

# Theory of the Ionization of Atoms by Electron Impact\*

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A review of the quantum theory of ionizing collisions is presented, with particular regard to recent theoretical developments. A discussion is given of quantal and classical approximations and their predictions compared with experimental data. Some useful empirical formulas are listed and compared, and in conclusion mention is made of the present inadequacies in the theory.

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## 1. INTRODUCTION

A great deal of experimental and theoretical work has been devoted in recent years to the study of ionization cross sections of atoms or ions by electron impact. The importance of an accurate evaluation of these cross sections is evidenced by the wide variety of physical phenomena, the interpretations of which demand a knowledge of reaction rates for ionization by electron impact. Examples of such phenomena arise in the fields of plasma physics, in the study of stellar atmospheres

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and the solar corona, in studies of gas discharges, and of the passage of shock waves through gases. A good deal of progress has been made in recent years by a number of different approaches towards obtaining an accurate knowledge of ionization cross sections. In the first place a substantial amount of experimental work has now been carried out in which single- or multiple-ionization cross sections of atoms or ions from their ground states have been measured. This work has been the subject of an earlier review by Kieffer and Dunn (1966). The available experimental data are far from exhaustive however. Many species remain to be investigated and there are difficulties in the experimental determination of ionization cross sections from excited states. Recourse in these cases has been made to theoretical studies. On the theoretical side the basic formulation of the problem has received a good deal of attention and it is found that the theory of ionizing collisions differs quite markedly from that for collisions involving excitation. At the same time a number of new approximate quantal methods of treating the problem have been investigated. Even so, quantal calculations are lengthy and not yet as accurate as could be wished. Alternative approaches have therefore been pursued with the aim of providing reasonably accurate estimates in a very simple fashion. Such approaches arise through using a classical rather than a quantal theory of collisions and from devising semiempirical formulas which represent known data and may be used, through the use of suitably defined parameters, to estimate as yet unmeasured or uncalculated data. This review examines the presently available theoretical procedures, with particular regard to the most salient features of the basic formulation and to deficiencies in approximate methods.

This article is confined to a study of ionization of atomic species by electron impact. In Sec. 2 the appropriate quantal theory is reviewed and this is followed in Sec. 3 by a discussion of quantal approximations. Section 4 describes classical approximations and Sec. 5 discusses some semiempirical formulas for single-ionization cross sections of atoms or ions by electron impact.

## 2. THE QUANTUM THEORY OF IONIZING COLLISIONS

The calculation of an ionization cross section even in a simple approximation is an arduous computational task, and on account of this little attention has been paid until fairly recently to developing the theory beyond that which has been described in earlier reviews by Bates, Fundaminsky, Leech, and Massey (1950) and by Massey (1956). A more recent and comprehensive review of ionization cross section calculations has been given by Veldre (1965). The problems of taking into account exchange in ionization processes and of developing proper integral expressions for the scattering amplitudes have now been considered in a number of papers by Peterkop [1960, 1961, 1962(a), 1962(b), 1963(a), 1963(b), 1965], by Seaton [1962(a)], and by Rudge and Seaton (1964, 1965).

The theory differs significantly from that for excitation processes and the most important features of the theory may be seen from consideration of the simplest case of ionization of atomic hydrogen by electron impact. This case is therefore discussed initially, the details being first prefaced by a brief outline of the theory. The discussion throughout is confined to the theory of ionization of atoms or ions by electron impact but applies with little modification to the case of ionization by other structureless charged particles.

The first step in the theory is to determine the asymptotic form of the wave function for an ionizing collision, i.e., the form of the wave function where both electrons are far removed from the nucleus and from each other. This involves, therefore, the determination of the behavior of the wave function where three charged particles are far removed from each other, in distinction to the case of excitation processes, where the behavior of the wave function is sought in a region where a single charged particle is removed from a neutral or positive system. The asymptotic form is developed as an expansion, from which only the leading term contributes to the current. Subject to boundary conditions, which define a collision event being satisfied, the coefficient of this leading term is the scattering amplitude, and the second step in the theory is to determine integral or variational expressions for it. The third step is to express the ionization cross section in terms of the scattering amplitude. Since, for single ionization, there are two free electrons in the final state, this involves constructing a current operator appropriate to the case of two particles rather than the single-particle current operator used in excitation problems. Finally, for the case of ionization by electron impact, consideration must be given to the exchange problem. Here again the situation differs from that for excitation, it being found that the "exchange" scattering amplitude is related to the "direct" scattering amplitude.

This is the program carried out in the cited papers by

Peterkop and Rudge and Seaton, and we first review their results for ionization of atomic hydrogen.

### 2.1. Notation

Atomic units are used ( $e$ , the electronic charge,  $m$ , the mass of electron, and  $\hbar$ , Planck's constant divided by  $2\pi$ , are taken as the fundamental units and therefore have the value unity);  $E$  denotes the total positive energy of the system in these units, and for reasons of convenience we also define  $\frac{1}{2}X^2 = E$ . Cross-section expressions and cross sections are however expressed in units of  $\pi a_0^2$ , where  $a_0$  is the first Bohr radius of atomic hydrogen ( $\pi a_0^2$  is  $8.797 \times 10^{-17}$  cm<sup>2</sup>). The coordinates of the  $i$ th electron denoted by  $\mathbf{r}_i$ ,  $\mathbf{k}_0$  is the momentum of the incident electron, and  $\mathbf{k}_1$  and  $\mathbf{k}_2$  are the momenta of the continuum electrons in the final state.

The electrostatic Hamiltonian of the system is written as  $\mathcal{H}$ , and in general for  $N$  electrons and a nucleus with charge  $Z$ , has the form

$$\mathcal{H} = \sum_{i=1}^N H_i + \sum_{j=i+1}^N \sum_{i=1}^{N-1} r_{ij}^{-1}, \quad (2.1)$$

where

$$H_i = -\frac{1}{2}\nabla_i^2 - Z/r_i \quad (2.2)$$

and

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|.$$

Bound-state hydrogenic eigenfunctions are written  $\psi(\gamma | \mathbf{r})$  ( $\gamma$  denoting collectively the quantum numbers  $n, l, m$ ) and satisfy

$$H\psi(\gamma | \mathbf{r}) = E\gamma\psi(\gamma | \mathbf{r}). \quad (2.3)$$

They are orthogonal and are taken to be normalized to unity.  $\gamma=0$  will be taken to refer to the initial state of the atom. The continuum eigenfunctions (Coulomb functions) satisfy

$$H\psi(z, \mathbf{k} | \mathbf{r}) = \frac{1}{2}k^2\psi(z, \mathbf{k} | \mathbf{r}) \quad (2.4)$$

and are taken to be normalized such that

$$\int \psi(z, \mathbf{k} | \mathbf{r}) \psi^*(z, \mathbf{k}' | \mathbf{r}) d\mathbf{r} = \delta(\mathbf{k} - \mathbf{k}'). \quad (2.5)$$

The continuum solutions are not uniquely defined through the normalization condition (2.5). It is shown in the cited papers that integral expressions for the scattering amplitude involve a particular solution of (2.4) defined by

$$\psi(z, \mathbf{k} | \mathbf{r}) = (2\pi)^{-3/2} \chi(z, -\mathbf{k} | \mathbf{r}), \quad (2.6)$$

where

$$\begin{aligned} \chi(z, -\mathbf{k} | \mathbf{r}) = & [2\pi\eta / (1 - e^{-2\pi\eta})]^{1/2} \exp [i\sigma_0(\eta)] \\ & \times \exp(-i\mathbf{k} \cdot \mathbf{r}) {}_1F_1[i\eta, 1, i(kr + \mathbf{k} \cdot \mathbf{r})]. \end{aligned} \quad (2.7)$$

In (2.7)  $\eta = Z/k$ ,  $\sigma_0(\eta) = \arg \Gamma(1 - i\eta)$ , and

$${}_1F_1(a, b, x) = \sum_{n=0}^{\infty} \frac{\Gamma(a+n)\Gamma(b)x^n}{\Gamma(b+n)\Gamma(a)\Gamma(n+1)}.$$

Asymptotically

$$\chi(z, -\mathbf{k} | \mathbf{r}) \sim \exp -i(\mathbf{k} \cdot \mathbf{r} + \eta \ln |kr + \mathbf{k} \cdot \mathbf{r}|) + [f(\theta)/r] \exp i(kr + \eta \ln 2kr), \quad r \rightarrow \infty, \quad (2.8)$$

where  $\cos \theta = -\hat{\mathbf{k}} \cdot \hat{\mathbf{r}}$  and

$$f(\theta) = \frac{\eta \Gamma(1 - i\eta) \exp 2i\eta \ln [\sin(\theta/2)]}{2k\Gamma(1 + i\eta) \sin^2(\theta/2)}. \quad (2.9)$$

The Schrödinger equation is

$$\mathfrak{H}\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}X^2\Psi(\mathbf{r}_1, \mathbf{r}_2). \quad (2.10)$$

It is convenient, when studying the asymptotic form of the wave function to write (2.10) in terms of hyperspherical coordinates. These are the set  $(\theta_1, \phi_1, \theta_2, \phi_2, \alpha, \rho)$ , where

$$\left. \begin{aligned} r_1 &= \rho \cos \alpha \\ r_2 &= \rho \sin \alpha \end{aligned} \right\} 0 \leq \alpha \leq \pi/2, \quad (2.11)$$

and  $(\theta_1, \phi_1, \theta_2, \phi_2)$  are the usual spherical polar coordinates. We also define

$$\zeta(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha) = (\sin \alpha)^{-1} + (\cos \alpha)^{-1} - (1 - \cos \theta_{12} \sin 2\alpha)^{-1/2}, \quad (2.12)$$

where  $\cos \theta_{12} = \hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2$ , so that

$$\zeta/\rho = 1/r_1 + 1/r_2 - 1/r_{12}. \quad (2.13)$$

### 2.2. The Asymptotic Form of the Wave Function

The form of  $\Psi$  in (2.10) is sought in the region where  $r_1 \rightarrow \infty$ ,  $r_2 \rightarrow \infty$ , and  $r_{12} \rightarrow \infty$ . Except at the points  $\alpha = 0$ ,  $\alpha = \pi/2$  ( $\alpha = \pi/4$ ,  $\theta_{12} = 0$ ), these conditions are met by taking  $\rho \rightarrow \infty$ . Accordingly (2.10) is written in terms of hyperspherical coordinates when, on making the substitution

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Phi(\mathbf{r}_1, \mathbf{r}_2)/\rho^{5/2}, \quad (2.14)$$

(2.10) reduces to

$$\mathfrak{L}\Phi = (\rho^{-2})\Lambda\Phi, \quad (2.15)$$

where

$$\mathfrak{L} = \partial^2/\partial\rho^2 + X^2 + 2\zeta/\rho - 15/4\rho^2 \quad (2.16)$$

and

$$\Lambda = (\sin^2 \alpha \cos^2 \alpha)^{-1} \{ \cos^2 \alpha L_2^2 + \sin^2 \alpha L_1^2 - (\partial/\partial\alpha) \times [\sin^2 \alpha \cos^2 \alpha (\partial/\partial\alpha)] \}, \quad (2.17)$$

with

$$L_i^2 = -(\sin \theta_i)^{-1} \frac{\partial}{\partial \theta_i} \left( \sin \theta_i \frac{\partial}{\partial \theta_i} \right) - (\sin^2 \theta_i)^{-1} \frac{\partial^2}{\partial \phi_i^2}. \quad (2.18)$$

Equation (2.15) may be solved formally by the method

of the Green's function in terms of the two linearly independent solutions of the homogeneous equation

$$\mathfrak{L} \begin{Bmatrix} F(\zeta, X, \rho) \\ H(\zeta, X, \rho) \end{Bmatrix} = 0. \quad (2.19)$$

These are radial Coulomb functions defined such that in the asymptotic region

$$\begin{aligned} F(\zeta, X, \rho) &\sim X^{-5/2} \sin [f(\rho)] & \rho \rightarrow \infty, \\ H(\zeta, X, \rho) &\sim X^{-5/2} \exp [if(\rho)] & \rho \rightarrow \infty, \end{aligned} \quad (2.20)$$

where

$$f(\rho) = X\rho + (\zeta/X) \ln (2X\rho) - \frac{3}{4}\pi + \arg \Gamma(\frac{5}{2} - i\zeta/X). \quad (2.21)$$

It is readily verified that (2.15) may now be written as the integral equation

$$\begin{aligned} \Phi(\zeta, X, \rho) &= -X^4 \left[ H(\zeta, X, \rho) \int_0^\infty \rho^{-2} F(\zeta, X, \rho) \right. \\ &\quad \times \Lambda \Phi d\rho + F(\zeta, X, \rho) \int_\rho^\infty \rho^{-2} H(\zeta, X, \rho) \Lambda \Phi d\rho \\ &\quad \left. - H(\zeta, X, \rho) \int_\rho^\infty \rho^{-2} F(\zeta, X, \rho) \Lambda \Phi d\rho \right]. \quad (2.22) \end{aligned}$$

For large  $\rho$  (and finite  $X$ ) the first term in (2.22) is the leading term in an asymptotic expansion so that on defining

$$\begin{aligned} f(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha) &= -\exp \left[ i \arg \Gamma \left( \frac{5}{2} - \frac{\zeta}{iX} \right) \right] \\ &\quad \times \int_0^\infty \rho^{-2} F(\zeta, X, \rho) \Lambda \Phi d\rho \end{aligned}$$

and using (2.14) and (2.20) we obtain the result that

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2) &\sim -i^{1/2} \left( \frac{X^3}{\rho^5} \right)^{1/2} f(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha) \\ &\quad \times \exp i[X\rho + (\zeta/X) \ln (2X\rho)], \quad (r_1, r_2) \rightarrow \infty. \quad (2.23) \end{aligned}$$

Examination of the neglected terms in (2.22) shows that the complete asymptotic expansion may be written in the form

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2) &\sim -i^{1/2} \left( \frac{X^3}{\rho^5} \right)^{1/2} \exp i \left[ X\rho + \frac{\zeta}{X} \ln (2X\rho) \right] \\ &\quad \times \sum_{n=0}^{\infty} \sum_{p=0}^{2n} A_{np}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha) \frac{(\ln \rho)^p}{\rho^n}, \quad (r_1, r_2) \rightarrow \infty. \quad (2.24) \end{aligned}$$

In (2.24) the leading term  $A_{00}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha)$  is the scattering amplitude  $f(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha)$ . The further terms  $A_{np}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha)$  may be obtained by substituting (2.24) into the Schrödinger equation [Peterkop (1960)]. Their values

may be expressed in terms of  $A_{00}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha)$ ,  $\zeta(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha)$  and their derivatives.

The integral equation (2.22) is valid for all  $\rho$  but the expressions (2.23) and (2.24) are valid only for  $\rho \gg \zeta/X^2$ , i.e.,  $r_1 \rightarrow \infty$ ,  $r_2 \rightarrow \infty$ , and  $r_{12} \rightarrow \infty$  as was specified at the outset. The scattering amplitude  $f(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha)$  is thus defined through (2.24) everywhere except at the singular points of  $\zeta$ , viz.,

$$[\alpha = 0, \alpha = \pi/2, (\alpha = \pi/4, \theta_{12} = 0)].$$

The complete scattering problem is defined once the asymptotic forms as  $r_1/r_2 \rightarrow \infty$  and  $r_2/r_1 \rightarrow \infty$  are also specified. These are well known and the behavior of the wave function in the entire asymptotic region is given by

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2) &\sim \psi(0 | \mathbf{r}_2) \exp i\mathbf{k}_0 \cdot \mathbf{r}_1 + \sum_{\gamma} \psi(\gamma | \mathbf{r}_2) f_{0\gamma}(\mathbf{k}_0, \hat{\mathbf{r}}_1) \\ &\quad \times \frac{\exp ik_{\gamma} r_1}{r_1} \quad (r_1/r_2) \rightarrow \infty \\ &\sim \sum_{\gamma} \psi(\gamma | \mathbf{r}_1) g_{0\gamma}(\mathbf{k}_0, \hat{\mathbf{r}}_2) \frac{\exp (ik_{\gamma} r_2)}{r_2} \\ &\quad (r_2/r_1) \rightarrow \infty \\ &\sim -i^{1/2} \left( \frac{X^3}{\rho^5} \right)^{1/2} f(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha) \\ &\quad \times \exp i \left[ X\rho + \frac{\zeta}{X} \ln (2X\rho) \right], \quad (r_1, r_2) \rightarrow \infty, \quad (2.25) \end{aligned}$$

where  $k_{\gamma}^2 = 2(E - E\gamma)$  and  $f_{0\gamma}(\mathbf{k}_0, \hat{\mathbf{r}}_1)$  and  $g_{0\gamma}(\mathbf{k}_0, \hat{\mathbf{r}}_2)$  are, respectively, the direct and exchange scattering amplitudes for excitation.

The asymptotic form of a symmetric or antisymmetric solution of the Schrödinger equation (2.10) may be obtained by appropriately symmetrizing (2.25). Thus

$$\begin{aligned} \Psi^{\pm}(\mathbf{r}_1, \mathbf{r}_2) &\sim \psi(0 | \mathbf{r}_2) \exp (i\mathbf{k}_0 \cdot \mathbf{r}_1) + \sum_{\gamma} \psi(\gamma | \mathbf{r}_2) \\ &\quad \times [f_{0\gamma}(\mathbf{k}_0, \hat{\mathbf{r}}_1) \pm g_{0\gamma}(\mathbf{k}_0, \hat{\mathbf{r}}_1)] [\exp (ik_{\gamma} r_1) / r_1] \\ &\quad (r_1/r_2) \rightarrow \infty \\ &\sim -i^{1/2} (X^3/\rho^5)^{1/2} \\ &\quad \times [f(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha) \pm f(\hat{\mathbf{r}}_2, \hat{\mathbf{r}}_1, \pi/2 - \alpha)] \\ &\quad \times \exp \{i[X\rho + (\zeta/X) \ln (2X\rho)]\}, \quad (r_1, r_2) \rightarrow \infty. \quad (2.26) \end{aligned}$$

The asymptotic form of the wave function at zero energy requires separate consideration. We define an operator

$$\mathcal{L}_0 = \partial^2 / \partial \rho^2 + 2A/\rho, \quad (2.27)$$

where  $A = A(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha)$  is for the moment arbitrary. The

equation

$$\mathcal{L}_0 \begin{Bmatrix} F_0(\alpha, \rho) \\ H_0(\alpha, \rho) \end{Bmatrix} = 0 \quad (2.28)$$

has fundamental solutions

$$F_0(\alpha, \rho) = (\pi\rho)^{1/2} J_1[(8A\rho)^{1/2}] \quad (2.29)$$

and

$$H_0(\alpha, \rho) = (\pi\rho)^{1/2} H_1[(8A\rho)^{1/2}], \quad (2.30)$$

where  $J_1$ , and  $H_1$  are, respectively, a Bessel function and a Hankel function of order one. Asymptotically

$$\begin{Bmatrix} F_0(\alpha, \rho) \\ H_0(\alpha, \rho) \end{Bmatrix} \sim \left( \frac{\rho}{2A} \right)^{1/4} \begin{Bmatrix} \sin \{ \phi_0(\rho) \} \\ -i \exp i \{ \phi_0(\rho) \} \end{Bmatrix} \rho \rightarrow \infty, \quad (2.31)$$

where

$$\phi_0(\rho) = (8A\rho)^{1/2} - \frac{1}{4}\pi.$$

Using the transformation (2.14) we may write

$$\mathcal{L}_0 \Phi(\mathbf{r}_1, \mathbf{r}_2) = (\Lambda_0/\rho^2) \Phi(\mathbf{r}_1, \mathbf{r}_2), \quad (2.32)$$

where

$$\Lambda_0 = \Lambda + 2(A - \zeta)\rho + 15/4. \quad (2.33)$$

A solution of (2.32) is

$$\begin{aligned} i\Phi(\mathbf{r}_1, \mathbf{r}_2) &= H_0(\alpha, \rho) \int_0^{\infty} \rho^{-2} F_0(\alpha, \rho) \Lambda_0 \Phi(\mathbf{r}_1, \mathbf{r}_2) d\rho \\ &\quad + F_0(\alpha, \rho) \int_{\rho}^{\infty} \rho^{-2} H_0(\alpha, \rho) \Lambda_0 \Phi(\mathbf{r}_1, \mathbf{r}_2) d\rho \\ &\quad - H_0(\alpha, \rho) \int_{\rho}^{\infty} \rho^{-2} F_0(\alpha, \rho) \Lambda_0 \Phi(\mathbf{r}_1, \mathbf{r}_2) d\rho. \quad (2.34) \end{aligned}$$

For large  $\rho$ , (2.34) tells us that

$$\begin{aligned} \Phi(\mathbf{r}_1, \mathbf{r}_2) &\sim f_0(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha) \rho^{1/4} \exp i\phi_0(\rho) - [(2A)^{-1/2} \rho^{1/4} / 2i] \\ &\quad \times \left\{ \exp [i\phi_0(\rho)] \int_{\rho}^{\infty} \rho^{-3/2} \exp [-i\phi_0(\rho)] \Lambda_0 [f_0(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha) \right. \\ &\quad \times \exp (i\phi_0(\rho))] d\rho - \exp [-i\phi_0(\rho)] \int_{\rho}^{\infty} \rho^{-3/2} \exp [i\phi_0(\rho)] \\ &\quad \times \Lambda_0 [f_0(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha) \exp (i\phi_0(\rho))] d\rho \left. \right\}, \quad (2.35) \end{aligned}$$

where

$$f_0(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha) = -(2A)^{-1/4} \int_0^{\infty} \rho^{-2} F_0(\alpha, \rho) \Lambda_0 \Phi(\mathbf{r}_1, \mathbf{r}_2) d\rho, \quad (2.36)$$

provided this integral converges.

The choice of  $A(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha)$  is now dictated by demanding that the remainder terms in (2.35) should behave as  $\rho^n$ , where  $n < \frac{1}{4}$ , i.e.,  $\Lambda_0 [f_0(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha) \exp i\phi_0(\rho)]$  must be of order  $\rho^m$ , where  $m < \frac{1}{2}$ . By imposing the condition that terms of order  $\rho^{-1/2}$  in the first integral of (2.35) vanish, we find that

$$A + A^{-1}(\mathbf{D}A)^2 = \zeta, \quad (2.37)$$

where

$$(\mathbf{D}A)^2 = \left(\frac{\partial A}{\partial \alpha}\right)^2 + (\cos^2 \alpha)^{-1} \left[ \left(\frac{\partial A}{\partial \theta_1}\right)^2 + (\sin^2 \theta_1)^{-1} \left(\frac{\partial A}{\partial \phi_1}\right)^2 \right] + (\sin^2 \alpha)^{-1} \left[ \left(\frac{\partial A}{\partial \theta_2}\right)^2 + (\sin^2 \theta_2)^{-1} \left(\frac{\partial A}{\partial \phi_2}\right)^2 \right]. \quad (2.38)$$

Consideration of terms of order  $\rho^{-1}$ , on the other hand, gives us the result

$$\mathbf{D} \cdot \{ [f_0(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha)]^2 \mathbf{D}(A)^{1/2} \} = 0, \quad (2.39)$$

where

$$\begin{aligned} \mathbf{D} \cdot (a \mathbf{D}b) = & (\sin^2 2\alpha)^{-1} \frac{\partial}{\partial \alpha} \left[ a \sin^2 2\alpha \frac{\partial b}{\partial \alpha} \right] + (\cos^2 \alpha)^{-1} \left[ (\sin \theta_1)^{-1} \frac{\partial}{\partial \theta_1} \left( a \sin \theta_1 \frac{\partial b}{\partial \theta_1} \right) + (\sin^2 \theta_1)^{-1} \frac{\partial}{\partial \phi_1} \left( a \frac{\partial b}{\partial \phi_1} \right) \right] \\ & + (\sin^2 \alpha)^{-1} \left[ (\sin \theta_2)^{-1} \frac{\partial}{\partial \theta_2} \left( a \sin \theta_2 \frac{\partial b}{\partial \theta_2} \right) + (\sin^2 \theta_2)^{-1} \left( \frac{\partial}{\partial \phi_2} a \frac{\partial b}{\partial \phi_2} \right) \right]. \end{aligned} \quad (2.40)$$

Hence the asymptotic form of the wave function at zero energy is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \sim (-i)^{1/2} f_0(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha) \rho^{-9/4} \exp i(8A\rho)^{1/2}, \quad \rho \rightarrow \infty, \quad (2.41)$$

provided Eqs. (2.37) and (2.39) are satisfied and (2.36) converges. In this treatment it has been assumed that  $A > 0$ . Solutions corresponding to negative  $A$  are exponentially decreasing at large  $\rho$  and therefore need not be considered. In a classical treatment of the problem Wannier (1953) assumed that the whole reaction at zero energy took place at  $\alpha = \pi/4, \theta_{12} = \pi$ , i.e., he assumed that the only path leading to ionization was that in which the electrons moved in opposite directions with equal energy. No proof of this has been given but a particular solution of Eqs. (2.37) and (2.39) is  $\mathbf{D}A = 0$  which gives,  $A = \zeta(\alpha = \frac{1}{4}\pi, \theta_{12} = \pi)$ .

### 2.3. An Integral Expression for the Scattering Amplitude

Knowledge of the asymptotic form (2.23) permits integral expressions to be developed for the scattering amplitude. Peterkop [1962(b)] and Rudge and Seaton (1965) have developed such an expression by considering the integral

$$I = \int \Psi(\mathbf{r}_1, \mathbf{r}_2) (\mathcal{H} - E) \Phi(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (2.42)$$

where  $\Psi(\mathbf{r}_1, \mathbf{r}_2)$  is the exact solution of the Schrödinger equation and has the asymptotic form (2.23) for finite energies, while  $\Phi(\mathbf{r}_1, \mathbf{r}_2)$  is a function the form of which is to be determined, and must be such that (2.42) converges to an expression involving the scattering amplitude. Equation (2.42) may be written

$$I = -\frac{1}{2} \lim_{\rho \rightarrow \infty} \rho^5 \int \left( \Psi \frac{\partial \Phi}{\partial \rho} - \Phi \frac{\partial \Psi}{\partial \rho} \right) \sin^2 \alpha \cos^2 \alpha d\alpha d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2, \quad \rho \rightarrow \infty, \quad (2.43)$$

and we consider a  $\Phi(\mathbf{r}_1, \mathbf{r}_2)$  with asymptotic form

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) \sim \phi_1(z_1, -\mathbf{k}_1 | \mathbf{r}_1) \phi_2(z_2, -\mathbf{k}_2 | \mathbf{r}_2) \quad \rho \rightarrow \infty, \quad (2.44)$$

where the functions  $\phi_1$  and  $\phi_2$  satisfy equations of the form

$$[\nabla^2 + k^2 + (2z_i/r) + V_i(r)] \phi_i(z_i, -\mathbf{k} | \mathbf{r}) = 0.$$

$V_1(r)$  and  $V_2(r)$  are any short-range potentials and the effective charges  $z_1$  and  $z_2$  are for the moment arbitrary. At large distances

$$\begin{aligned} \phi(z, -\mathbf{k} | \mathbf{r}) \sim & (2\pi/ikr) \{ \alpha(\hat{\mathbf{k}}, \hat{\mathbf{r}}) \\ & \times \exp i[kr + (z/k) \ln(2kr)] - \delta(\hat{\mathbf{k}} - \hat{\mathbf{r}}) \\ & \times \exp -i[kr + (z/k) \ln(2kr)] \}, \quad r \rightarrow \infty, \end{aligned} \quad (2.45)$$

where

$$\alpha(\hat{\mathbf{k}}, \hat{\mathbf{r}}) = \delta(\hat{\mathbf{k}} + \hat{\mathbf{r}}) + (ik/2\pi) f_{e1}(-\hat{\mathbf{k}}, \hat{\mathbf{r}}), \quad (2.46)$$

and  $f_{e1}$  denotes the elastic scattering amplitude.

Jeffreys and Jeffreys (1956) give theorems of stationary phase, which state that

$$\begin{aligned} \int_a^b f(x) \exp [iRg(x)] dx \sim & f(x_0) \left[ \frac{2\pi}{R|g''(x_0)|} \right]^{1/2} \\ & \times \exp i[g(x_0)R + \frac{1}{4}\pi \operatorname{sgn}(g''(x_0))], \quad R \rightarrow \infty, \end{aligned} \quad (2.47)$$

provided  $g'(x_0) = 0, a \leq x_0 \leq b$ . If such a point does not exist or if  $f(x_0) = 0$ , then

$$\int_a^b f(x) \exp [iRg(x)] dx \sim \left\{ \frac{f(x) \exp iRg(x)}{iRg'(x)} \right\} \Big|_{x=a}^{x=b} \quad R \rightarrow \infty. \quad (2.48)$$

We therefore define

$$\left. \begin{aligned} k_1 &= X \cos \beta \\ k_2 &= X \sin \beta \end{aligned} \right\} 0 \leq \beta \leq \frac{1}{2}\pi, \quad (2.49)$$

and use (2.45) and the stationary-phase theorems (2.47) and (2.48) to perform the  $\alpha$  integration. It is then seen that the terms involving  $\alpha(\hat{\mathbf{k}}_1, \hat{\mathbf{r}}_1)$  and  $\alpha(\hat{\mathbf{k}}_2, \hat{\mathbf{r}}_2)$  give no contribution, while the remaining term has a point of stationary phase, where  $\alpha = \beta$  and may

be evaluated to give

$$I = -(2\pi)^{5/2} f(\mathbf{k}_1, \mathbf{k}_2) (\sin \beta)^{-2iz_2/k_2} (\cos \beta)^{-2iz_1/k_1} \\ \times \lim_{\rho \rightarrow \infty} \exp \{ i[\zeta(\hat{\mathbf{k}}_1, \hat{\mathbf{k}}_2, \beta)/X - z_1/k_1 - z_2/k_2] \ln(2X\rho) \}, \quad (2.50)$$

In order that the integral I shall have no divergent-phase factor it is therefore necessary that

$$z_1/k_1 + z_2/k_2 = \zeta(\hat{\mathbf{k}}_1, \hat{\mathbf{k}}_2, \beta)/X,$$

i.e.,

$$z_1/k_1 + z_2/k_2 = 1/k_1 + 1/k_2 - 1/|\mathbf{k}_1 - \mathbf{k}_2|. \quad (2.51)$$

The integral expression therefore is

$$f(\mathbf{k}_1, \mathbf{k}_2) = -(2\pi)^{-5/2} \exp[i\Delta(\mathbf{k}_1, \mathbf{k}_2)] \\ \times \int \Psi(\mathcal{H} - E) \Phi d\mathbf{r}_1 d\mathbf{r}_2, \quad (2.52)$$

where  $z_1$  and  $z_2$  are defined by (2.51) and

$$\Delta(\mathbf{k}_1, \mathbf{k}_2) = 2[(z_1/k_1) \ln(k_1/X) + (z_2/k_2) \ln(k_2/X)]. \quad (2.53)$$

The entire contribution to the integral arises from the stationary-phase point  $\alpha = \beta$ , i.e., from the points

$$r_1/k_1 = r_2/k_2 = t, \quad (2.54)$$

where  $t$  is a constant and classically is the time. Equation (2.51) may therefore be read as

$$z_1/r_1 + z_2/r_2 \sim 1/r_1 + 1/r_2 - 1/|\mathbf{r}_1 - \mathbf{r}_2|, \quad (2.55)$$

and the interpretation of the charges  $z_1$  and  $z_2$  is that they are angle-dependent quantities which asymptotically take full account of the Coulomb potentials.

The phase factor  $\Delta(\mathbf{k}_1, \mathbf{k}_2)$  is of importance when the effects of exchange are included (see Sec. 2.5).

#### 2.4. The Current Operator and Cross-section Expressions

The current operator is

$$\mathbf{j} = (1/2i) [\Psi^* \nabla \Psi - \Psi \nabla \Psi^*], \quad (2.56)$$

and the ionization cross section, in units of  $\pi a_0^2$ , is given by

$$Q = (1/\pi k_0) \int \mathbf{j} \cdot d\mathbf{S}. \quad (2.57)$$

In the case of single ionization the gradient operator and surface elements are those appropriate to a six-dimensional space.

The gradient operator is

$$\nabla = (\partial/\partial\rho) \hat{\rho} + \{\text{terms of order } (1/\rho)\}, \quad (2.58)$$

and the surface element is

$$dS = \rho^5 \sin^2 \alpha \cos^2 \alpha d\alpha d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2. \quad (2.59)$$

Hence

$$Q = \frac{X^4}{\pi k_0} \int_0^{\pi/2} \sin^2 \alpha \cos^2 \alpha d\alpha \int |f(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha)|^2 d\hat{\mathbf{r}}_1 d\hat{\mathbf{r}}_2. \quad (2.60)$$

Expressed in terms of the momenta of the final-state electrons on averaging over directions of the incident electron, (2.60) becomes

$$Q = (\pi k_0)^{-1} \int_0^E k_1 k_2 \sigma(k_1, k_2) d(\frac{1}{2} k_2^2), \quad (2.61)$$

where

$$\sigma(k_1, k_2) = (4\pi)^{-1} \int |f(\mathbf{k}_1, \mathbf{k}_2)|^2 d\hat{\mathbf{k}}_0 d\hat{\mathbf{k}}_1 d\hat{\mathbf{k}}_2. \quad (2.62)$$

Expressions (2.61) and (2.62) are those appropriate to the ionization problem when exchange may be neglected, that is, when dealing with "distinguishable" electrons.

#### 2.5. The Effects of Exchange in Hydrogenic Systems

We introduce spin variables defining a spin quantum number  $\mu = \pm \frac{1}{2}$ , a spin coordinate  $\sigma = \pm \frac{1}{2}$ , and a spin function  $\delta(\mu | \sigma)$ , which is unity for  $\mu = \sigma$ , and zero otherwise. To denote both space and spin coordinates we use  $\mathbf{x} = (\mathbf{r}, \sigma)$ . The requirement of the Pauli principle for the  $e$ -H system is therefore that

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1). \quad (2.63)$$

A total spin function for two electrons is written

$$\chi(S, M_S | \sigma_1, \sigma_2) = \sum_{\mu_1 \mu_2} C(\frac{1}{2}, \frac{1}{2}, S; \mu_1, \mu_2, M_S) \\ \times \delta(\mu_1 | \sigma_1) \delta(\mu_2 | \sigma_2), \quad (2.64)$$

where the  $C$  is a Clebsch-Gordan coefficient.

It follows from (2.64) that

$$\chi(S, M_S | \sigma_1, \sigma_2) = (-1)^{S+1} \chi(S, M_S | \sigma_2, \sigma_1). \quad (2.65)$$

The asymptotic form of a wave function satisfying (2.63) is now

$$\Psi(S | \mathbf{x}_1, \mathbf{x}_2) \sim -i^{1/2} (X^3/\rho^5)^{1/2} \chi(S, M_S | \sigma_1, \sigma_2) \\ \times f(S | \hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha) \exp[i[X\rho + (\zeta/X) \ln(2X\rho)]] \\ (r_1, r_2) \rightarrow \infty, \quad (2.66)$$

where

$$f(S | \hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha) = f(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha) + (-1)^S f(\hat{\mathbf{r}}_2, \hat{\mathbf{r}}_1, \pi/2 - \alpha). \quad (2.67)$$

Corresponding to a given total spin  $S$  the ionization cross section is given by

$$Q(S) = (\pi k_0)^{-1} \int_0^E k_1 k_2 \sigma(S | k_1, k_2) d(\frac{1}{2} k_2^2), \quad (2.68)$$

where

$$\sigma(S | k_1, k_2) = (4\pi)^{-1} \int d\hat{\mathbf{k}}_0 d\hat{\mathbf{k}}_1 d\hat{\mathbf{k}}_2 |f(S | \mathbf{k}_1, \mathbf{k}_2)|^2 \quad (2.69)$$

and

$$f(S | \mathbf{k}_1, \mathbf{k}_2) = f(\mathbf{k}_1, \mathbf{k}_2) + (-1)^S f(\mathbf{k}_2, \mathbf{k}_1). \quad (2.70)$$

For random spin orientations the ionization cross section is given by

$$Q(E) = (\pi k_0)^{-1} \int_0^{E/2} \frac{1}{4} (k_1 k_2) \times [\sigma(0 | k_1, k_2) + 3\sigma(1 | k_1, k_2) d(\frac{1}{2} k_2^2)]. \quad (2.71)$$

We must integrate over all distinct final states which lead to the process of ionization. In (2.68) there is a distinction arising from the electron spins but in the case where the spin is not fixed the only distinction is that between the velocities of the two final-state electrons. Hence the integration is performed only over all relative velocities of the final-state electrons and the integration in (2.71) is therefore cut off at  $E/2$  rather than at  $E$ . The integrand in (2.71) is equal to

$$(k_1 k_2 / 4) \{ |f(\mathbf{k}_1, \mathbf{k}_2)|^2 + |f(\mathbf{k}_2, \mathbf{k}_1)|^2 - \text{Re} [f(\mathbf{k}_1, \mathbf{k}_2) f^*(\mathbf{k}_2, \mathbf{k}_1)] \}, \quad (2.72)$$

and from the symmetry of this integrand we may therefore also write

$$Q(E) = (2\pi k_0)^{-1} \int_0^E \frac{1}{4} (k_1 k_2) \times [\sigma(0 | k_1, k_2) + 3\sigma(1 | k_1, k_2) d(\frac{1}{2} k_2^2)], \quad (2.73)$$

and the distribution in energy of all electrons following an ionizing collision is symmetric about  $E/2$ .

An integral expression for  $f(S | \mathbf{k}_1, \mathbf{k}_2)$  is

$$f(S | \mathbf{k}_1, \mathbf{k}_2) = \frac{1}{2} [-(2\pi)^{-5/2}] \exp i\Delta(\mathbf{k}_1, \mathbf{k}_2) \times \int \Psi(S | \mathbf{r}_1, \mathbf{r}_2) (\mathcal{H}C - E) \Phi(\mathbf{r}_1, \mathbf{r}_2) + (-1)^S \Phi(\mathbf{r}_2, \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.74)$$

$$= f(\mathbf{k}_1, \mathbf{k}_2) + (-1)^S g(\mathbf{k}_1, \mathbf{k}_2), \quad (2.75)$$

where

$$g(\mathbf{k}_1, \mathbf{k}_2) = -(2\pi)^{-5/2} \exp i\Delta(\mathbf{k}_1, \mathbf{k}_2) \int \Psi(\mathbf{r}_1, \mathbf{r}_2) \times (\mathcal{H}C - E) \phi_1[z_1(\mathbf{k}_1, \mathbf{k}_2), -\mathbf{k}_1 | \mathbf{r}_2] \times \phi_2[z_2(\mathbf{k}_1, \mathbf{k}_2), -\mathbf{k}_2 | \mathbf{r}_1] d\mathbf{r}_1 d\mathbf{r}_2. \quad (2.76)$$

In (2.76)  $z_2(\mathbf{k}_1, \mathbf{k}_2)$  may be replaced by  $z_1(\mathbf{k}_2, \mathbf{k}_1)$  and  $z_1(\mathbf{k}_1, \mathbf{k}_2)$  may be replaced by  $z_2(\mathbf{k}_2, \mathbf{k}_1)$ , since the relationship (2.51) will still be satisfied, and  $\Delta(\mathbf{k}_1, \mathbf{k}_2)$  is then replaced by  $\Delta(\mathbf{k}_2, \mathbf{k}_1)$ . Thus

$$g(\mathbf{k}_1, \mathbf{k}_2) = f(\mathbf{k}_2, \mathbf{k}_1), \quad (2.77)$$

and the expression (2.74) is in agreement with (2.70).

The exchange states for ionization are those states wherein the "ejected" electron has a greater velocity than the "scattered" electron. The effects of exchange are large when both electrons have similar velocities.

## 2.6. The Effects of Exchange in Nonhydrogenic Systems

For single ionization of nonhydrogenic systems there is a new possibility in that "classical" exchange can occur, i.e., the incident electron may be captured into a bound state while two initially bound electrons are ejected. Let us consider first the ionization of a helium atom which is the simplest case for which this possibility can arise. The eigenfunctions of helium may be denoted by  $\psi(n, S_A | \mathbf{r}_2, \mathbf{r}_3)$ , where  $n$  denotes the configuration and  $S_A$  the total spin of the atom. Let us now denote by  $\psi(\gamma | \mathbf{r})$  the eigenfunctions of  $\text{He}^+$  which belong to eigenvalue  $E\gamma$  and extend the notation already used by defining

$$\rho_{ij}^2 = r_i^2 + r_j^2,$$

$$\tan \alpha_{ij} = r_i / r_j,$$

$$\zeta_{ij}(\hat{\mathbf{r}}_i, \hat{\mathbf{r}}_j, \alpha_{ij}) = (\cos \alpha_{ij})^{-1} + (\sin \alpha_{ij})^{-1} - (1 - \sin 2\alpha_{ij} \cos \theta_{ij})^{-1/2},$$

$$S_{ij} = X\gamma\rho_{ij} + (\zeta_{ij}/X\gamma) \ln(2X\gamma\rho_{ij}),$$

$$X_\gamma^2 = 2(E - E_\gamma).$$

The spatial dependence of the wave function  $\Psi(\mathbf{r}_2, \mathbf{r}_3; \mathbf{r}_1)$ , which satisfies

$$\Psi(\mathbf{r}_3, \mathbf{r}_2; \mathbf{r}_1) = (-1)^{S_A} \Psi(\mathbf{r}_2, \mathbf{r}_3; \mathbf{r}_1), \quad (2.78)$$

may be investigated in a manner similar to that already used in studying the ionization of hydrogen. The asymptotic forms of interest are

$$\begin{aligned} \Psi(\mathbf{r}_2, \mathbf{r}_3; \mathbf{r}_1) &\sim \psi(0, S_A | \mathbf{r}_2, \mathbf{r}_3) \exp(i\mathbf{k}_0 \cdot \mathbf{r}_1) + \sum_n \psi(n, S_A | \mathbf{r}_2, \mathbf{r}_3) f_{0n}(\mathbf{k}_0, \hat{\mathbf{r}}_1) \frac{\exp(ik_n r_1)}{r_1}, \quad r_1 \rightarrow \infty \\ &\sim -\sqrt{2} i^{1/2} \sum_\gamma \left[ \frac{X_\gamma^3}{\rho_{12}^5} \right]^{1/2} \psi(\gamma | \mathbf{r}_3) f_\gamma(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha_{12}) \exp(iS_{12}), \quad (r_1, r_2) \rightarrow \infty \\ &\sim (-1)^{S_A+1} \sqrt{2} i^{1/2} \sum_\gamma \left[ \frac{X_\gamma^3}{\rho_{13}^5} \right]^{1/2} \psi(\gamma | \mathbf{r}_2) f_\gamma(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_3, \alpha_{13}) \exp(iS_{13}), \quad (r_1, r_3) \rightarrow \infty \\ &\sim -\sqrt{2} i^{1/2} \sum_\gamma \left[ \frac{X_\gamma^3}{\rho_{23}^5} \right]^{1/2} \psi(\gamma | \mathbf{r}_1) \omega_\gamma(\hat{\mathbf{r}}_2, \hat{\mathbf{r}}_3, \alpha_{23}) \exp(iS_{23}), \quad (r_2, r_3) \rightarrow \infty, \end{aligned} \quad (2.79)$$

where the integral expressions are:

$$f_\gamma(\mathbf{k}_1, \mathbf{k}_2) \left. \vphantom{f_\gamma} \right\} = -(2\pi)^{-5/2} \exp i\Delta(\mathbf{k}_1, \mathbf{k}_2) \int \Psi(\mathbf{r}_2, \mathbf{r}_3; \mathbf{r}_1) (\mathcal{H} - E) \left. \vphantom{\Psi} \right\} \begin{cases} \Phi(\mathbf{r}_3, \mathbf{r}_1, \mathbf{r}_2) \\ \Phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \end{cases} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \quad (2.80)$$

In (2.80)  $\mathcal{H}$  is the Hamiltonian for the  $e$ -He system,  $\Delta(\mathbf{k}_1, \mathbf{k}_2)$  is the phase factor defined by (2.53) and

$$\Phi(\mathbf{r}_3, \mathbf{r}_1, \mathbf{r}_2) \sim \psi^*(\gamma | \mathbf{r}_3) \phi_1(z_1, -\mathbf{k}_1 | \mathbf{r}_1) \phi_2(z_2, -\mathbf{k}_2 | \mathbf{r}_2) \quad (r_1, r_2) \rightarrow \infty, \quad (2.81)$$

where  $z_1$  and  $z_2$  satisfy (2.51).

Introducing spin coordinates, a totally antisymmetric wave function is

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = \sum_{\text{cyclic permutations}} \chi(S_A, M_{S_A} | \sigma_2, \sigma_3) \delta(\mu_1 | \sigma_1) \Psi(\mathbf{r}_2, \mathbf{r}_3; \mathbf{r}_1), \quad (2.82)$$

which has the asymptotic form

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \sim -\sqrt{2}(i)^{1/2} \sum_{\mu_1' \mu_2' \mu_3'} \delta(\mu_1' | \sigma_1) \delta(\mu_2' | \sigma_2) \delta(\mu_3' | \sigma_3) \sum_\gamma [X_\gamma^3 / \rho_{12}^5]^{1/2} f_\gamma(S_A, M_{S_A}, \mu_1 | \mu_1' \mu_2' \mu_3'; \hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha_{12}) \times \exp(iS_{12}) \quad (r_1, r_2) \rightarrow \infty, \quad (2.83)$$

where, using (2.79),

$$f_\gamma(S_A, M_{S_A}, \mu_1 | \mu_1' \mu_2' \mu_3'; \mathbf{k}_1, \mathbf{k}_2) = C(\frac{1}{2}, \frac{1}{2}, S_A; \mu_2', \mu_3', M_{S_A}) \delta_{\mu_1 \mu_1'} f_\gamma(\mathbf{k}_1, \mathbf{k}_2) + (-1)^{S_A} C(\frac{1}{2}, \frac{1}{2}, S_A; \mu_3', \mu_1', M_{S_A}) \times \delta_{\mu_1 \mu_2'} f_\gamma(\mathbf{k}_2, \mathbf{k}_1) + C(\frac{1}{2}, \frac{1}{2}, S_A; \mu_1', \mu_2', M_{S_A}) \delta_{\mu_1 \mu_3'} w_\gamma(\mathbf{k}_1, \mathbf{k}_2). \quad (2.84)$$

Defining

$$q_\gamma(\mathbf{k}_1, \mathbf{k}_2) = [2(2S_A + 1)]^{-1} \sum_{\mu_1 M_{S_A}, \mu_1' \mu_2' \mu_3'} |f_\gamma(\mu_1, S_A, M_{S_A} | \mu_1' \mu_2' \mu_3'; \mathbf{k}_1, \mathbf{k}_2)|^2,$$

the ionization cross section is given by

$$Q_\gamma(E) = \frac{2}{\pi k_0} \int_0^{x_\gamma^{2/4}} k_1 k_2 d\frac{1}{2}(k_2^2) \int q_\gamma(\mathbf{k}_1, \mathbf{k}_2) d\hat{\mathbf{k}}_1 d\hat{\mathbf{k}}_2. \quad (2.85)$$

From (2.84) it follows that

$$q_\gamma(\mathbf{k}_1, \mathbf{k}_2) = |f_\gamma(\mathbf{k}_1, \mathbf{k}_2)|^2 + |f_\gamma(\mathbf{k}_2, \mathbf{k}_1)|^2 + |w_\gamma(\mathbf{k}_1, \mathbf{k}_2)|^2 - \text{Re} [f_\gamma(\mathbf{k}_1, \mathbf{k}_2) f_\gamma^*(\mathbf{k}_2, \mathbf{k}_1)] - \text{Re} \{w_\gamma^*(\mathbf{k}_1, \mathbf{k}_2) [f_\gamma(\mathbf{k}_2, \mathbf{k}_1) + (-1)^{S_A} f_\gamma(\mathbf{k}_1, \mathbf{k}_2)]\}. \quad (2.86)$$

If the "capture" term  $w_\gamma(\mathbf{k}_1, \mathbf{k}_2)$  is assumed to be zero, then (2.85) and (2.86) reduces to the same form as for hydrogen except for a factor of 2, which arises because there are two equivalent electrons. In calculations so far on two-electron systems this has been assumed to be the case [Sloan (1965) and Rudge (1964)].

In the more general case of ionization of an atom with an outer shell of  $n$  equivalent electrons, the scattering amplitude is given by a straightforward generalization of the theory, so that

$$f(\mathbf{k}_1, \mathbf{k}_2) = -(2\pi)^{-5/2} \exp i\Delta(\mathbf{k}_1, \mathbf{k}_1) \int \Psi(\mathbf{x}_1 \cdots \mathbf{x}_{n+1}) (\mathcal{H} - E) \Phi(\mathbf{x}_1 \cdots \mathbf{x}_{n+1}) d\mathbf{x}_1 \cdots d\mathbf{x}_{n+1}, \quad (2.87)$$

antisymmetry with respect to the core electrons being ignored. Using the symmetry properties of the wave functions, the integral in (2.87) may be written

$$I = n^{1/2} \int \Psi(\mathbf{x}_2 \cdots \mathbf{x}_{n+1}; \mathbf{x}_1) (\mathcal{H} - E) [\psi(\mathbf{x}_3 \cdots \mathbf{x}_{n+1}) \{1 - P_{12}\} \{\phi_1(z_1, -\mathbf{k}_1 | \mathbf{x}_1) \phi_2(z_2, -\mathbf{k}_2 | \mathbf{x}_2)\} + (n-1) \psi(\mathbf{x}_1, \mathbf{x}_4 \cdots \mathbf{x}_{n+1}) \phi_1(z_1, -\mathbf{k}_1 | \mathbf{x}_2) \phi_2(z_2, -\mathbf{k}_2 | \mathbf{x}_3)] d\mathbf{x}_1 \cdots d\mathbf{x}_{n+1}. \quad (2.88)$$

If the radial wave functions of the initial and final bound states are assumed to be identical and are denoted by  $P_{nl}(r)/r$ , then

$$\psi(\mathbf{x}_3 \cdots \mathbf{x}_{n+1}) = \chi[l^{n-1}(\alpha_1, S_1, L_1) \hat{\mathbf{x}}_3 \cdots \hat{\mathbf{x}}_{n+1}] \prod_{i=3}^{n+1} \frac{P_{nl}(r_i)}{r_i}, \quad (2.89)$$

$$\phi_1(z_1, -\mathbf{k}_1 | \mathbf{x}_1) = \phi_1(z_1, -\mathbf{k}_1 | \mathbf{r}_1) \delta(\mu_1' | \sigma_1),$$

$$\phi_2(z_2, -\mathbf{k}_2 | \mathbf{x}_2) = \phi_2(z_2, -\mathbf{k}_2 | \mathbf{r}_2) \delta(\mu_2' | \sigma_2), \quad (2.90)$$

and

$$\Psi(\mathbf{x}_2 \cdots \mathbf{x}_{n+1}; \mathbf{x}_1) = \phi_0(\mathbf{k}_0 | \mathbf{r}_1) \prod_{i=2}^{n+1} \frac{P_{nl}(r_i)}{r_i} \delta(\mu_1 | \sigma_1) \chi \times [l^n(\alpha, S, L) \hat{\mathbf{x}}_2 \cdots \hat{\mathbf{x}}_{n+1}]. \quad (2.91)$$

In these equations  $(\alpha, S, L)$  denotes the initial term of the atom and  $(\alpha_1, S_1, L_1)$  the term of the final state of the ion.



Following Racah (1943) we can write

$$\chi[l^n(\alpha, S, L)\hat{\mathbf{x}}_2 \cdots \hat{\mathbf{x}}_{n+1}] = \sum_{\alpha', S', L'} [l^{n-1}(\alpha', S', L')lSL | \{l^n\alpha, S, L\}] \sum_{M_L, M_S; m, \mu_2} C(L', l, L; M_L, m, M) \times C(S', \frac{1}{2}, S; M_{S'}, \mu_2, M_S) Y_{lm}(\hat{\mathbf{r}}_2) \delta(\mu_2 | \sigma_2) \chi[l^{n-1}(\alpha', S', L')\hat{\mathbf{x}}_3 \cdots \hat{\mathbf{x}}_{n+1}] \quad (2.92)$$

using the usual notation for a fractional parentage coefficient. Using Eqs. (2.89)–(2.92), (2.88) may be reduced to two electron integrals. In particular if the “capture” term in (2.88) is ignored and the wave functions  $\phi_1(-\mathbf{k}_1 | \mathbf{r}_1)$ ,  $\phi_2(-\mathbf{k}_2 | \mathbf{r}_2)$  are orthogonal to  $[P_{nl}(r)/r]Y_{lm}(\hat{\mathbf{r}}_2)$ , then (2.88) reduces to

$$I = n^{1/2} [l^{n-1}(\alpha_1, S_1, L_1)lSL | \{l^n\alpha SL\}] \sum_{m, \mu_2} C(L_1, l, L; M_1, m, M) C(S_1, \frac{1}{2}, S; M_{S_1}, \mu_2, M_S) \times \{ \delta_{\mu_1 \mu_1'} \delta_{\mu_2 \mu_2'} I_1 - \delta_{\mu_2 \mu_1'} \delta_{\mu_1 \mu_2'} I_2 \}, \quad (2.93)$$

where

$$(I_1, I_2) = \int \frac{P_{nl}(r_2)}{r} \phi_0(\mathbf{k}_0 | \mathbf{r}_1) Y_{lm}(\hat{\mathbf{r}}_2) [H(1, 2) + E_f - E] \begin{cases} \phi_1(z_1, -\mathbf{k}_1 | \mathbf{r}_1) \phi_2(z_2, -\mathbf{k}_2 | \mathbf{r}_2) \\ \phi_1(z_1, -\mathbf{k}_1 | \mathbf{r}_2) \phi_2(z_2, -\mathbf{k}_2 | \mathbf{r}_1) \end{cases} d\mathbf{r}_1 d\mathbf{r}_2, \quad (2.94)$$

$H(1, 2)$  being the two-particle Hamiltonian and  $E_f$  the energy of the final state of the ion. The quantity of interest in computing the cross section is

$$[2(2L+1)(2S+1)]^{-1} \sum_{M_L M_S, M_{L_1} M_{S_1}} |I|^2 = n [l^{n-1}(\alpha_1, S_1, L_1)lSL | \{l^n\alpha SL\}]^2 \{ |I_1|^2 + |I_2|^2 - \text{Re}(I_1 I_2^*) \}. \quad (2.95)$$

Thus, in this case we again reduce to the same expression as for the ionization of hydrogen, except for the factor

$$n [l^{n-1}(\alpha_1, S_1, L_1)lSL | \{l^n\alpha SL\}]^2.$$

Summing over all  $S_1$  and  $L_1$  yields a factor of  $n$ , the number of equivalent electrons. The evaluation of (2.87) can be carried through quite readily when assumptions of orthogonality are relaxed and when the “capture” term is taken into account. This term is essential when considering ionization for example from an  $(\alpha, S, L) = P^3(^4S)$  state to an  $(\alpha_1, S_1, L_1) = P^2(^1S)$  state.

### 2.7. Threshold Laws for Single Ionization

The threshold law for ionization has been the subject of investigations by Wannier (1953), by Geltman (1956), and by Rudge and Seaton (1964).

The method used by Wannier (1953) consists of asserting that the threshold dependence of the ionization cross section is given by the rate of change of the available volume of phase space which leads to ionization. In order to compute this quantity, he considers the equations of motion for zero angular momentum classically and shows that at small energies the reaction takes place near  $\alpha = \pi/4$  and  $\theta_{12} = \pi$ . He then solves Hamilton’s equations for  $\alpha, \theta_{12}$  and their conjugate momenta by using a Taylor expansion for  $\zeta(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha_{12})$  about this point. His method then leads to a threshold dependence for ionization of atomic hydrogen given by

$$Q \propto (E - I)^{1.127}.$$

Wannier considers that the argument is not rigorous but that nevertheless the above relationship is the correct one. For the case of a hydrogenic ion with nuclear charge  $Z \rightarrow \infty$ , Wannier obtains a linear result and as-

cribes the nonlinearity of the above threshold dependence as being due to the effect of electron correlation.

The assumption of Wannier in applying classical and statistical methods is open to question and it is therefore desirable that a quantal derivation of the threshold law should be given. Such an approach was used by Rudge and Seaton (1964), who deduce that for ionization of hydrogenic systems

$$Q \propto (E - I) \quad (2.96)$$

near threshold.

Adopting pure Coulomb functions for the final state, (2.52) becomes

$$f(\mathbf{k}_1, \mathbf{k}_2) = (2\pi)^{-5/2} \exp(i\Delta(\mathbf{k}_1, \mathbf{k}_2)) \times \int \Psi \left( \frac{1-z_1}{r_1} + \frac{1-z_2}{r_2} - \frac{1}{r_{12}} \right) \chi(z_1, -\mathbf{k}_1 | \mathbf{r}_1) \times \chi(z_2, -\mathbf{k}_2 | \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (2.97)$$

At low velocities

$$\chi(z, -k | r) \propto k^{-1/2} \quad z > 0 \\ \propto k^{-1/2} \exp(-\pi/k) \quad z < 0. \quad (2.98)$$

The dominant contribution to  $f(\mathbf{k}_1, \mathbf{k}_2)$  at low velocities is therefore from the region where  $z_1 > 0$  and  $z_2 > 0$  and therefore near the threshold

$$f(\mathbf{k}_1, \mathbf{k}_2) \propto (k_1 k_2)^{-1/2},$$

provided (2.97) converges. This then leads to the threshold law (2.96).

The result (2.96) does not depend on a knowledge of the angular and energy distributions of the electrons, as was needed by Wannier in his treatment of the problem. In the result of Rudge and Seaton (1964) correlation between the outgoing electrons is accounted for through the angle dependence of the charges  $z_1$  and  $z_2$ .

In their treatment, the effect of correlation does not change the threshold law from that which arises in the case  $Z \rightarrow \infty$ , though it undoubtedly exerts some influence on the shape of the cross section near threshold. The essential difference between the two results is that Wannier predicts a zero derivative for the ionization cross section of atomic hydrogen at threshold, while Rudge and Seaton predict a finite derivative at threshold.

Earlier, Geltman (1956) also predicted a linear-threshold law but based his argument on a final-state wave function with  $z_1 = z_2 = 1$ . Such a choice does not comply with Eq. (2.51) however.

If it were incorrectly assumed that the choice  $z_1 = 0, z_2 = 1$  yielded a proper expression for the scattering amplitude (this being frequently adopted and referred to as "Born's approximation"), then the threshold law would be

$$Q \propto (E-I)^{3/2}.$$

A classical analysis of near-threshold ionization of atomic hydrogen, similar to the work of Wannier, has been carried out by Vinkalns and Gailitis (1967), who deduce that there is a departure from linearity of about 1%. The work of Rudge and Seaton (1964) has been criticized by Temkin (1964) on the basis that the asymptotic form (2.24) is not valid at  $\theta_{12} = 0$ ; he derives a  $\frac{3}{2}$  power law for a model problem and infers that this is the correct result for  $e$ -H ionization threshold behavior.

For detachment from negative ions the situation is different. Here the only Coulomb potential operating in the final state is the repulsion between the two free electrons or, for detachment by positron impact (for example), there is a Coulomb attraction between the two free particles. In this case the threshold laws are [Rudge (1964), Hart, Gray, and Guier (1957)]

$$Q \propto (E-I)^{3/2} \quad (2.99)$$

for detachment from a negative ion by a positively charged particle and

$$Q \propto (E-I)^{3/2} \exp -[\gamma \cdot (E-I)^{-1/2}], \quad (2.100)$$

where  $\gamma$  is a constant, for detachment from a negative ion by a negatively charged particle.

Little has been predicted theoretically about the range of validity of threshold laws. The linear law for example states that the first derivative of the ionization cross section is nonvanishing at threshold but does not say what the relative magnitudes of the first to higher derivatives are in the near-threshold region.

## 2.8. Multiple Ionization

The simplest case to consider is the double ionization of helium. Consideration has been given to this problem by Peterkop (1961, 1965). The theory may be extended in an obvious manner to the case of double ionization and the integral expression for this case will take the form

$$2^{-1/2} f(\mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_1) = (2\pi)^{-4} \exp [i\Delta(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)] \int \Psi(\mathbf{r}_2, \mathbf{r}_3; \mathbf{r}_1) (\mathcal{H}C - E) \phi_1(z_1, -\mathbf{k}_1 | \mathbf{r}_1) \\ \times \phi_2(z_2, -\mathbf{k}_2 | \mathbf{r}_2) \phi_3(z_3, -\mathbf{k}_3 | \mathbf{r}_3) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3, \quad (2.101)$$

where

$$\frac{z_1}{k_1} + \frac{z_2}{k_2} + \frac{z_3}{k_3} = \frac{2}{k_1} + \frac{2}{k_2} + \frac{2}{k_3} - |\mathbf{k}_1 - \mathbf{k}_2|^{-1} - |\mathbf{k}_1 - \mathbf{k}_3|^{-1} - |\mathbf{k}_2 - \mathbf{k}_3|^{-1} \quad (2.102)$$

and

$$\Delta(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) = \frac{2z_1}{k_1} \ln \left( \frac{k_1}{X} \right) + \frac{2z_2}{k_2} \ln \left( \frac{k_2}{X} \right) + \frac{2z_3}{k_3} \ln \left( \frac{k_3}{X} \right). \quad (2.103)$$

Making use of the symmetry of the initial state and introducing spin variables, it follows that

$$2^{-1/2} f(S_A, M_{S_A}, \mu_1; \mu_1' \mu_2' \mu_3' | \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) = \delta_{\mu_1 \mu_1'} C(\frac{1}{2}, \frac{1}{2}, S_A; \mu_2', \mu_3', M_{S_A}) f(\mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_1) + \delta_{\mu_1 \mu_2'} C(\frac{1}{2}, \frac{1}{2}, S_A; \mu_3', \mu_1', M_{S_A}) \\ \times f(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) + \delta_{\mu_1 \mu_3'} C(\frac{1}{2}, \frac{1}{2}, S_A; \mu_1', \mu_2', M_{S_A}) f(\mathbf{k}_3, \mathbf{k}_1, \mathbf{k}_2). \quad (2.104)$$

Defining

$$q(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) = [2(2S_A + 1)]^{-1} \sum_{\mu_1 M_{S_A}, \mu_1' \mu_2' \mu_3'} |f|^2, \quad (2.105)$$

it is found that

$$q(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) = 2 \{ |f(\mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_1)|^2 + |f(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)|^2 + |f(\mathbf{k}_3, \mathbf{k}_1, \mathbf{k}_2)|^2 - (-1)^{S_A} \\ \times \text{Re} [f(\mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_1) f^*(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) + f(\mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_1) f^*(\mathbf{k}_3, \mathbf{k}_1, \mathbf{k}_2) + f(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) f^*(\mathbf{k}_3, \mathbf{k}_1, \mathbf{k}_2)] \}. \quad (2.106)$$

As in the case of single ionization the cross-section expression must represent the number of ions formed in the final state; or equivalently we can say that only the electron current corresponding to all possible relative momenta of the three electrons must be counted. Defining

$$\sigma(k_1, k_2, k_3) = \int q(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) d\hat{\mathbf{k}}_1 d\hat{\mathbf{k}}_2 d\hat{\mathbf{k}}_3, \quad (2.107)$$

we can write the double-ionization cross section in two equivalent forms. The first of these is

$$Q(E) = (\pi k_0)^{-1} \int_0^{E/3} k_3 d(\frac{1}{2}k_3^2) \times \int_{(1/2)k_3^2}^{(1/4)(2E-k_3^2)} k_2 \sigma(k_1, k_2, k_3) d(\frac{1}{2}k_2^2), \quad (2.108)$$

the limits of integration ensuring that  $k_3^2 \leq k_2^2 \leq k_1^2$ . The second form is

$$Q(E) = (\pi 3! k_0)^{-1} \int_0^E k_3 d(\frac{1}{2}k_3^2) \times \int_0^{E-(1/2)k_3^2} k_2 \sigma(k_1, k_2, k_3) d(\frac{1}{2}k_2^2). \quad (2.109)$$

The only restriction placed on the limits of integration in (2.109) are those arising from energy conservation. Included therefore is a sum over  $3!$  permutations of the momenta which correspond to identical events. A division by  $3!$  is therefore included in (2.109) and in general for an  $n$ -fold ionization the corresponding expression to (2.109) must include a factor of  $1/(n+1)!$  (Peterkop, 1961).

### 3. QUANTAL APPROXIMATIONS

Most of the essential features of the various quantal approximations which have been used may be discussed for the particular case of the ionization of atomic hydrogen. In this case, quantal approximations for the scattering amplitude consist in making a choice of the functions  $\Psi$  and  $\Phi$  of Eq. (2.52). This equation however, depends on equation (2.51) being satisfied, in which case the phase factor  $\Delta(\mathbf{k}_1, \mathbf{k}_2)$  is defined through (2.53). In many methods which have been used to calculate ionization cross sections, (2.51) is not satisfied and hence in these cases approximations are made to this phase as well as to the functions appearing in the integral expression (2.52). In describing each approximation therefore we list the  $\Psi$ ,  $\Phi$ , and  $\Delta(\mathbf{k}_1, \mathbf{k}_2)$  which when used in (2.52) give rise to each approximate scattering amplitude.

#### 3.1. Born Approximations

The usual interpretation of "Born's approximation," as applied for example to excitation problems, is that separable wave functions are used, which correctly

describe all the long-range forces, and that the effects of exchange are ignored. In work on ionizing collisions however the phrase "Born's approximation" has been used where this is not the case, but rather the choice  $z_1=0, z_2=1$  has been adopted. Thus for atomic hydrogen the method consists in adopting the approximations

$$\begin{aligned} \Psi_B &= \psi(0 | \mathbf{r}_2) \exp(i\mathbf{k}_0 \cdot \mathbf{r}_1), \\ \Phi_B &= \chi(1, -\mathbf{k}_2 | \mathbf{r}_2) \exp(-i\mathbf{k}_1 \cdot \mathbf{r}_1), \\ \Delta(\mathbf{k}_1, \mathbf{k}_2) &= 0. \end{aligned} \quad (3.1)$$

This gives

$$f_B(\mathbf{k}_1, \mathbf{k}_2) = (2\pi)^{-5/2} \int \psi(0 | \mathbf{r}_2) \exp(i\mathbf{k}_0 \cdot \mathbf{r}_1) \times [ (r_1)^{-1} - (r_{12})^{-1} ] \chi(1, -\mathbf{k}_2 | \mathbf{r}_2) \exp(-i\mathbf{k}_1 \cdot \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2. \quad (3.2)$$

The choice  $z_1=0, z_2=1$  is not a serious defect at high energies, since with increasing energy it is found that the main contribution to the cross section comes increasingly from the region where  $k_2$  is small and  $k_1$  is large. At sufficiently high energies therefore Born's approximation becomes exact but at very low energies (Sec. 2.7) gives rise both to substantial errors in the cross section and an incorrect threshold behavior.

The second feature of Born's approximation, the neglect of exchange, has also been treated rather differently in work on ionizing collisions from what it has been in problems of excitation. Referring to Eq. (2.72) we see that "neglecting exchange" means that all terms involving  $f(\mathbf{k}_2, \mathbf{k}_1)$  should be excluded to give the expression

$$Q[\text{Born (b)}] = (\pi k_0)^{-1} \int_0^{E/2} k_1 k_2 d(\frac{1}{2}k_2^2) \times \int d\hat{\mathbf{k}}_1 d\hat{\mathbf{k}}_2 |f_B(\mathbf{k}_1, \mathbf{k}_2)|^2. \quad (3.3)$$

However an expression frequently used has been

$$Q[\text{Born (a)}] = (\pi k_0)^{-1} \int_0^E k_1 k_2 d(\frac{1}{2}k_2^2) \times \int d\hat{\mathbf{k}}_1 d\hat{\mathbf{k}}_2 |f_B(\mathbf{k}_1, \mathbf{k}_2)|^2. \quad (3.4)$$

Equation (3.4) is the correct expression to use if we are dealing with ionization involving distinguishable particles. In the case of ionization by electron impact, with random spin orientations, (3.4) would correspond to neglecting only the interference term of (2.72) while retaining the  $|g(\mathbf{k}_1, \mathbf{k}_2)|^2 = |f(\mathbf{k}_2, \mathbf{k}_1)|^2$  term. This procedure is clearly inconsistent and Eq. (3.3) is the more acceptable definition. The Born (b) approximation should therefore be used if exchange is to be neglected and will always yield a better result in those circumstances when, as is usually the case, the effects of

exchange are to reduce the cross section. In Fig. 1 the two approximations are compared for the cases of ionization of atomic hydrogen [Rudge and Seaton (1965)] from its ground state, a curve representing a mean of the experimental measurements of Fite and Brackmann (1958), Boksenberg (1960), and Rothe *et al.* (1963) being also shown, and in Fig. 2 the same comparison is shown for ionization of helium from its ground state [Sloan (1965)].

In the case of ionization of a hydrogenic positive ion of nuclear charge  $Z$  by electron impact, the appropriate expression for  $f_B$  is

$$f_B(\mathbf{k}_1, \mathbf{k}_2) = (2\pi)^{-5/2} \int \psi(0 | \mathbf{r}_2) \chi(Z-1, \mathbf{k}_0 | \mathbf{r}_1) \\ \times [ (r_1)^{-1} - (r_{12})^{-1} ] \chi(Z, -\mathbf{k}_2 | \mathbf{r}_2) \\ \times \chi(Z-1, -\mathbf{k}_1 | \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2. \quad (3.5)$$

The phrase ‘‘Coulomb–Born’’ approximation is appropriate to this case to distinguish it from calculations where plane waves have been used to describe the incident and scattered electrons. This latter treatment is very unsatisfactory at low and intermediate energies but becomes equal to (3.5) at high energies. In no circumstances may plane waves be used to describe the ejected electron.

Recent calculations in the Born (a) approximation have been reported by Omidvar (1965) for ionization of hydrogen from an initial state with principal quantum number  $n$  running from 1–10; for  $\text{He}^+$  in the  $1s$  and  $2s$  states by Burke and Taylor (1965); for helium in the ground state by Peach (1965) and by Dalgarno and McDowell (1956), the latter authors calculating also cross sections for excited states of the helium ion with  $(n, l) = 2p, 3p, 4p, 3d, 4d$ ; for Li by McDowell *et al.* (1965) and by Peach (1965); for Be by Peach (1965); for Ne by Inokuti (1961). Inner-shell ionization of Ni, Ag, and Hg in the Born approximation neglecting relativistic effects have been calculated by Burhop (1940). Arthurs and Moiseiwitsch (1958) have included relativistic effects in calculating the inner-shell

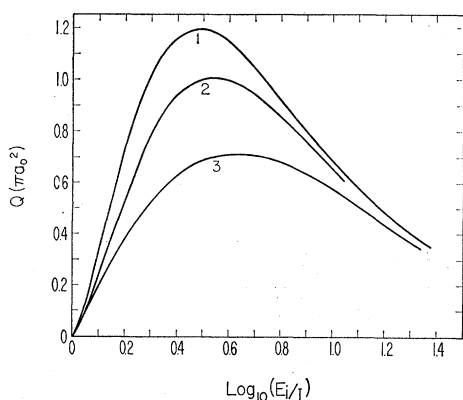


FIG. 1. Ionization cross sections for  $\text{H}(1s)$  comparing (1) the Born (a) and (2) the Born (b) approximation [Rudge and Seaton (1965)] with (3) ‘‘experimental’’ data.

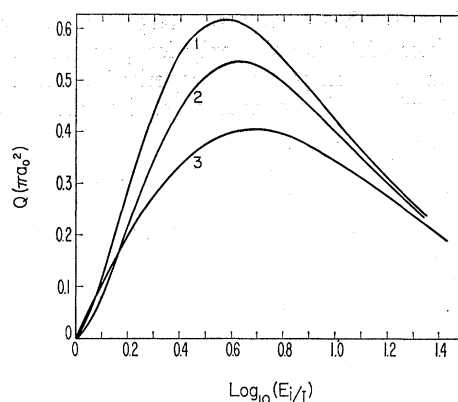


FIG. 2. Ionization cross sections for  $\text{He}(1s^2)$  comparing (1) the Born (a) and (2) the Born (b) approximation [Sloan (1965)] with (3) ‘‘experimental’’ data.

ionization of Ni, and Perlman (1960) has similarly calculated inner-shell ionization of Ni and Hg.

The Born (b) approximation has been used for ionization of the following species by the authors indicated:  $\text{H}(1s)$  [Rudge and Seaton (1965)];  $\text{H}(2s)$ ,  $\text{He}^+(1s)$ , and  $\text{He}^+(2s)$  [Rudge and Schwartz (1966a)];  $\text{Fe}^{XV}$  and  $\text{Fe}^{XVI}$  [Rudge and Schwartz (1966b)]; He, Li, Be [Peach (1965)]; and Na [Bates *et al.* (1965)].

In all the calculations of ionization of nonhydrogenic systems, further approximations are involved in the description of the bound-state wave functions and the wave functions for the ejected electron.

### 3.2. The Bethe Approximation

The Bethe approximation [Bethe (1930)] is a simple version of the Born approximation, its chief usefulness lying in the fact that it allows a determination to be made of the form of the ionization cross section at high energies. The principal features of the approximation may be seen by examining the case of atomic hydrogen. Performing the integration in (3.2) gives

$$f_{\text{Born}}(\mathbf{k}_1, \mathbf{k}_2) = (-2^{-1/2} \pi^{-3/2} / q^2) \langle 0 | \exp(i\mathbf{q} \cdot \mathbf{r}) | -\mathbf{k}_2 \rangle, \quad (3.6)$$

where  $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}_1$  and we define the notation

$$\langle 0 | \exp(i\mathbf{q} \cdot \mathbf{r}) | -\mathbf{k}_2 \rangle = \int \psi(0 | \mathbf{r}) \\ \times \exp(i\mathbf{q} \cdot \mathbf{r}) \chi(1, -\mathbf{k}_2 | \mathbf{r}_2) d\mathbf{r}.$$

Expanding  $\exp(i\mathbf{q} \cdot \mathbf{r})$  as a power series, using orthogonality, and assuming  $q$  small, we obtain the result that

$$f_{\text{Bethe}}(\mathbf{k}_1, \mathbf{k}_2) = (-2^{-1/2} \pi^{-3/2} i / q) \langle 0 | z | -\mathbf{k}_2 \rangle, \quad (3.7)$$

where  $\hat{\mathbf{q}}$  is taken as the quantization axis. Transforming the  $\hat{\mathbf{k}}_1$  integration of (3.3) to one over  $q$  gives the ionization cross section as

$$Q_{\text{Bethe}} = \frac{\pi^{-3}}{k_0^2} \int_0^{E/2} k_2 d(\frac{1}{2} k_2^2) \int_{q_{\text{min}}}^{q_{\text{max}}} \frac{dq}{q} \int d\hat{\mathbf{k}}_2 | \langle 0 | z | -\mathbf{k}_2 \rangle |^2. \quad (3.8)$$

In (3.8)  $q_{\min}=k_0-k_1$  and the largest value of  $q$  is  $k_0+k_1$ . Since (3.7) is valid only for  $q$  small, the value of  $q_{\max}$  in (3.8) may more properly be taken to be  $\tau(k_0+k_1)$ , where  $\tau$  is a constant less than unity, to give

$$Q = \frac{\pi^{-3}}{k_0^2} \int_0^{E/2} \ln \frac{\tau(k_0+k_1)}{k_0-k_1} |\langle 0 | z | -\mathbf{k}_2 \rangle|^2 d\mathbf{k}_2. \quad (3.9)$$

Since the main contribution to (3.9) arises from the region where  $k_2$  is small, we may approximate further by writing

$$k_0^2 - k_1^2 \simeq 2I, \quad (3.10)$$

where  $I$  is the ionization potential, so that

$$\begin{aligned} (k_0 - k_1) &\simeq 2I / (k_0 + k_1) \\ &\simeq I / k_0, \end{aligned} \quad (3.11)$$

and (3.9) becomes

$$Q_{\text{Bethe}} = \frac{\pi^{-3}}{k_0^2} \ln \left( \frac{2\tau k_0^2}{I} \right) \int_0^{E/2} |\langle 0 | z | -\mathbf{k}_2 \rangle|^2 d\mathbf{k}_2. \quad (3.12)$$

Writing  $E_i = 1/2k_0^2$ , (3.12) takes the form

$$Q = A \ln E_i / E_i + B / E_i, \quad (3.13)$$

where

$$\begin{aligned} A &= \frac{1}{2} \pi^{-3} \int_0^{E/2} |\langle 0 | z | -\mathbf{k}_2 \rangle|^2 d\mathbf{k}_2, \\ B &= A \ln (4\tau / I) + \text{const.} \end{aligned} \quad (3.14)$$

The additional constant in (3.14) arises from the neglected terms in approximating (3.6) by (3.7). The constant  $A$  thus depends on the optical properties of the atom and can fairly readily be evaluated, but the constant  $B$  depends on a full Born calculation since it is determined through the cut-off parameter  $\tau$  and the neglected terms. Using sum rules proved by Bethe (1930) and averaging over the  $m$  states, the constant  $A$  may be written (for large  $E$ )

$$A = \frac{4}{3} \left[ \langle r_{nl}^2 \rangle_{\text{Av}} - \sum_{n'} \left\{ \frac{l+1}{2l+1} (R_{n,l}{}^{n',l+1})^2 + \frac{l}{2l+1} (R_{n,l}{}^{n',l-1})^2 \right\} \right], \quad (3.15)$$

where

$$\psi(0 | \mathbf{r}) = R_{n,l}(r) Y_{lm}(\hat{\mathbf{r}}), \quad (3.16)$$

$$R_{nl}{}^{n'l'} = \int_0^\infty r^3 R_{nl}(r) R_{n'l'}(r) dr, \quad (3.17)$$

and

$$\langle r_{nl}^2 \rangle_{\text{Av}} = \int_0^\infty r^4 R_{nl}(r) R_{nl}(r) dr. \quad (3.18)$$

Alternatively, we may write

$$A = 4 \left[ \frac{1}{3} \langle r_{nl}^2 \rangle_{\text{Av}} - \sum_{n'l'} \frac{\bar{f}_{n'l, nl}}{2 | E_n - E_{n'} |} \right], \quad (3.19)$$

where  $\bar{f}_{n'l, nl}$  is the average oscillator strength defined by Bethe and Salpeter (1957). In both (3.15) and (3.19) the sums over  $n'$  include  $n=n'$ .

The Bethe approximation may also be derived for ionization of ions. In this case an equivalent method may be used [Seaton (1962)], which replaces  $(1/r_1 - 1/r_{12})$  in (3.5) by  $-(r_2/r_1^2) P_1(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$ . The only essential difference which arises is in the "Gaunt factor"  $\ln \tau(k_0+k_1)(k_0-k_1)$  appearing in (3.14). This becomes modified due to the charge on the ion, and formulas for the appropriate "Gaunt factor" in this case are given by Grant (1958).

The Bethe theory applies equally to complex atoms when the appropriate formula for  $A$  is

$$A = 4 \left[ \frac{1}{3} \langle (\sum_i \mathbf{r}_i)^2 \rangle_{\text{Av}} - \sum_{n'l'} \frac{\bar{f}_{n'l, nl}}{2 | E_n - E_{n'} |} \right]. \quad (3.20)$$

In the case of  $\text{H}^-$  for example it follows from (3.20) that the constant  $A$  corresponding to the total detachment cross section is  $\frac{4}{3} \langle (\mathbf{r}_1 + \mathbf{r}_2)^2 \rangle_{\text{Av}}$  and is large. In the case of the alkali metals on the other hand the predominant contribution to the sum over oscillator strengths in (3.20) arises from the resonance levels and in these cases  $A$  may be expected to be small. In the case of hydrogen  $A$  decreases with increasing  $l$  for given  $n$  [Bethe (1930)] but averaged over  $l$  is proportional to  $n$  [Kingston (1965b)].

It is often convenient to write the Bethe formula in terms of the photoionization cross section  $a(W)$ , where  $W$  is the energy of the ejected electron. Equation (3.9) may then be expressed in the form [Seaton (1959)]

$$Q_{\text{Bethe}}(E) = \frac{I_{\text{H}}}{\pi \alpha E} \int_0^{E/2-I} \frac{a(W)}{I+W} \ln \left( \frac{4E\tau}{I+W} \right) dW, \quad (3.21)$$

$\alpha$  being the fine-structure constant. The constant  $A$  may then be expressed as

$$A = I_{\text{H}} / \pi \alpha \int_0^\infty \frac{a(W) dW}{I+W}. \quad (3.22)$$

The above and (3.20) are not always equivalent. Thus (3.20) represents the total continuum contribution to the sum rule including, therefore, multiple-ionization processes. The above expression for  $A$  does not include multiple-ionization processes if  $a(W)$  is taken to be the single photoionization cross section. Only in unusual circumstances does the Bethe theory yield good estimates of the ionization cross section. A useful procedure has been given by Seaton (1959) however based on the Bethe theory which allows reasonable estimates of ionization cross sections to be made. Referring to (3.21) it can be seen that if we have two atoms  $A$  and  $B$  whose photoionization cross sections have the same slope then, in the Bethe approximation,

$$I_A Q_A(E) / a_A(0) = I_B Q_B(E) / a_B(0). \quad (3.23)$$

Equation (3.23) is a useful relation since it involves ratios which may be quite accurate even though the

individual cross sections may be a good deal less so. Equation (3.23) is of most value when considering ionization of systems where there is a substantial contribution from the optically allowed transitions to the continuum. Such cases include, for example, the inert gases or detachment from negative ions but not ionization of the alkalis. The relationships (3.23) has been used by Seaton (1959) to calculate ionization cross sections for Ne, O, and N, and McDowell and Williamson (1964) have used the Bethe approximation [Eq. (3.21)] to calculate the detachment cross section for  $H^-$ .

### 3.3. The Born–Oppenheimer Approximation

In this approximation, exchange is taken into account by adopting the following expression for the scattering amplitudes:

$$f(S | \mathbf{k}_1, \mathbf{k}_2) = -(2\pi)^{-5/2} \int \Psi_B(\mathbf{r}_1, \mathbf{r}_2) (\mathcal{H} - E) \times [\Phi_B(\mathbf{r}_1, \mathbf{r}_2) + (-1)^S \Phi_B(\mathbf{r}_2, \mathbf{r}_1)] d\mathbf{r}_1 d\mathbf{r}_2. \quad (3.24)$$

The ionization cross section is then obtained through use of (2.69) and (2.71). From (2.71) it is seen that  $k_1 \geq k_2$ , and so in this approximation the faster electron is taken to be completely screened by the slower one. In other words Eq. (2.51) is approximately satisfied by excluding, in an expansion of  $1/|\mathbf{k}_1 - \mathbf{k}_2|$  in a series of Legendre polynomials, all terms other than the first. The approximation is inherently bad however, owing to the fact that  $\Psi_B(\mathbf{r}_1, \mathbf{r}_2)$  and  $\Phi_B(\mathbf{r}_2, \mathbf{r}_1)$  are not orthogonal. The lack of orthogonality means, for example, that if a constant were added to the Hamiltonian (corresponding to a zero force), the cross section calculated in this approximation would change, a situation which is clearly absurd [Schiff (1952)]. Numerically it is confirmed that, for example, in calculating an ionization cross section from an initial atomic  $s$  state in the Born–Oppenheimer approximation, contributions to the cross section arising from  $s$  states of the scattered electron are spuriously large. A fairly typical result in this approximation is shown in Fig. 3. Equation (3.24) is a poor approximation, although Burke and Taylor (1965) show that the method is much better in the case of ionization of positive ions than it is for neutral species. Some improvement may be effected by replacing  $\Phi_B(\mathbf{r}_2, \mathbf{r}_1)$  in (3.24) by

$$\Phi(\mathbf{r}_2, \mathbf{r}_1) = \Phi_B(\mathbf{r}_2, \mathbf{r}_1) - \psi(0 | \mathbf{r}_2) \int \Phi_B(\mathbf{r}_2, \mathbf{r}_1) \psi(0 | \mathbf{r}_2) d\mathbf{r}_2. \quad (3.25)$$

The Born–Oppenheimer approximation has been used by Burke and Taylor (1965) for calculating the ionization cross sections of  $H(1s)$ ,  $H(2s)$ ,  $He^+(1s)$ , and  $He^+(2s)$ , by Trefftz (1963) for  $O^{+5}$ , by Malik and Trefftz (1961) for  $O^{+4}$ , and by Geltman (1960) for  $H^-$ .

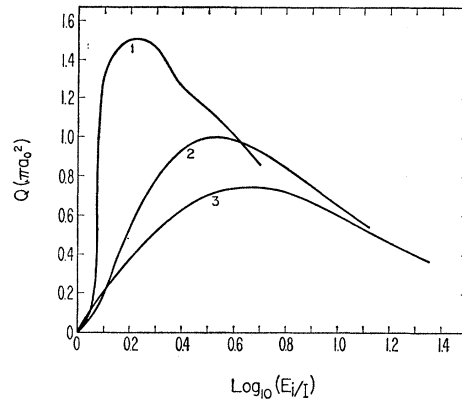


FIG. 3. Ionization cross section for  $H(1s)$  comparing (1) the Born–Oppenheimer approximation [Burke and Taylor (1965)] with (2) the Born (b) approximation [Rudge and Seaton (1965)] and (3) “experimental” data.

### 3.4. The Born–Exchange Approximation

In the Born approximation to the scattering amplitude there are no orthogonality difficulties. An alternative approximation to the Born–Oppenheimer method therefore is to make use of Eq. (2.77), which relates the exact direct and exchange amplitudes. Although by using the Born-approximation Eq. (2.51) is not satisfied, a reasonable procedure is to make use of Eq. (2.77) for the magnitudes of the respective scattering amplitudes and introduce a phase factor into the relationship, so that the approximation reads

$$g_{B-E}(\mathbf{k}_1, \mathbf{k}_2) = \exp [i\tau(\mathbf{k}_1, \mathbf{k}_2)] f_{\text{Born}}(\mathbf{k}_2, \mathbf{k}_1). \quad (3.26)$$

Two distinct approximations are apparent in this method therefore, one for the magnitude of  $g(\mathbf{k}_1, \mathbf{k}_2)$  and the other for its phase relative to that of  $f(\mathbf{k}_1, \mathbf{k}_2)$ . The method is an improvement over the Born–Oppenheimer approximation in that there are no orthogonality difficulties, but it suffers from the inaccuracies inherent in adopting the Born approximation for  $f(\mathbf{k}_1, \mathbf{k}_2)$  and these are likely to be greatest where  $k_2 > k_1$ , which is the region where (3.26) is applied. Thus  $g(\mathbf{k}_1, \mathbf{k}_2)$  calculated from (3.26) may not be accurate nor should it be very inaccurate. The choice of  $\tau(\mathbf{k}_1, \mathbf{k}_2)$  decides the value of  $|g|^2 - \text{Re}(fg^*)$ , and so the approximation is most useful in those circumstances in which the choice of  $\tau(\mathbf{k}_1, \mathbf{k}_2)$  leads to compensation of errors. We mention three possible choices which have been made for this phase factor. The first of these, suggested by Peterkop [1962(a)], is to define

$$\tau_1(\mathbf{k}_1, \mathbf{k}_2) = \arg f(\mathbf{k}_1, \mathbf{k}_2) - \arg f(\mathbf{k}_2, \mathbf{k}_1). \quad (3.27)$$

This corresponds to maximum interference and therefore gives the smallest cross section in any approximation for  $f$ .

A second choice which has been frequently used [Peterkop (1962a), Geltman, Rudge, and Seaton

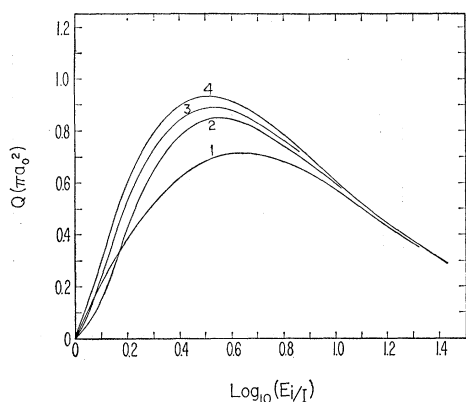


FIG. 4. Ionization cross sections for H(1s) in the Born-exchange approximation: (1) "experimental" curve, (2) Born-exchange with phase factor (3.27) [Peterkop (1962)], (3) Born-exchange results of Rudge and Schwartz [1966(a)], (4) Born-exchange with phase factor (3.28) [Geltman *et al.* (1963)].

(1963), and Sloan (1965)] is to define

$$\tau_2(\mathbf{k}_1, \mathbf{k}_2) = \arg \Gamma(1 - iZ/k_1) - \arg \Gamma(1 - iZ/k_2), \quad (3.28)$$

where  $Z$  is the net change on the new ion produced (unity for hydrogen).

A third choice, which is useful when partial-wave expansions are used, has been described by Burgess and Rudge (1963) and by Rudge and Schwartz [1966(a)].

In Fig. 4, we compare the three approximations for the case of ionization of atomic hydrogen from its ground state. Figure 5 shows the results of Sloan (1965) for ionization of helium using the phase choice (3.28) and in Fig. 6 we show the results of Rudge and Schwartz [1966(a)] for He<sup>+</sup> using the third phase choice.

It can be seen that the Born-exchange method gives a substantial improvement over Born calculations. This indicates the importance of including exchange in calculating ionization cross sections. The Born-exchange method, with various choices of  $\tau(k_1, k_2)$  has been used by Peterkop [1962(a)] and Geltman, Rudge, and

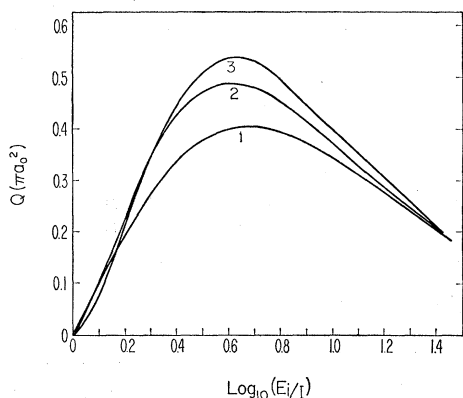


FIG. 5. Ionization cross sections for He(1s<sup>2</sup>) showing: (1) experiment, (2) Born-exchange with phase factor (3.28) [Sloan (1965)], (3) Born (b) [Sloan (1965)].

Seaton (1963) for ionization of H(1s), by Rudge and Schwartz [1966(a), (b)] for H(2s), He<sup>+</sup>(1s), He<sup>+</sup>(2s), Fe<sup>XV</sup>, and Fe<sup>XVI</sup>, by Sloan (1965) for He(1s<sup>2</sup>), and by Peach [1966(a), (b)] for ionization of He, Li, Be, Na, and Mg from their ground states.

### 3.5. The Born-Ochkur Approximation

In this approximation, an alternative expression is sought for the exchange-scattering amplitude, while again retaining the Born approximation for the direct-scattering amplitude. A number of different formulas have been proposed, the first is an expression given by Ochkur (1964) appropriate to excitation problems and the second, another formula by Ochkur (1965) appropriate to ionization problems. The expression of Ochkur for excitation has been modified by Rudge (1965), who derives a third expression by a different argument.

Ochkur (1964) and (1965) argues that the Oppenheimer expression for the exchange scattering amplitude [Eq. (3.24)] is correct at high energies and asserts that it is therefore better to retain just the leading term in an expansion of  $g_{B.O.}(\mathbf{k}_1, \mathbf{k}_2)$  in power of  $1/k_0$  rather

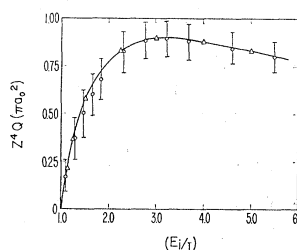


FIG. 6. Reduced ionization cross section for He<sup>+</sup>(1s) in the "Born-exchange" approximation [Rudge and Schwartz (1966(a))] compared with experimental data [Dolder *et al.* (1961)].

than use the full Oppenheimer expression. In the case of excitation he deduces, by this procedure, the result that for neutral species

$$g_{Och}^{(1)} = (q^2/k_0^2)f_{Born} \quad (3.29)$$

(where  $q = \mathbf{k}_0 - \mathbf{k}_1$ ). Using expression (3.29) for certain singlet-triplet transitions in helium, Ochkur (1964) obtained good results. In the case of ionization Prasad (1965) has adopted the results (3.29), and refers to this as the Born-Ochkur approximation, but Ochkur himself (1965) in extending his analysis to the ionization case deduces the expression

$$g_{Och}^{(2)}(\mathbf{k}_1, \mathbf{k}_2) = (q^2/|\mathbf{k}_0 - \mathbf{k}_2|^2)f_{Born}(\mathbf{k}_1, \mathbf{k}_2). \quad (3.30)$$

Ochkur (1965) further simplifies the result (3.30) by replacing  $|\mathbf{k}_0 - \mathbf{k}_2|^2$  by  $(k_0^2 - k_2^2)$  to give a third approximation

$$g_{Och}^{(3)}(\mathbf{k}_1, \mathbf{k}_2) = [q^2/(k_0^2 - k_2^2)]f_{Born}(\mathbf{k}_1, \mathbf{k}_2). \quad (3.31)$$

He argues that (3.31) should differ inappreciably from the result (3.30).

The derivation of Ochkur's results is of an *ad hoc* nature and it is not altogether clear why it yields a

marked improvement over the Born–Oppenheimer method. The  $1/r$  term in the Born–Oppenheimer method which gives a large contribution due to the nonorthogonality of the initial and final states has simply been discarded in this approach. This probably accounts for some of the improvement, but in, for example, the problem of proton–hydrogen atom, charge transfer, the discarding of this term leads to worse results rather than improved ones [Bates and Dalgarno (1952)]. It is therefore desirable to reexamine the approximations from a variational standpoint and find what approximate wave functions yield results which are similar to those of Ochkur. With regard to the excitation problem Rudge (1965) found that a trial function for the final state could be found which was orthogonal to the initial state and gave a result similar to (3.29), viz.,

$$g = [q^2 / (k_1^2 - iI^{1/2})^2] f_{\text{Born}}, \quad (3.32)$$

where  $I$  is the ionization potential of the initial state. Similar, but not identical, considerations apply to the ionization problem. The result (3.30) can be regarded as a modification of the Born–exchange method. We consider the scattering amplitude based on the trial functions

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2) &= \psi(0 | \mathbf{r}_2) \exp(i\mathbf{k}_0 \cdot \mathbf{r}_1), \\ \Phi(\mathbf{r}_1, \mathbf{r}_2) &= -\chi(z_2, -\mathbf{k}_2 | \mathbf{r}_2) \\ &\quad \times \frac{\nabla_1^2 [\chi(z_1, -\mathbf{k}_1 | \mathbf{r}_1) \exp(i\mathbf{k}_0 \cdot \mathbf{r}_1)]}{\exp(i\mathbf{k}_0 \cdot \mathbf{r}_1) |\mathbf{k}_0 - \mathbf{k}_1|^2}. \end{aligned} \quad (3.33)$$

With  $\Delta(\mathbf{k}_1, \mathbf{k}_2) = 0$  we then have the result that

$$\begin{aligned} f(\mathbf{k}_1, \mathbf{k}_2) &= -(2\pi)^{-5/2} \int \Phi(\mathcal{H}C - E) \Psi d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{-2^{-1/2} \pi^{-3/2}}{|\mathbf{k}_0 - \mathbf{k}_1|^2} \int \psi(0 | \mathbf{r}) \chi(z_2, -\mathbf{k}_2 | \mathbf{r}) \\ &\quad \times [\chi(z_1, -\mathbf{k}_1 | \mathbf{r}) \exp(i\mathbf{k}_0 \cdot \mathbf{r}) - \chi(z_1, -\mathbf{k}_1 | 0)] d\mathbf{r}. \end{aligned} \quad (3.34)$$

With the choice  $z_2 = 1, z_1 = 0$ , we regain the Born approximation, but with the more physical choice

$$\begin{aligned} z_2 &= 1; & z_1 &= 0 & \text{if } k_2 < k_1, \\ z_2 &= 0; & z_1 &= 1 & \text{if } k_2 > k_1, \end{aligned}$$

we obtain the result that

$$\begin{aligned} f(\mathbf{k}_1, \mathbf{k}_2) &= f_{\text{Born}}(\mathbf{k}_1, \mathbf{k}_2), \quad \text{if } k_1 > k_2 \\ &= [|\mathbf{k}_0 - \mathbf{k}_2|^2 / |\mathbf{k}_0 - \mathbf{k}_1|^2] f_{\text{Born}}(\mathbf{k}_2, \mathbf{k}_1), \quad \text{if } k_1 < k_2, \end{aligned} \quad (3.35)$$

provided that the terms arising from the nonorthogonality of  $\chi(z_2, -\mathbf{k}_2 | \mathbf{r}_2)$  and  $\psi(0 | \mathbf{r}_2)$  are ignored. The

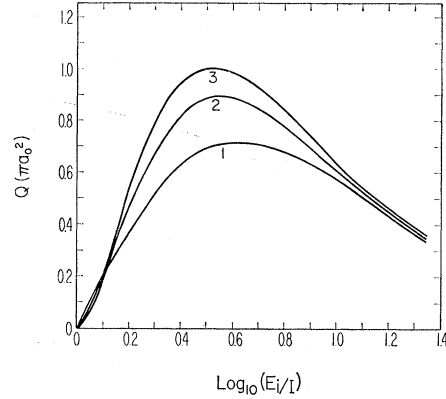


FIG. 7. Ionization cross section for H(1s) (1) “experiment,” (2) Born–Ochkur [Ochkur (1965)], and (3) Born (b) [Rudge and Seaton (1965)].

exchange–scattering amplitude is then given by

$$\begin{aligned} g(\mathbf{k}_1, \mathbf{k}_2) &= f(\mathbf{k}_2, \mathbf{k}_1) \\ &= [q^2 / |\mathbf{k}_0 - \mathbf{k}_2|^2] f_{\text{Born}}(\mathbf{k}_1, \mathbf{k}_2), \end{aligned} \quad (3.36)$$

where  $k_2 > k_1$ . This is in accord therefore with Eq. (3.30). The above derivation shows that (3.30) may be justified approximately, but that more correctly in the exchange term  $\chi(z_2, -\mathbf{k}_2 | \mathbf{r}_2)$  should be orthogonalized to  $\psi(0 | \mathbf{r}_2)$  and that then the result shows the best features of the Born–Oppenheimer and Born–exchange methods, viz., on the one hand a more realistic treatment of the appropriate Coulomb fields and on the other the avoidance of nonorthogonality difficulties. The results (3.29) and (3.31) are less satisfactory, though they are the only approximations for which calculations have been carried out. A comparison of results using the expression (3.31) [Ochkur (1965)] with the Born (b) approximation and experiment is shown in Fig. 7.

The Born–Ochkur method [Eq. (3.31)] has been used by Ochkur (1965) for ionization of H(1s); the Born–Ochkur method [Eq. (3.29)] has been used by Prasad (1965) for H(1s), H(2s), and H(2p) and by Peach [1966(a), (b)] for ionization of He, Li, Be, Na, and Mg from their ground states.

### 3.6. Improved Final-State Approximations

None of the previous approximations is in harmony with the theory presented in Sec. 2 as regards its treatment of the final state. It is essential however, in a proper treatment of the problem, that Eq. (2.51) should be satisfied and calculations have been carried out by Rudge and Schwartz (1966) in which these conditions are met. They use the approximation

$$\begin{aligned} \Psi &= \psi(0 | \mathbf{r}_2) \exp(i\mathbf{k}_0 \cdot \mathbf{r}_1), \\ \Phi &= \chi(z_1, -\mathbf{k}_1 | \mathbf{r}_1) \chi(1, -\mathbf{k}_2 | \mathbf{r}_2), \end{aligned} \quad (3.37)$$

with

$$z_1 = 1 - (k_1 / |\mathbf{k}_1 - \mathbf{k}_2|). \quad (3.38)$$



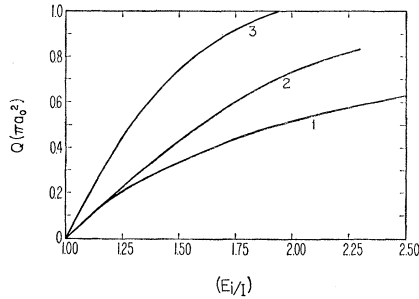


FIG. 8. Theoretical calculations for ionization for H(1s) using an improved final-state function [Rudge and Schwartz (1966(a))]. (1) Experiment, (2) results without exchange, and (3) results with exchange.

With this choice a linear-threshold behavior is obtained but, in order to evaluate the cross section, one more numerical integration is needed than in the previous approximations. Results obtained in this approximation are shown in Fig. 8, two curves being shown, the one where exchange is taken into account and the other where it is neglected. Some improvement is obtained in the agreement between theory and experiment in the case where exchange is neglected and for energies below  $E_i/I=1.5$ , where  $E_i$  is the energy of the incident electron, theory and experiment are in accord allowing for experimental uncertainty. A linear-threshold behavior is obtained. At higher energies however there is a discrepancy and this discrepancy between theory and experiment is increased with inclusion of exchange. The reason for this may be due to the choice of charge in (3.38). Clearly in an approximate calculation of the scattering amplitude it is advantageous to guarantee that as  $k_2 \rightarrow 0$ ,  $z_1 \rightarrow 0$  and  $z_2 \rightarrow 1$  corresponding to screening in this limit. Equation (3.38) guarantees this behavior and the nonexchange results are quite reasonable. Also one should guarantee that as  $k_1 \rightarrow 0$ ,  $z_1 \rightarrow 1$  and  $z_2 \rightarrow 0$ . This is not given by the choice (3.38) and we may therefore expect the exchange-scattering amplitude to be less accurate. Further work is needed to establish what choice of  $z_1$  and  $z_2$  satisfying (2.51) is most appropriate in approximate calculations.

### 3.7. The Distorted-Wave Born–Oppenheimer Method

In all the above methods the initial state was represented as a product of an initial atomic function and an undistorted plane wave for the incident electron. Burke and Taylor (1965) have carried out calculations in which the initial state is represented in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = [1 + (-1)^s P_{12}] \sum_{\gamma} \psi(\gamma | \mathbf{r}_2) F_{\gamma}(\mathbf{r}_1),$$

where  $\gamma=1s, 2s, 2p$  and the  $F_{\gamma}(\mathbf{r}_1)$  are determined through the Hartree–Fock equations

$$\int \psi^*(\gamma | \mathbf{r}_2) (H - E) \Psi(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = 0. \quad (3.39)$$

The final state was chosen as in the Born–Oppenheimer

approximation. A comparison of this approximation with the Born, Born-exchange approximation, and experiment for ionization from the ground state is given in Fig. 9. It is seen that, despite the much greater complexity of Eq. (3.39), in this case there is little improved agreement with experiment, indicating that a better description of the final state is also necessary. For ionization from the 2s state, however, Burke and Taylor (1965) find that the effects of close coupling in the initial state are of much greater significance. Work similar to that of Burke and Taylor (1965) has been carried out by Veldre and Vinkalns (1963).

### 3.8. Other Approximations

#### a. Impulse Approximation

The approximation has been described by Akerib and Borowitz (1961) and applied by them to both excitation and ionization. Their excitation work has been criticized by Coleman and McDowell (1966). These criticisms apply *a fortiori* to the ionization calculations where a factor of 2 has also been omitted. The approximation in its present form cannot be regarded as in any way well founded.

#### b. Geltman Approximation

In the work of Geltman (1956) both continuum electrons were represented as Coulomb waves belonging to charge  $Z$ , with  $Z$  the charge on the new ion produced. This procedure was also adopted by Treftz (1963) and by Malik and Treftz (1961) in considering the ionization of  $O^{4+}$  and  $O^{5+}$ . A linear-threshold behavior is obtained in this way but the effect of this choice is to overestimate the cross section at low energies. The approximation has been investigated in most detail by Veldre and Vinkalns (1963) both including and neglecting exchange. Their results are shown in Fig. 10.

#### c. Plane-Wave Approximation

In contrast to the Geltman approximation, in this method plane waves are used to describe both con-

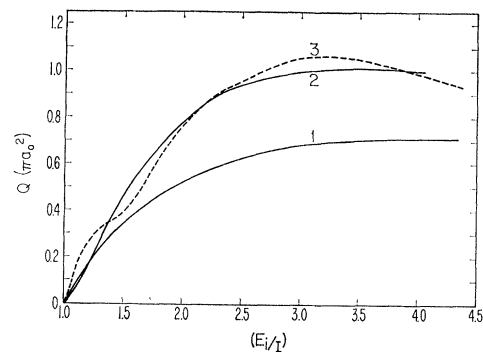


FIG. 9. A comparison of the distorted-wave Born–Oppenheimer calculation [Burke and Taylor (1965)] (3) with (2) the Born (b) approximation and with (1) “experimental” data.

tinuum electrons, one of these being orthogonalized to the ground state of the atom concerned. The approximation has been used by Michael (1963), who considers the ionization of hydrogen and cesium. The approximation is a very poor one. It gives rise to a threshold behavior like  $E^2$ , which yields results which are too low at low energies, while it overestimates in the region of the maximum of the cross section. Results of Michael (1963) for hydrogen are shown in Fig. 11.

### 3.9 Multiple Ionization

Little theoretical work has been carried out on multiple ionization owing to the numerical difficulty of a full quantal calculation. Geltman (1956) has carried out calculations for the double ionization of helium taking just the  $s$  wave into account, using for the final state of the atom the function

$$\psi_f \text{ atom} = \chi(2, -\mathbf{k}_2 | \mathbf{r}_2) \chi(2, -\mathbf{k}_3 | \mathbf{r}_3) \delta(\mathbf{k}_2 + \mathbf{k}_3), \quad (3.40)$$

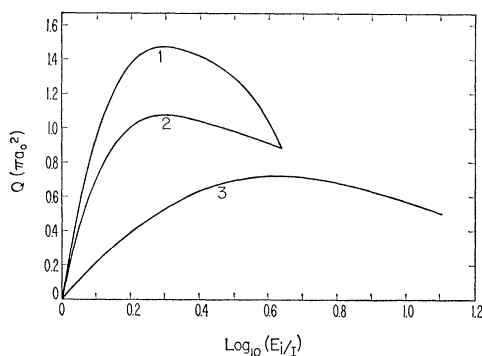


FIG. 10. Results for the ionization cross sections of H(1s) in the Geltman approximation [Veldre and Vinkalns (1963)]. (1) Without exchange, (2) with exchange, and (3) "experiment."

the insertion of the  $\delta$  function in (3.40) being based on the assumption that the dominant contribution to the cross section will arise from states in which two of the electrons move in opposite directions. Since only  $s$  waves were included the calculations are only useful very near threshold, where the behavior of the cross sections is as  $(E-I)^2$ . Geltman showed that this was in accord with experimental data and inferred an  $(E-I)^n$  threshold law for  $n$ -fold ionization. More recently Mittleman (1966) and Byron and Joachain (1966) have given expressions for the ratio of the single to double ionization cross section valid at high energies. They use what is essentially a form of the Bethe approximation. Using a Hartree-Fock function for the initial state of helium, Mittleman (1966) finds a ratio  $Q_{\text{single}}/Q_{\text{double}}=198$ , a result which is compared with experiment in Fig. 12. Byron and Joachain (1966) show, however, that this ratio is strongly dependent on the form assumed for the initial- and final-state wave functions.

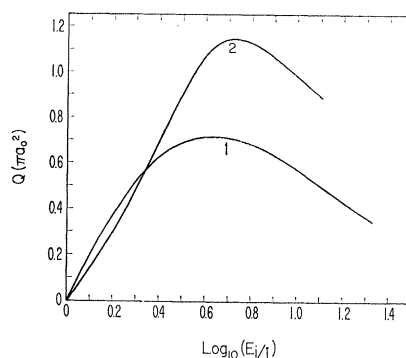


FIG. 11. A comparison of (2) the plane-wave approximation [Michael (1963)] with (1) "experiment" for H(1s).

## 4. CLASSICAL APPROXIMATIONS

The use of classical mechanics to describe an ionizing collision has a greater appeal than it has in the case of an excitation problem. In the first place, the final atomic state lies in the continuum, a concept which is defined both classically and quantally. Secondly, one is not concerned with a final atomic state having a definite angular momentum but rather with the sum over all possible angular momenta, and moreover, as quantal calculations show, a significant number of angular momenta contribute appreciably to this sum. For these reasons it might be expected that classical approximations can play a useful role in estimating ionization cross sections.

In treating ionizing collisions by classical methods three basic approximations are involved. They are:

(1) A classical description must be found for the initial state of the bound electron. In practice, several prescriptions have been used. In the simplest methods the atomic electron is assumed either to be at rest prior to the collision or else to have a fixed velocity, an average then being taken over the direction of this velocity. A second technique is to ascribe a velocity distribution to the atomic electron; several such distributions have been proposed.

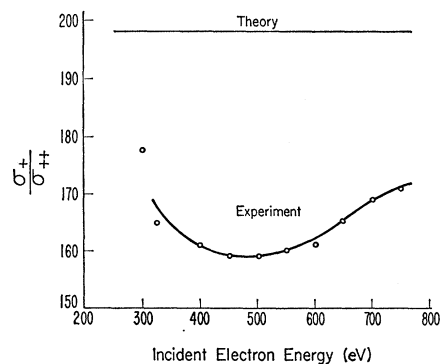


FIG. 12. Experimental results for the ratio of the single to double ionization cross section of He compared with a theoretical high-energy limit [Mittleman (1966)].

(2) The collision is described in terms of the classical Newtonian Laws of motion. This implies that no account can be taken of quantal-interference effects.

(3) For the simplest case of  $e$ -H ionization the classical problem is still a difficult three-body problem, and so in most treatments the equations have been simplified further by treating the collision process as though it were a two-body one.

The classical methods differ from one another in their choice of approximations (1) and (3). Semi-classical methods have been introduced which only partially make use of approximation (2). We consider first the earliest treatment of ionizing collisions, presented by Thomson (1912), and then turn to the various modifications which have been made to his theory.

### 4.1. The Thomson Theory

Thomson (1912) considered classically the ionization of an atom by a charged particle of mass  $m_1$  and charge  $qe$ . He approximates by taking the (classical) Hamiltonian of the system to be

$$H = (p_1^2/2m_1) + (p_2^2/2m) - (qe^2/|\mathbf{r}_1 - \mathbf{r}_2|) \quad (4.1)$$

and, assuming the appropriate initial condition to be that the atomic electron is at rest, calculates the energy transferred to it in the course of a collision in which the incident particle has speed  $v$  and impact parameter  $R$  (relative to the atomic electron). Classical orbit theory then gives the result that the energy transferred is

$$\Delta T = [4mm_1E_i/(m+m_1)^2] \sin^2(\theta/2), \quad (4.2)$$

where  $E_i = \frac{1}{2}m_1v^2$  and  $\theta$  is the angle between the initial and final relative velocities. Expressed in terms of the impact parameter, (4.2) becomes

$$\Delta T = \frac{2mm_1^2v^2}{(m+m_1)^2[1+(R^2v^4/q^2e^4)(mm_1/m+m_1)^2]}. \quad (4.3)$$

Thomson's expression for the cross section is now given by

$$Q = 2\pi \int_0^{R_{\max}} R dR, \quad (4.4)$$

with  $R_{\max}$  chosen such that  $\Delta T = I$ , the ionization potential.

Restricting ourselves for the moment to the case of electron impact, (4.4) gives the result that

$$Q = (\pi e^4/E_i)(1/I - 1/E_i) \text{ (cm}^2\text{)}.$$

Introducing a reduced energy  $x = E_i/I$ , this becomes

$$Q = 4(I_H/I)^2(1/x)(1 - 1/x)(\pi a_0^2), \quad (4.5)$$

where  $I_H$  is the Rydberg. Before discussing the result (4.5) it is of interest to note that (4.4), through the use of (4.3), can be expressed rather differently. Writing  $\Delta T = I + \frac{1}{2}k_2^2$  and  $v^2 = k_0^2$ , a change of variable in (4.4)

gives the result that

$$Q = \frac{2}{k_0^2} \int_0^{1/2k_0^2 - I} \frac{d(k_2^2/2)}{(I + k_2^2/2)^2}. \quad (4.6)$$

In this form (4.6) is reminiscent of the Born( $a$ ) quantal expression for the ionization cross section. Again, if the variable of integration in (4.4) is changed from  $R$  to  $\phi = \theta/2$ , it is found that

$$Q = \frac{4}{k_0^4} \int_{\sin^{-1}(I/E_i)^{1/2}}^{\pi/2} \frac{\sin(2\phi)d\phi}{\sin^4\phi}. \quad (4.7)$$

Equation (4.7) is simply an integration over the Rutherford differential cross section. These results are pertinent to extensions of the Thomson formula to be discussed in Sec. 4.3. For the present we return to (4.5). In deriving (4.5) it was assumed that only a single electron was available for removal from the atom. For the case of ionization from a shell of  $n$  equivalent electrons (4.5) should be multiplied by  $n$ , and the first prediction of the Thomson theory is that ionization cross sections obey a scaling law expressed by saying that

$$\tilde{Q}(x) = n^{-1}(I/I_H)^2Q \quad (4.8)$$

is a universal function of  $x$ .  $\tilde{Q}(x)$  is referred to as the reduced ionization cross section. The result is a useful one and a comparison with experimental data for H, He, and  $\text{Na}^+$  is shown in Fig. 13. Similar comparisons have been effected by Seaton [1962(a), 1964]. It is seen that for these species at low and intermediate energies the prediction is in good accord with the data. (4.5) however does not represent the correct shape of the ionization curve. According to (4.5) the maximum of the cross section should occur at  $x=2$ , while experimental evidence shows that this occurs at higher values. More seriously the Bethe theory shows that at high energies the cross section behaves like  $A \ln E_i/E_i + B/E_i$ , but in (4.5) there is no such logarithmic dependence. Since for high-enough energies the logarithmic term is dominant, this is a severe drawback. It is also of some interest to exhibit predictions of the Thomson theory for ionization by other particles, for

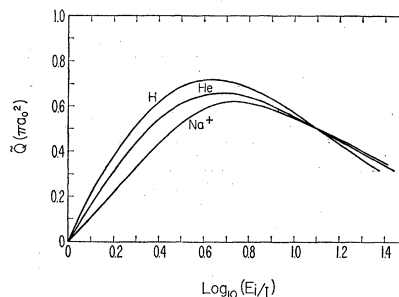


FIG. 13. A comparison of some reduced ionization cross sections showing a mean experimental curve for hydrogen, the results of Smith (1930) for helium, and the results of Hooper *et al.* (1966) for  $\text{Na}^+$ .

example, protons or alpha particles. In these cases the Thomson formula is

$$Q = (4I_H^2 q^2 / v^4) \{ (2v^2/I) - [(1+m_1)/m_1]^2 \}. \quad (4.9)$$

Equation (4.9) has one obvious fault in that it predicts a threshold where

$$\frac{1}{2} m_1 v^2 = (I/4m_1) (1+m_1)^2, \quad (4.10)$$

a result which is only correct for electrons with  $m_1=1$ .

The prediction of an incorrect threshold energy is a feature of the two-body approximation. Denoting the mass of the atom by  $M$  the correct relationship is

$$\frac{1}{2} [M m_1 / (M + m_1)] v^2 = I, \quad (4.11)$$

so that for ionization of atomic hydrogen by proton impact, for example, at threshold  $v^2 \approx 4I/M$  while in the Thomson theory  $v^2 \approx I/2$ . Equation (4.9) is of interest in that it shows that the ionization cross section is a function of the velocity of the incident particle rather than its energy. Thus the cross section for ionization by proton impact, for example, approaches from above the cross section for ionization by an electron having the same velocity, as the velocity increases. This prediction is compared with experiment in Fig. 14. The same result may be derived from quantal expressions for the ionization cross section, but Thomson was the first to deduce this relationship. Through the  $q^2$  factor in (4.9) the classical theory is also seen to predict that the cross section for ionization by alpha-particle impact, for example, will be about four times that for ionization by a proton having the same velocity. Thus an extremely simple theory makes a number of important qualitative predictions. It has therefore been of interest to pursue the theory further with a view to obtaining formulas whose quantitative aspects are in better accord with quantal theory and experiment.

#### 4.2. Improved Classical Approximations

Gryzinski (1959), as in the earlier work of Williams (1927) and Thomas (1927), sought to improve the Thomson theory by adopting different initial conditions in the classical description of the problem. He ascribes in the first instance an initial velocity to the atomic electron and then interprets an ionizing collision as being one in which the incident electron loses an

FIG. 14. A comparison of ionization cross sections for He(b) by electron impact [Smith (1930)] and (a) by proton impact [Hooper *et al.* (1962)]. The curves correspond to equal velocities of the incident particles.

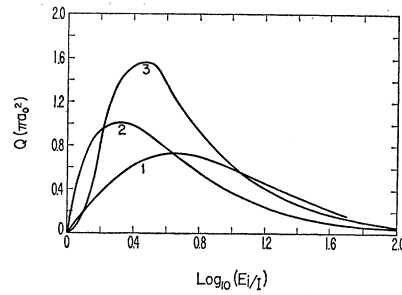
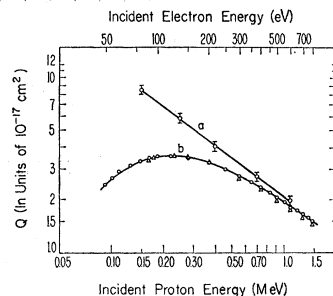


FIG. 15. Ionization cross sections for H(1s): (1) "experiment," (2) Thomson classical theory, and (3) Stabler-Gryzinski classical theory [Eq. (4.12)].

amount of energy greater than or equal to the ionization potential of the atom concerned. A calculation consistent with these assumptions was not carried out by Gryzinski (1959), who in the course of his analysis made the simplifying approximation of replacing the true relative speed of the two electrons  $V = |\mathbf{v}_1 - \mathbf{v}_2|$  by its average value  $(v_1^2 + v_2^2)^{1/2}$ . This approximation was later removed by Ochkur and Petrunkin (1963) and by Stabler (1964). Defining  $E_2$  as the initial kinetic energy of the atomic electron, introducing another reduced variable  $y = E_2/I$ , and assuming an isotropic distribution of electron velocities, the result of Stabler for the ionization cross section is

$$Q = 4n(I_H/I)^2 (1/x) [1 + (2y/3) - (x-y)^{-1}] \quad x \geq y+1$$

$$= (8n/3) (I_H/I)^2 (1/x) [(x-1)^3/y]^{1/2} \quad 1 \leq x \leq y+1. \quad (4.12)$$

With the further approximation mentioned above and taking  $y=1$ , the Gryzinski result is

$$Q = 4n(I_H/I)^2 (x/x+1)^{3/2}$$

$$\times \begin{cases} (5/3x - 2/x^2) & x \geq 2 \\ (4\sqrt{2}/3x) (1-1/x)^{3/2} & 1 \leq x \leq 2. \end{cases} \quad (4.13)$$

The effect of the new initial condition is expressed through (4.12) and, far from improving the Thomson theory, in fact makes it worse (as shown in Fig. 15). The shape of the curve is still in error at high energies and the position of the maximum still incorrect, while at low energies the behavior of the cross section is now like  $(x-1)^{3/2}$  rather than  $(x-1)$ , as given quantally and in the Thomson theory. The subsidiary approximation introduced by Gryzinski to give (4.13) suffers from the same defects at high and low energies, though for hydrogen the position of the maximum is more correct and numerical values are in better accord at intermediate energies (see Fig. 16).

Neither formula is very satisfactory above the maximum of the cross section and it may be concluded that neither (4.12) nor (4.13) represents a substantial improvement over the Thomson theory.

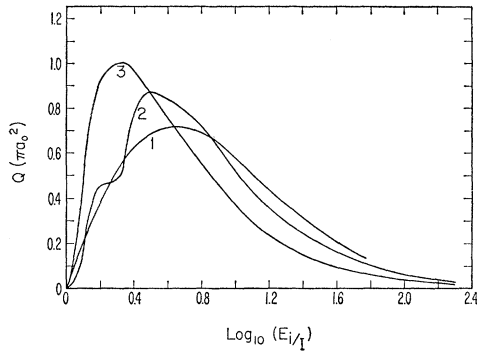


FIG. 16. Ionization cross sections for H(1s): (1) "experiment," (2) Gryzinski classical theory [Eq. (4.13)], and (3) Thomson classical theory.

In order to obtain a logarithmic decrease in the ionization section Gryzinski reconsidered the problem in a series of papers [1965(a), (b), (c)] by assuming that the atomic electron had a continuous velocity distribution. He introduced an empirical distribution function whose form ( $\sim v^{-3}$ ) was chosen so that, on averaging over this distribution, a logarithmic term would be obtained. Explicitly he assumed that the atomic electron had a velocity distribution given by

$$f(v) = (\bar{v}/v)^3 \exp(-\bar{v}/v), \quad (4.14)$$

with  $\bar{v}$  equal to the mean velocity. On averaging over this distribution, he finds that

$$Q = 4n(I_H/I)^2(1/x)[(x-1)/(x+1)]^{3/2} \times \{1 + \frac{2}{3}(1-1/2x) \ln [2.7 + (x-1)^{1/2}]\}. \quad (4.15)$$

Equation (4.15) may be criticized because it again has an incorrect form at the threshold. At high energies there is now a logarithmic term, but the coefficient multiplying it is in general incorrect, the correct factor being given by the expression (3.15). This is illustrated in Fig. 17, where  $x(x+1)Q(x)/(x-1)$  is plotted against  $\log(x)$  for Ar. There is no *a priori* justification for the averaging procedure or the choice (4.14), which is simply an *ad hoc* device for producing the logarithmic term of (4.15). Equation (4.15) may be regarded however as a semiempirical formula which has some advantage over that expressed by (4.12).

In a later note Gryzinski [1965(d)] reconsidered the problem of what velocity distribution should be used for the atomic electron. He argues that the appropriate velocity distribution is that for an electron of a Bohr atom in which it has only radial motion, corresponding to a degenerate line ellipse. The velocity distribution in this case is

$$f(v) = (4/\pi)v_n^3/(v^2+v_n^2)^2, \quad (4.16)$$

where  $v_n^2/2 = |En|$ , where  $En$  is the energy at the initial state with principal quantum number  $n$ . No

calculations have been reported with this velocity distribution. Kingston (1964) has made calculations in which he takes the velocity distribution to be that of the quantal momentum wave functions and compared these calculations with various forms of the Gryzinski's theory. McDowell (1966) has performed a similar calculation.

Mapleton (1966) and Abrines and Percival (1966) have investigated the relationship between quantal velocity distributions and classical velocity distributions which are obtained from statistical mechanics. The quantal distribution for atomic hydrogen is given by [Fock (1935)]

$$4\pi/n^2 \sum_{lm} |\phi_{nlm}(\mathbf{v})|^2 v^2 dv = [32v_n^5 v^2 dv / \pi(v^2 + v_n^2)^4], \quad (4.17)$$

where  $\phi_{nlm}(\mathbf{v})$  is a momentum wave function.

Mapleton (1966) and Abrines and Percival (1966) show that the result (4.17) is obtained also from the classical microcanonical distribution provided that an integration is performed over the classical angular momentum. On the other hand, if such an integration is not performed, then, for a degenerate line ellipse, Mapleton (1966) shows that Gryzinski's result (4.16) is obtained. Since the ground state of hydrogen is known to be spherically symmetric, while classical states of fixed angular momentum are not, it seems most reasonable that the averaged classical velocity distribution, which coincides with the quantal result (4.17), should be used. The calculations of Kingston (1964) wherein such a distribution was adopted were restricted by the approximation of assuming a binary collision. This approximation is only necessary insofar as it gives rise to simple formulas for the cross sections. However, Abrines and Percival (1966), Percival and Valentine (1966), and Abrines, Percival, and Valentine (1966) have considered a more precise classical treatment. In their method the classical equations of motion are integrated exactly, thus discarding the binary-collision approximation. The initial velocity distribution was taken to be that given by (4.17) and a Monte Carlo technique was applied to average over initial classical states of the system. For  $p$ -H ionization Percival and Valentine (1966) show that the effect of removing the

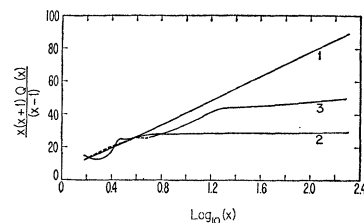


FIG. 17.  $x(x+1)Q(x)/(x-1)$  vs  $\log_{10} x$  for Ar. (1) experiment, (2) Gryzinski [Eq. (4.15)], and (3) Gryzinski [Eq. (4.13)].

binary-collision approximation is to reduce the cross section by a factor of 2 at its maximum. A comparison of the results of Abrines, Percival, and Valentine (1966) for  $e$ -H ionization with experimental values is shown in Fig. 18, wherein the error bars refer to the statistical errors in the calculation. Very reasonable agreement with experiment is obtained. At low energies however the results are too high, which reflects the absence of interference effects in the classical treatment while at high energies the results are too low reflecting the wrong asymptotic dependence on energy.

**4.3. The Exchange-Classical Approximation**

In a treatment of the problem introduced by Burgess (1963) and (1964), it is argued from the outset that in order to improve the Thomson theory certain features of the quantal treatment must be incorporated into the approximation. The first of these is that the effects of exchange must be allowed for. This is clearly impossible in a purely classical approach but the Thomson cross section expression in the form of Eq. (4.6) or Eq. (4.7) make a convenient basis for a semiclassical modification to the theory. Referring to Eq. (4.7), it is seen that an integration is performed over the Rutherford scattering cross section with neglect of exchange. Including exchange means that  $1/\sin^4 \phi$  is replaced by the Mott formula

$$[1/\sin^4 \phi + 1/\cos^4 \phi - (1/\sin^2 \phi \cos^2 \phi) \times \cos(e^2/\hbar v \ln \tan^2 \phi)].$$

$$Q = \frac{2}{(k_0^2 + 2I)} \int_0^{(k_0^2/2 - I)} \left\{ (2I + k_2^2)^{-2} + (2I + k_1^2)^{-2} - (2I + k_1^2)(2I + k_2^2)^{-1} \right. \\ \left. \times \cos\left(\frac{1}{(k_0^2 + 2I)^{1/2}} \ln \frac{2I + k_2^2}{2I + k_1^2}\right) \right\} d(k_2^2). \quad (4.19)$$

If the argument of the cosine is assumed constant and equal to  $\gamma$ , then (4.19) becomes

$$Q = 4(I_H/I)^2 \cdot (x+1)^{-1} \{ 1 - x^{-1} - [\cos \gamma \ln x/(1+x)] \}. \quad (4.20)$$

In the more detailed treatments presented by Burgess (1964) and by Vriens (1966) the atomic electron is

With this substitution in (4.7) the ionization cross section may be expressed by

$$Q = \frac{8}{k_0^2} \int_0^{\frac{1}{2}(k_0^2 - I)} \left\{ (2I + k_2^2)^{-2} + (k_1^2)^{-2} - [k_1^2(2I + k_2^2)]^{-1} \cos\left(k_0^{-1} \ln \frac{2I + k_2^2}{k_1^2}\right) \right\} d(\frac{1}{2}k_2^2), \quad (4.18)$$

with the usual energy relation

$$k_0^2 - 2I = k_1^2 + k_2^2,$$

and where the upper limit of integration has been chosen to be in harmony with quantal theory. Equation (4.18) is unsatisfactory however in that the integrand is not symmetric, i.e., the relationship  $f(\mathbf{k}_1, \mathbf{k}_2) = g(\mathbf{k}_2, \mathbf{k}_1)$  is not satisfied [Burgess (1963)]. Alternatively if the integration in (4.18) is extended over the full energy range and a factor of  $\frac{1}{2}$  is introduced, this being an equivalent procedure in a quantal treatment, it is seen that (4.18) diverges. In order to circumvent this difficulty Burgess (1963) makes the additional assumption that the incident electron gains an amount of kinetic energy equal to  $I$ , before it interacts with the atomic electron, and loses an equivalent amount of potential energy. This procedure is similar to one employed by De la Rippelle (1949). In this way (4.18) is replaced by an expression symmetric for interchange of  $k_1$  and  $k_2$ . Explicitly (4.18) becomes

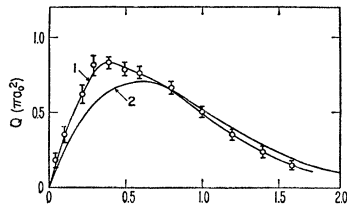
assumed to have an initial kinetic energy. This complicates the analysis and the results of Burgess (1964) and Vriens (1966) do not appear to coincide. However the result of Vriens (1966), on carrying through the procedure of Burgess (1964), is

$$Q_{EC} = \frac{4(I_H/I)^2}{(x+W/I)} \left[ 1 - x^{-1} + \frac{2}{3}\gamma(1-x^{-2}) - \frac{\cos \gamma \ln x}{1+x} \right], \quad (4.21)$$

where  $W$  is the gain in kinetic energy of the incident electron and in order to allow an explicit evaluation of an expression similar to (4.19), the argument of the cosine has been taken as a constant, which Vriens recommends be taken as

$$\gamma = [1/2I(x+1)]^{1/2} \ln x. \quad (4.22)$$

FIG. 18. Ionization cross sections for H(1s): (1) "Exact" classical calculations of Abrines, Percival, and Valentine (1966) and (2) experiment.



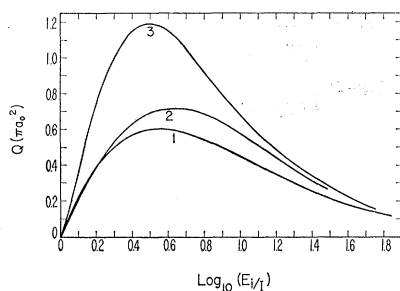


FIG. 19. Ionization cross section for atomic hydrogen: (1) ECIP [Burgess (1964)], (2) "experimental," (3) Born (a).

With  $W=I$  and  $y=0$  (4.21) is identical with (4.20) as it should be. Burgess chooses  $W=I$  while Vriens chooses  $W=I(y+1)$ .

The expressions (4.20) and (4.21) are a significant improvement in the theory, removing as they do one of the major defects of the Thomson expression. It does not however have the correct behavior at high energies.

#### 4.4. Exchange-Classical Impact-Parameter (ECIP) Approximation

Burgess (1963) and (1964) has suggested a means of improving the Thomson theory further by combining the previous theory with an impact-parameter formulation. In the previous sections the close electron-electron encounters have been treated correctly, indeed exactly if the influence of the nucleus may be ignored. In the impact parameter method on the other hand [Alder *et al.* (1965) and Seaton 1962(b)], the distant collisions are treated in a good approximation. A combination of the two methods has therefore an obvious appeal. Calculations by Burgess (1964) indicate considerable success for this method and a fairly typical result is displayed in Fig. 19 for hydrogen. The method does not give rise to any simple formula such as those obtained previously. It is a nice treatment in that the correct behavior at low and high energies is obtained while the quantitative predictions are also sound. The exchange-classical approximation may also be improved in a more empirical fashion, yielding a simple formula, and a discussion of this approach is given in Sec. 5. The main difficulty of the method is that it involves choosing a value of the impact parameter  $R_0$ , such that for  $R > R_0$  the impact-parameter method is used, while for  $R < R_0$  the exchange-classical method is used. Vriens [1966(a)] has suggested an alternative procedure which involves a cutoff on the momentum transfer.

### 5. EMPIRICAL FORMULAS FOR IONIZATION CROSS SECTIONS

In view of the need for reasonable estimates of ionization cross sections and the present incompleteness of

experimental or theoretical data, it is necessary to develop semiempirical formulas. In so doing certain criteria should be met, these being:

(a) To provide a good fit to the known data. In this respect it is important that to be of general usefulness the fit should be good at all energies. This implies that the functional form chosen to represent the data should show the correct behavior in the region near threshold and have the asymptotic dependence predicted by the Bethe theory at high energies.

(b) To predict variations in the ionization cross sections for members of isoelectronic sequences.

(c) To display the variations in the cross sections as a function of the quantum numbers of the initial state.

A considerable number of empirical formulas have appeared in the literature. Many of them however are only of limited usefulness and have been superseded by the later formulas which we discuss here.

The most recent and extensive list of formulas for ionization cross sections and for reaction rates for ionization has been compiled by Lötzt (1967). Lötzt writes the ionization cross section in the form

$$Q = \zeta_1 \frac{a \ln(E/I_1)}{I_1 E} \quad \text{if } I_1 \leq E \leq I$$

$$= \sum_{j=1}^N \zeta_j \frac{a \ln(E/I_j)}{I_j E} = \bar{\zeta} \frac{a \ln(E/\bar{I})}{\bar{I} E} \quad \text{if } E > I_N.$$
(5.1)

The formula (5.1) applies to an atom or ion containing several shells of electrons, the  $I_j$  being successive ionization potentials;  $a$  is a fixed constant, and the  $\zeta_i$  are numbers, the relevant values of which Lötzt tabulates for three energy regions of the ionization curve. For the high energy part of the curve the  $\zeta_i$  are equal to the number of electrons in each shell. The constants are calculated from experimental data and apply to ionization from the ground state.

The form of the function (5.1) derives from an earlier and rather successful formula of Drawin (1961), who writes the reduced cross section of Eq. (4.8) in the form

$$\tilde{Q}(x) = 2.66 f_1 [(x-1)/x] \ln(1.25 f_2 x), \quad (5.2)$$

where  $x$  is the reduced energy and  $f_1$  and  $f_2$  are constants which, in the absence of further data, Drawin recommends be taken equal to unity. It is seen that (5.2) has a linear behavior near threshold and a functional form at high energies, which agrees with the Bethe theory. The formula (5.2) provides a very reasonable estimate of the ionization cross section for a large number of species from their ground states but (with the recommended choice of  $f_1=f_2=1$ ) is less accurate for ionization from excited states.

Percival (1966) has given formulas which represent the average cross section for ionization from excited states of hydrogen and of hydrogenic positive ions. Percival's formula for the average ionization cross section from a state of hydrogen with principal quantum number  $n$  is

$$\begin{aligned} \bar{Q}(x) &= (1.19 \ln x + 5.26)(x-1)/(x^2 + 1.67x + 3.57) \\ &\quad \text{if } n=1 \\ &= \{[1.28n^{-1} \ln(xn^{-2}) + 6.67]/(x^2 + 1.67x + 3.57)\} \\ &\quad \times (x-1) \quad \text{if } n \geq 2. \quad (5.3) \end{aligned}$$

For hydrogen the coefficient  $A$  in (3.13) of the logarithmic term is well known from oscillator strengths [Bethe and Salpeter (1957), Kingston (1965)]. The appropriate constant in (5.3) has been approximated by Percival (1966) in the form  $1.28/n$ . For large  $n$  and large  $x$ , (5.3) gives  $\bar{Q}(x) \sim 6.67/x$ , a form which derives from the Gryzinski or exchange-classical approximations when the initial kinetic energy of the bound electron is taken equal to  $I$ . Abrines and Percival [1966(b)] have shown for large  $n$ , the classical and quantal cross sections are equal when expressed in terms of the reduced energy, and the calculations of Abrines, Percival, and Valentine (1966) agree with the exchange-classical results at high energies. For the reduced ionization cross section of hydrogenic positive ions, Percival (1967) writes

$$\bar{Q}_z = 1 + \frac{2.3}{(1-1/z)^2 + 2(x-1)^2} [\bar{Q}_1(x)], \quad (5.4)$$

where  $z$  is the nuclear charge.

The exchange-classical formula (4.20) may be used as a basis for a semiempirical formula, provided a logarithmic term is included. Such a formula is

$$\begin{aligned} \bar{Q}(x) &= [1/(x+1)][1 - 1/x - \cos \gamma \ln x/(1+x)] \\ &\quad \times (4\alpha + \beta \ln x), \quad (5.5) \end{aligned}$$

where  $\gamma = \ln x/(1+x)^{1/2}$ ,  $\alpha$  is a constant, approximately 1.5, and  $\beta = AI/I_H^2$ , where  $A$  is given by (3.22). For ionization from the  $1s$  state of hydrogen,  $\alpha = 1.39$  gives agreement with the greater part of the experimental data and agrees with Percival's result  $\alpha = 5/3$  for large values of  $n$ . In Table I values of  $\beta$  are tabulated for the first few states of hydrogen.

Table I shows that the logarithmic dependence of the reduced cross section decreases with increasing  $n$  and for given  $n$  decreases with increasing  $l$ . For ionization of hydrogen the logarithmic term only begins to dominate the cross section where  $x$  is of the order of a few hundred. Classical approximations for ionization of atomic hydrogen, wherein there is either no logarithmic term or

TABLE I. Empirical formula (5.5) for the ionization of atomic hydrogen ( $\alpha \approx 1.4$ ).

$n$	Initial state $l$	$\beta$
1	0	1.134
2	0	0.824
2	1	0.532
3	0	0.652
3	1	0.552
3	2	0.280
4	0	0.550
4	1	0.512
4	2	0.372
4	3	0.150
5	0	0.482
5	1	0.468
5	2	0.396
5	3	0.244
5	4	0.082

one with an incorrect coefficient appear misleadingly good on this account.

The reduced ionization cross sections for positive ions are greater than for the neutral member of the given isoelectronic sequence as a result of the focusing of the incident electron beam by the attractive Coulomb field of the ion. If  $Z_{in}$  is the initial charge on the ion, then a focusing factor  $F$  can be defined by

$$F = 1 + Z_{in}/xI^{1/2}, \quad (5.6)$$

and the reduced ionization cross section for the isoelectronic sequence can be written

$$\bar{Q}_{Z_{in}}(x) = F\bar{Q}_0(x). \quad (5.7)$$

For the hydrogen isoelectronic series either (5.7) or (5.4) give a good representation of the variation of the reduced cross section with  $Z$ .

The hydrogen sequence is a special case in that the constant  $\beta$  is the same for all members of the sequence. In other sequences this is not so and a simple focusing function does not completely represent the variation of the reduced cross section. In the neon sequence, for example, the reduced cross sections for  $\text{Na}^+$  and  $\text{Ne}$  are quite different at high energies [Hooper *et al.* (1966)].

The only other cases for which these are good theoretical data for the high-energy dependence of the ionization cross section are the inert gases. The constant  $A$  for them has been obtained by Kingston [1965(a)]. A comparison with high-energy experimental data by Kingston, Schram, and de Heer (1965) shows satisfactory agreement. Vriens (1965) has given semiempirical formulas for ionization cross sections for the inert gases. Kingston's (1965) values for  $A$  were used to



TABLE II. Values of  $\beta$  for the inert gases.

Element	$I$	$\beta$
He	0.903	1.76
Ne	0.794	1.75
Ar	0.579	3.17
Kr	0.514	3.78
Xe	0.445	4.21

calculate the values of  $\beta$  for the inert gases which are shown in Table II.

In contrast to the situation for atomic hydrogen, in the case of Ar, for example, the logarithmic term begins to dominate the cross section in the region close to the maximum of the cross section. It is therefore readily understood why classical theories either with no logarithmic term or with such a term having the wrong coefficient, are inadequate in such a case.

In contrast to the inert gases in the case of ionization of the alkalis there is only a very small coefficient of the logarithmic term arising from removal of the valence electron owing to the strength of the resonance transition for these elements. At high energies there is a substantial contribution from removal of an inner-shell electron. McFarland (1966) has computed Gryzinski cross sections for the alkalis.

Figure 20 shows a comparison of the available experimental data for ionization of H(1s) [Fite and Brackmann (1958), Boksenberg (1960), and Rothe *et al.* (1962)] with the Born (b) approximation, the Drawin formula (5.2), the Percival formula (5.3), and formula (5.5), with  $\alpha=1.39$ . The earlier comparisons with "experiment" have been referred to a curve giving slightly more weight to the data of Rothe *et al.* (1962) by taking  $\alpha=1.3$ .

In Fig. 21 the formula (5.5) with  $\alpha=1.3$  is compared with some theoretical results for ionization of H(2s), and in Fig. 22 are shown theoretical and semiempirical estimates of the average ionization cross section for the  $n=2$  states of hydrogen.

Figure 23 illustrates the behavior of the reduced ionization cross section in the hydrogen isoelectronic sequence. For other species reference may be made to

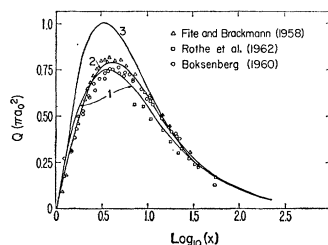


FIG. 20. Empirical formulas for ionization of H(1s): (1) Eq. (5.5),  $\alpha=1.3925$ , (2) Percival (1966) [Eq. (5.3)], and (3) Born (b).

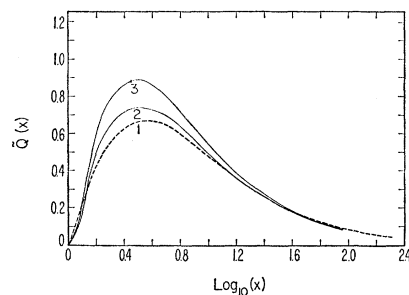


FIG. 21. Reduced ionization cross section for H(2s): (1) semi-empirical formula (5.5) with  $\alpha=1.3$ , (2) Born-Ochkur [Prasad (1965)], and (3) Born (b) [Prasad (1965)].

the work of Lötzer (1967). There therefore exists a number of satisfactory semiempirical formulas. In order to improve on these, further theoretical work is needed to establish the high-energy behavior of ionization cross sections, while more experimental work is needed to establish their low-energy behavior.

## 6. CONCLUDING REMARKS

Theoretical treatments of ionizing collisions have improved in recent years but many problems remain. In the first instance, there is still a need for fairly simple but effective means of performing quantal-ionization calculations. The Born approximation and its variations which take account of exchange effects are reasonably successful in predicting total cross sections, provided the near-threshold region is excluded. What is needed however is a treatment which gives the correct threshold behavior and correct angular distributions of the reaction products. No discussion has been given of theoretical angular distributions because there is at present no experimental data with which to compare these. It is clearly unlikely however that theoretical treatments

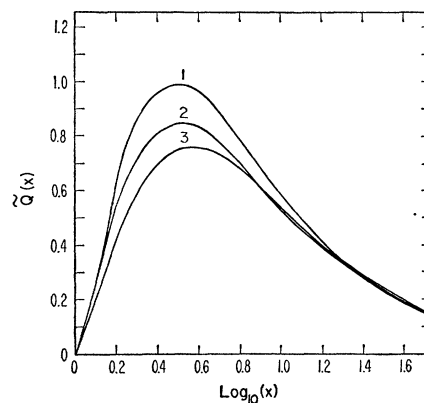


FIG. 22. Average cross section for ionization from the  $n=2$  state of atomic hydrogen: (1) Born (b) [Prasad (1966)], (2) Born-Ochkur [Prasad (1965)], and (3) Percival formula (5.3).

which do not take proper account of the Coulomb interactions in the final state will give rise to correct angular distributions. It is therefore necessary to devise a technique which will do this. As regards threshold behavior, there is little doubt that the Born approximation and its variations are inadequate. There has recently however been intensive experimental study at  $e$ -H near threshold ionization [McGowan and Clarke (1967)], which suggests that the linear result, given by the theory presented in this review, is incorrect. If this should indeed prove to be the case, then further theoretical effort will be necessary to explain the experimental results.

Besides the need for a simple effective theoretical treatment, there is a much greater need for a systematic scheme for calculating ionization cross sections whereby, as in the close coupling method for excitation problems, a consistent improvement to the calculations may be effected, both in principle and in practice. Such a scheme is at present lacking.

For ionization of complex atoms there are further problems distinct from those arising in the case of ionization of hydrogen. Thus the evidence of Burke and Taylor (1965) suggests that coupling in the initial state for H is of importance for ionization from excited states, and Bates *et al.* (1965) conjecture that this may also be the case for ionization of alkalis such as Na from their ground states. Again for alkalis it is essential that an accurate description should be given of the motion of the ejected electron in the field of the residual ion and a sensitive test of this is provided by comparison of theoretical and experimental photoionization data. It is also of importance in some cases to take account, in the final state, of doubly excited autoionizing levels. Kaneko and Kanamota (1963), for example, attribute structure in the ionization cross section of Ca as being due to the influence of autoionizing levels.

Thus a really adequate theoretical approach to the calculations of single ionization cross sections is still lacking and as regards multiple ionization the situation is a good deal worse where virtually the only available estimates are those of Gryzinski.

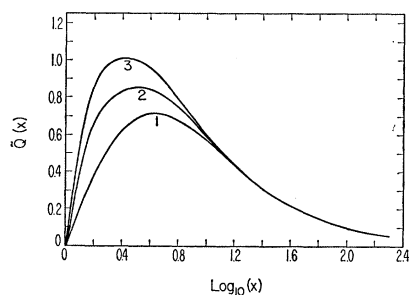


FIG. 23. Reduced ionization cross sections in the hydrogen isoelectronic sequence: (1) mean curve for hydrogen, (2)  $\text{He}^+$  [Dolder *et al.* (1963)], and (3) theoretical curve for  $Z=128$  [Rudge and Schwartz (1966a)].

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