THEORY OF ELECTRON-ATOM COLLISIONS*

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I. INTRODUCTION

The collision of electrons with atoms (including ions as special cases) is not only of interest to atomic physics itself but also has important applications in other fields such as astrophysics, plasma physics, and radiation physics.

Although the main emphasis of this conference is on the interaction with ions, this lecture will cover interactions with both neutral atoms and ions because:

(a) Electron-atom collisions are better understood, and
(b) More is learned by comparing the similarities and differences between electron-atom and electron-ion collisions.

The systematics peculiar to electron-ion collisions are primarily due to the presence of an attractive potential and infinitely many

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bound states between the colliding particles. We shall use the word "atoms" to include "ions" hereafter unless specified otherwise.

Collisions of electrons with atoms can be classified into two broad categories, slow and fast collisions, depending on the speed of the incident electron compared to the orbital speed of the bound electron participating in the collision.

In a slow collision, the incident electron and the target atom form a compound state, and strong coupling exists among alternative compound states as well as among the various channels of separation after the collision. As a result, both the incident and target particles must be described on equal footing, i.e., the interaction between them cannot be treated as a perturbation compared to the interactions among the bound electrons. The R-matrix and close-coupling methods are examples of theories describing such systems. Slow collisions still pose severe difficulties (and challenges) to theorists.

Fast collisions, on the other hand, are easier to formulate and better understood than slow collisions. The incident electron behaves differently from atomic electrons, and hence it can be described separately from the bound electrons. The collision occurs mostly at large impact parameters, and the interaction is weak. The interaction between the incident electron and the target is represented as an impulse and is treated in the framework of a perturbation theory. For the perturbation treatment to succeed, the collision should be dominated by small impulse—or momentum transfer—compared to the average momenta of the bound electrons. Dipole-allowed transitions clearly belong to this class, and this is the main reason that the Born approximation works better for dipole-allowed transitions than dipole-forbidden ones, as we shall see later.

Also, there is a close relationship between collisions of photons and fast electrons with atoms. The cross sections for various bare incident particles (e.g., e⁻, e⁺, p, alpha, etc.) can be scaled from each other at high incident energies. These simplifications for fast projectiles are essential features of the first Born approximations.

A major departure of electron-ion collision process from electron-atom collisions occurs in the threshold behavior. For the excitation of a neutral atom by an electron, the cross section vanishes at the threshold, whereas for the excitation of an ion, it starts with a finite value. The excitation cross section for an ion usually has its maximum at the threshold.

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In the next few lectures, we shall discuss:

(c) Theory of fast collisions, with emphasis on the systematics and relationships to other types of collisions;
(d) Electron-impact ionization including the systematics of secondary electrons;
(e) Relativistic and correlation effects in collision cross sections;
(f) Theory for slow collisions; and
(g) Conclusion.

II. THEORY OF FAST COLLISIONS: THE BORN APPROXIMATION

A. Derivation of the Basic Formulas of the FBA

As was mentioned briefly in the Introduction, the first order perturbation theory is adequate to describe collisions of fast electrons—and other fast charged particles—with atoms, as long as the collision is dominated by weak interactions. In this case, the Coulomb interaction between the projectile and the target \( H_{\text{int}} \) can be treated as a perturbation compared to the sum of the total energy of the target \( H_{\text{a}} \) and the kinetic energy of the incident electron \( H_{\text{k}} \).

In this chapter, we shall derive the basic formulas of the first Born approximation (FBA) and discuss their qualitative features and relationships to photon-atom interaction.

1. Preliminaries

We first consider the excitation of an atom from its ground state 0 to a discrete excited state \( n \). This will allow us to understand the basic structure of the FBA without being encumbered by mathematical details.

There are three basic forms of the FBA: the plane-wave Born approximation, The Coulomb Born approximation, and the distorted-wave Born approximation. They are different in what part of \( H_{\text{int}} \) is included in the unperturbed Hamiltonian \( H_{0} \).

For an atom of nuclear charge \( Z \) with \( N \) electrons, \( H_{a} \) is given by

\[
H_{a} = \sum_{j=1}^{N} \left[ \frac{p_{j}^{2}}{2m} - \frac{Ze_{j}^{2}}{r_{j}} + \sum_{k>j}^{N} \frac{e_{j}^{2}}{r_{jk}} \right],
\]  

(1)
where \( \mathbf{p}_j \) and \( \mathbf{r}_j \) are the momentum and position vectors of the jth electron, respectively, \( r_{jk} = |\mathbf{r}_j - \mathbf{r}_k| \), and \( e \) and \( m \) are the charge and the rest mass of the electron, respectively. For the projectile electron,

\[
H_e = \frac{p_e^2}{2m},
\]

and

\[
H_{ei} = \frac{p_i^2}{2m},
\]

\[
H_{ef} = \frac{p_f^2}{2m} = H_{ei} - E_n,
\]

where \( E_n \) is the excitation energy gained by the target atom. The interaction Hamiltonian is given by

\[
H_{int} = \sum_{j=1}^{N} \frac{\frac{Ze^2}{r_{ej}}}{r_{ej}}
\]

where \( r_{ej} \) is the distance between the projectile and the target nucleus, and \( r_{ej} = |\mathbf{r}_{ej} - \mathbf{r}_j| \). Here we have assumed that the target nucleus is so heavy that the center of mass during the collision coincides with the nucleus. For a heavy projectile, this assumption may be invalid. Then, theory must be derived in the center of mass frame and cross sections must be transformed to the laboratory frame for comparison with experiment.

2. The Plane-Wave Born Approximation (PWBA)

In the simplest—and the most popular—form of the FBA, the unperturbed Hamiltonian of the colliding particles, \( H_0 \), is the sum of \( H_a \) and \( H_e \). The perturbed Hamiltonian, \( H' \), therefore, includes both electron-electron and electron-nucleus interactions in \( H_{int} \), Eq. (4):

\[
H_e = H_a + H_e,
\]

\[
H' = H_{int}.
\]

Since \( H_0 \) does not include any interaction between the projectile and the target, the appropriate wave function \( \psi_0 \) for \( H_0 \) is a product

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of the atomic wave function \( \psi_a \) and that for a free electron \( \psi_e \), i.e., a plane wave:

\[
\psi_0 = \psi_a \psi_e.
\]

The interaction matrix element for the excitation to the state \( n \) is

\[
M_n = \langle \psi_0 | H' | \phi_0 \rangle = \langle \psi_0 | \sum_j \sum_k e^{-2/r_{ej}} | \phi_j \rangle = < \psi_0 | < \phi_j | Z e^{-2/r_e} | \phi_0 > .
\]

Aside from a normalization factor, we denote the plane wave by

\[
\psi_e = \exp(i \mathbf{p} \cdot \mathbf{r}_0) = \exp(i \mathbf{k} \cdot \mathbf{r}_0).
\]

Then, the projectile-dependent terms in Eq. (8) can be integrated out using the relation

\[
\int \frac{e^{i \mathbf{k} \cdot \mathbf{r'}}}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r'} = \frac{4\pi}{2} \frac{e^{i \mathbf{k} \cdot \mathbf{r}}}{|\mathbf{r} - \mathbf{r}_j|}.
\]

With Eq. (10) we get

\[
M_n = \left( 4\pi^2/k_e^2 \right) \left[ \psi_n | \sum_j e^{i \mathbf{k} \cdot \mathbf{r}_j} | \psi_0 > - \mathbf{Z} \delta_n 0 \right],
\]

where \( \mathbf{k} \) is defined in terms of the momentum transfer,

\[
\mathbf{k} = \mathbf{p}_1 - \mathbf{p}_f.
\]

The Kronecker delta in Eq. (11) results from the orthonormality of the atomic wave functions, and it contributes only to elastic scattering. Now we can write the cross section in the PWBA using Fermi's golden rule:

\[
\frac{d\sigma}{d\Omega} = \frac{4a e^2}{(k\mathbf{r})^4} \frac{v_f}{2} \frac{Z \delta_n 0 - \psi_n | \sum_j e^{i \mathbf{k} \cdot \mathbf{r}_j} | \psi_0 > |^2}{2}
\]

\[
= \frac{k \mathbf{e}^2}{k (k\mathbf{r}_0)^4} \frac{Z \delta_n 0 - \psi_n | \sum_j e^{i \mathbf{k} \cdot \mathbf{r}_j} | 0 > |^2}.
\]
where \( \vec{v}_i \) and \( \vec{v}_f \) are the initial and final velocities of the projectile, and \( a_0 = \frac{\hbar^2}{2me^2} = 5.291 \text{ Å} \) is the Bohr radius. Note that \( K_0 \) is dimensionless, and hence all terms in the last line of Eq. (13) are explicitly dimensionless except for the term \( 4a_0^2 \), which carries the correct dimension of a cross section.

Equation (13) is the cross section for the angular distribution of the projectile. The relationship between \( d\Omega \) and \( K \) is nontrivial; it involves both the scattering angle \( \Theta \) and the energy loss \( E_n \). From Fig. 1, we have

\[
K_0^2 = k_i^2 + k_f^2 - 2k_ik_f \cos \Theta,
\]

and from Eqs. (3a) and (3b),

\[
k_i^2 = k_0^2 - \frac{2mE}{n} \mu_n^2.
\]

Substitution of Eq. (14b) into (14a) yields

\[
(K_0)^2 = 2(\frac{T}{R})[1 - \frac{E}{2T} - (1 - \frac{E}{T})^{1/2} \cos \Theta],
\]

where

\[
T = \frac{mv_i^2}{2},
\]

and \( R = \frac{m^2}{\mu_i^2} = 13.6 \text{ eV} \) is the Rydberg energy. Note again that Eq. (15) is presented in a dimensionless form, and \( T \) defined by Eq. (16) reduces to the nonrelativistic kinetic energy of the incident electron. Also, Eq. (13) can be expressed in terms of \( T \) and \( K \), using Eq. (14a):

\[
\frac{d\sigma}{d\Omega} = \frac{4\pi a_0^2}{T/R} \left[ \frac{z\delta_{n0} - n|\sum_j \phi_j^+ r_j^+ |0>|^2}{(K_0)^4} \right].
\]

Equations (14) and (17) are the basic formulas for the PWBA we shall work with.

3. The Coulomb Born Approximation (CBA)

When the target is an ion, particularly with high ionicity,

\[
\zeta = Z - N,
\]

the nuclear interaction term, \(-Ze^2/r_e\), in \( H_{\text{int}} \) [Eq. (4)] is more important than the electronic interaction term \( \sum_j e^2/r_{ej}\). In this case, it may be better to include the nuclear term into the unperturbed Hamiltonian, \( H_0 \). Then,

\[
H_0 = H + e\frac{Ze^2}{r_e}.
\]

\[
H' = \sum_j e^2/r_{ej}.
\]

Equation (19a), however, still does not contain any interaction term between bound and incident electrons. Thus, the appropriate wave function \( \Psi_0 \) for \( H_0 \) is still a product of \( \Phi_a \) and \( \Phi_\infty(Z) \); \( \Phi_\infty(Z) \) now must satisfy

\[
(\frac{2}{2m} - Ze^2/r_e)\Phi_\infty(Z) = e\Phi_\infty(Z).
\]

The solution of Eq. (21a) is the hydrogenic Coulomb function with continuum energy \( e\zeta \). The interaction matrix element [Eq. (8)] now contains only the interelectronic term:

\[
M_{n} \propto |\langle \psi_n | j \Phi_e^{-1} | 0, n \rangle |^2.
\]

The CBA uses Eq. (22a) as the interaction matrix element in deriving the cross section formula from Fermi's golden rule again:

\[
\frac{d\sigma}{d\Omega} = \frac{2}{4\pi a_0^2} \left| \frac{1}{n} \phi_j^+ r_j^+ \phi_0^+ |0, n \rangle \right|^2.
\]
Dimension of the matrix element in Eq. (23) is \((\text{length})^2\) and the correct dimension for the cross section is preserved.

Of course, one can use a screened nuclear charge, e.g., the ionicity \(\zeta\) instead of the nuclear charge \(Z\) in Eq. (21a), in which case Eqs. (19a)-(22a) should be replaced by

\[
\begin{align*}
H_0 &= H_0 + \frac{e^2}{r_e} - \zeta e^2/r_e, \\
H' &= \sum_j \frac{e^2}{r_{ej}} - (Z - \zeta) e^2/r_e = \sum_j \frac{e^2}{r_{ej}} - Ne^2/r_e, \\
(p_e^2/2m - \zeta^2 e^2/r_e)\psi_\zeta(e, \zeta) &= e^2 \phi_\zeta(e, \zeta),
\end{align*}
\]

and

\[
M = \sum_{n} \frac{e^2}{\alpha_f} (\zeta) \left| \sum_{j} \frac{e^2}{r_{ej}} \right| \psi_\zeta(e, \zeta) \left| \psi_{n}^0 \phi_\zeta(e, \zeta) >
\]

will contribute only for a few values of \(\lambda\) owing to the selection rules for angular momentum eigenstates. This in turn will reduce the number of nonvanishing integrals involving the projectile states,

\[
\sum_{n} \left| \psi_{n}^0 \phi_\zeta(e, \zeta) >
\]

to a single series sum though both \(\phi_\zeta\) and \(\phi_\zeta\) are represented by infinite series [Eq. (25)].

For ionizing collisions, however, these simplifications do not occur, and the interaction matrix element requires double series summation. In practice, of course, these series are truncated to save computational burden.

As we can see from the above discussion, a different choice of \(\zeta\) will result in a different cross section. Limited experience with existing theoretical and experimental data suggests that net ionicity defined by Eq. (18) is preferable to the bare nuclear charge \(Z\).

4. The Distorted-Wave Born Approximation (DWBA)

A further improvement on the CBA can be made by replacing a constant ionicity (or screened charge) \(\zeta\) by a screening function. In practice, we solve a Schrödinger equation for the projectile in the field of bound electrons and the nucleus of the target atom. The screened charge distribution in the target atom can be represented by a local or nonlocal potential — e.g., Hartree-Fock potentials. For brevity, we choose a local potential, \(V(r_e)\), to represent the screening of the target nuclear charge by bound electrons. Then, instead of Eqs. (19)-(22), we have

\[
\begin{align*}
H_0 &= H_0 + \frac{e^2}{r_e} [Z/r - V(r_e)], \\
H' &= \sum_j \frac{e^2}{r_{ej}} - Ne^2/r_e, \\
(p_e^2/2m - e^2 [Z/r_e - V])\psi_\zeta(V) &= e^2 \phi_\zeta(V).
\end{align*}
\]
and

\[ M_n = e^2 \langle \psi_n \phi(V) | \Sigma_j e^{iK \cdot r_j} - V| \phi_0 \psi(V) \rangle = e^2 \langle \psi_n \phi(V) | \Sigma_j e^{iK \cdot r_j} - \delta_{n0} \phi(V) | V(r) | \phi_0 \psi(V) \rangle. \]

\[ (22c) \]

Again, the choice of the screening function explicitly enters in \( M_n \) only for elastic scattering. For inelastic scattering, \( M_n \) will depend on \( V \) indirectly through \( \phi(V) \) in the first matrix element of Eq. (22c). The basic numerical technique to evaluate \( M_n \) and hence the DWBA cross section, which is the same form as Eq. (23), is to expand the continuum functions into partial waves and \( r_j \) into products of spherical harmonics as was done for the CBA.

One can develop different versions of the DWBA by choosing different \( V(r) \) as well as constructing total wave functions \( \psi_0 \) out of \( \phi_0 \) and \( \phi_e \)-e.g., with or without antisymmetrization.

5. Generalized Oscillator Strength—The Photon Connection

For an inelastic scattering, Eq. (17) can be written as

\[ \frac{d\sigma}{d(Ka_0)^2} = \frac{4\pi a_0^2}{T/R} \frac{R}{E_n} \frac{f(K)}{(Ka_0)^2}, \]

\[ (27) \]

where the generalized oscillator strength (GOS), \( f_n(K) \), is defined as

\[ f_n(K) = \frac{E_n}{R} \frac{|\langle \psi_n | e^{iK \cdot r_j} | \psi_0 \rangle|^2}{(Ka_0)^2}. \]

\[ (28) \]

Some simple and useful properties of the GOS are listed below.

(a) The GOS is an even function of \( K \)—this is obvious from the definition, Eq. (28).

(b) The GOS reduces to the well-known dipole oscillator strength, \( f_d \), at \( K = 0 \)—we can prove this by expanding \( e^{iK \cdot r_j} \) in Eq. (28) into n-

power series and by taking the limit \( K \to 0; \)

\[ e^{iK \cdot r} = 1 + iK \cdot r - (K \cdot r)^2/2 + \ldots \]

and

\[ \lim_{K \to 0} |n| e^{iK \cdot r} |0 \rangle^2/(Ka_0)^2 = \lim_{K \to 0} |n| x/a_0 |0 \rangle^2/(Ka_0)^2 \]

\[ = |n| x/a_0 |0 \rangle^2. \]

In the last step, we took \( K \) to be parallel to the \( x \) axis. The GOS now reduces to

\[ \lim_{K \to 0} \frac{f(K)}{R} = \frac{E_n}{R} \frac{|n| x/a_0 |0 \rangle^2}{(Ka_0)^2} \equiv f_n. \]

\[ (29) \]

(c) Similar to the Thomas-Kuhn-Reiche sum rule for \( f_n \), we have the Bethe sum rule

\[ \sum \frac{f(K)}{n} = N \quad \text{for all} \ K, \]

\[ (30) \]

where \( f_n \) denotes summation over all excitations (including ionization and inner-shell excitations) and \( N \) is the total number of electrons in the atom. The proof of the Bethe sum rule is given in the classic article by Bethe\(^3\) and other standard textbooks.\(^4,5\) In this context, the Thomas-Kuhn-Reiche sum rule is a special case (\( K = 0 \)) of the Bethe sum rule. The Bethe sum rule is valid for ions, as long as the number of bound electrons is used for \( N \), not the nuclear charge.

The fact that the GOS reduces to \( f_n \) at \( K = 0 \) provides a very important link between electron-impact and photon-impact cross sections. This connection exists only through PWBA, and hence it can be exploited only when the FWBA is valid—i.e., when the incident electron speed far exceeds those of the bound electrons, particularly the orbital speed of the electron being excited or ionized.

Note that \( f_n(K) \) as defined by Eq. (28) is a function of \( K \) only and does not depend on the incident energy. Hence, the GOS needs to be calculated only once for a given transition as a function of \( K \). Then, one can calculate the FWBA cross section, \( d\sigma/d\Omega \) for all incident energies. Again, this simplification occurs only for the PWBA.
In comparing experiment with theory, one can derive an "experimental" GOS by using the measured angular distribution on the left-hand side (LHS) of Eq. (27) and solving it for $f_{\alpha}(K)$. If "experimental" GOS for different incident energies form a universal curve, it is a good indication that the FWBA is valid for the experiment. As is evident from Eq. (28), however, the theoretical values of $f_{\alpha}(K)$ depend on the target wave functions used. Any comparison of the FWBA and experiment, therefore, must be done with a realistic estimate of the wave function effect, even when the incident energy is high enough for the FWBA to be valid.

![He (2\textsuperscript{1}P)](image)

Fig. 2. Generalized oscillator strength for the $1\text{S} + 2\text{P}$ excitation of He. The solid curve was computed from highly correlated wave functions (Ref. 6) and the broken curve from less correlated wave functions (Ref. 7). The circles are electron-impact experimental data by Lassettre et al. (Refs. 7,8), the squares are those by J. Geiger, (Rev. 9), and the triangles are those by Vriens et al. (Ref. 10). Experimental incident energies vary from 200 eV to 25 keV. (From Ref. 6).

![He (2\textsuperscript{1}S)](image)

Fig. 3. Generalized oscillator strength for the $1\text{S} + 2\text{S}$ excitation of He. The solid curve was computed from highly correlated wave functions (Ref. 6). The circles are electron-impact experimental data by Lassettre et al. (Ref. 7) and the triangles are those by Vriens et al. (Ref. 10). Experimental incident energies vary from 400 eV to 600 eV. (From Ref. 6)

In Figs. 2 and 3, we compare theoretical GOS \textsuperscript{6,7} and "experimental" ones\textsuperscript{8-10} for the excitation of He to the $2\text{P}$ and $2\text{S}$ states, respectively. The solid curves were computed from highly accurate wave functions, uncertainties from which are expected to be less than the thickness of the curves drawn. Figure 2 shows an excellent agreement between theory and experiment for an allowed transition, whereas Fig. 3 indicates that the FWBA is not reliable at the incident energies of 300-500 eV for a forbidden transition.
Frequently, the ratio of incident energy to excitation energy, \( u = T/E_0 \), is used as a sole criterion for the validity of the PWBA. Such a practice is unjustified because the values of \( u \) for the experimental data presented in Figs 2 and 3 are similar (\( u = 15-25 \)) but the figures clearly indicate different degrees of validity of the PWBA. For the resonance transition of Na, the experimental data\(^{11}\) in Fig. 4 were measured at \( u = 50-70 \), but agreement with theory\(^{12}\) is far as good as in the resonance transition of He presented in Fig. 2. Although the wave functions used for Na (Hartree-Fock) are inferior to those for He (50-term Hylleraas), the theoretical uncertainty in Fig. 4 is \( \pm 1\% \), far smaller than the scatter in the experimental data.

The fact that \( f_0(K) \) reduces to the dipole \( f_n \) as \( K = 0 \) can be used in judging the reliability of theoretical \( f_0(K) \). The broken curve\(^7\) in Fig. 2 is calculated using wave functions which are inferior to those used for the solid curve. We see that the two curves differ most for small values of \( K \), i.e., at small scattering angles. The theoretical GOS in Fig. 4 reduced to \( f_0(0) = 0.987 \) as compared to the value \( f_0 = 0.982 \) recommended in the NBS tabulation of atomic transition probabilities.\(^{13}\)

This is one example of using photoabsorption data \( f_n \) to assess reliability of electron-impact data, both theoretical and experimental. More examples of the "photon connection" will be presented later.

For ionizing collisions, accurate theoretical GOS are difficult to calculate because, for the continuum wave functions, we cannot match the accuracy of bound-state wave functions. One exception is the hydrogenic case, of course. In Fig. 5, we present the continuum GOS of the hydrogen atom.\(^{14}\) For ionization, the cross section is not only differential in scattering angles, but also in the energy of the ejected electron. The GOS for the discrete excitation is dimensionless; the continuum GOS is defined per energy loss of the incident electron, as is done in Fig. 5. Hence, actual values of the continuum GOS, \( df(K)/dE \), depend on the unit of energy for \( E \); Rydberg energy is used in Fig. 5.

The continuum GOS near the ionization threshold resembles those for discrete excitations. However, a sharp peak at \( (K\alpha)^2 \approx E/R \) emerges as \( E \) becomes much larger than the binding energy of the ejected electron. If the target electron were free and at rest, the momentum-energy conservation laws would have required the GOS to be a delta function with its peak at \( (K\alpha)^2 = E/R \). The peak in the continuum GOS is referred to as the Bethe ridge or the binary peak.

Another point to remember is that \( df(K)/dE \) describes the angular distribution of scattered electron and not the ejected electron. In fact, \( df(K)/dE \) is obtained by integrating over the angles of the ejected electron.

B. Integrated Cross Sections

Often experimental arrangement is such that it is easier to measure integrated cross sections rather than angular distributions. Theoretically, one simply integrates over the angular distribution of the scattered electron. Bethe developed\(^3\) a simple but powerful method for integrating the PWBA angular distribution. The Bethe approximation for the integrated cross section not only retains essential physics contained in the PWBA, but it also provides a compact form for the cross section—in terms of two to three constants constants that are independent of the incident energy. This form is particularly useful for applications in which the cross sections for a wide range of incident energies are needed.
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where the limits of integration [cf. Eqs. (14a) and (15)]

\[ Q_{\text{min}} = (k_i - k_f)^2 a_0^2 \]
\[ = \frac{E_n^2}{4TR} \left[ 1 + \frac{E_n}{2T} + O\left(\frac{E_n^2}{T^2}\right) \right], \]  

(34)

and

\[ Q_{\text{max}} = (k_i + k_f)^2 a_0^2 \]
\[ = \frac{4T}{R} \left[ 1 - \frac{E_n}{2T} + O\left(-\frac{E_n^2}{T}\right) \right]. \]  

(35)

Equation (33) can easily be visualized by plotting \( f_n(Q) \) vs. \( \ln Q \) as is done in Fig. 2. Then, the area under the GOS curve bounded by \( Q_{\text{min}} \) and \( Q_{\text{max}} \) is the integral on the RHS of Eq. (33), i.e.,

\[ \sigma_n = \frac{4\pi a_0^2}{T/E_n} \int_{\ln Q_{\text{min}}}^{\ln Q_{\text{max}}} f_n(Q) \, d(\ln Q) \]  

(36)

The integral \( G \) depends, as it should, on \( E_n \) and \( T \) through \( Q_{\text{min}} \) and \( Q_{\text{max}} \). A straightforward procedure to obtain \( \sigma_n \) is to evaluate \( G \) by numerical integration for each value of \( T \) of interest.

The Bethe approximation concerns the evaluation of \( G \) for high \( T \) in such a way that its \( T \) dependence is factored out and numerical integration is used only once. For this purpose, we note that for \( E_n/T \ll 1 \),

\[ Q_{\text{min}} = \frac{E_n^2}{4TR}, \]  

(34a)

and

\[ Q_{\text{max}} = 4T/R. \]  

(35a)

When \( T \) is large, \( Q_{\text{min}} \ll 1 \) and for a dipole-allowed transition, \( f_n(Q) \approx f_n \) in the vicinity of \( Q_{\text{min}} \). Also, \( Q_{\text{max}} \) becomes sufficiently large that it can be replaced by \( a_0 \). The first step in the Bethe

1. Integrated Cross Section in the PWBA

Integration over the angles in the PWBA is equivalent to integration over \((Knq)^2\) in Eq. (27), or essentially integration of the GOS between the minimum and maximum momentum transfer. Let

\[ Q \equiv (Kq)^2. \]  

(31)

Then, Eq. (27) can be rewritten as

\[ d\sigma_n = \frac{4\pi a_0^2}{T/E_n} \frac{E_n}{Q} \frac{f_n(Q)}{Q} \, dQ, \]  

(32)

and the integrated cross section is given by

\[ \sigma_n = \int_{Q_{\text{min}}}^{Q_{\text{max}}} d\sigma_n = \frac{4\pi a_0^2}{T/E_n} \int_{Q_{\text{min}}}^{Q_{\text{max}}} \frac{f_n(Q)}{Q} \, dQ, \]  

(33)
approximation is to express $G$ in terms of these simpler but approximate limits of integration:

$$G = \int_{\ln(E_n^2/4TR)}^\infty f_n(Q) d\ln(Q).$$  \hspace{1cm} (37)

Then, we choose $Q_0 > Q_{\text{min}}$ such that the area of a rectangle bounded between $Q = E_n^2/4TR$ and $Q_0$ with height $f_n$ becomes the same as $G$. This procedure is illustrated in Fig. 6. The correct value of $G$ is the sum of areas I and II, excluding the shaded parts. The value $Q_0$ is chosen such that areas II and III, including the shaded upper left corner, are the same. Both shaded areas contribute to higher order corrections, from which the leading dependence on $E_n$ and $T$ can also be factored out. One numerical integration of $f_n(Q)$ is necessary to determine $Q_0$ accurately. Once $Q_0$ is known,

$$G = \int_{\ln(E_n^2/4TR)}^{Q_0} f_n(Q) d\ln(Q) = f_n \left[ \ln(T/R) + \ln(4K_0^2/E_n^2) \right]$$

and

$$\sigma_n = \frac{4\pi a_0^2}{T/R} \left[ A_n \ln(T/R) + B_n \right],$$  \hspace{1cm} (38)

where $A_n$ and $B_n$ are defined by

$$A_n \equiv f_n R/E_n,$$  \hspace{1cm} (39)

$$B_n \equiv A_n \ln(4K_0^2/E_n^2).$$  \hspace{1cm} (40)

Bethe parameters $A_n$ and $B_n$ depend only on the target property and not on the type of incident particle as long as it is structureless. For a bare ion of charge $z$ and speed $v_i$, corresponding $C_n$ is given by

$$\sigma_n = \frac{4\pi a_0^2}{T/R} \left[ A_n \ln(T/R) + B_n \right].$$  \hspace{1cm} (38a)

where $T$ should be evaluated with $v_i$ as specified in Eq. (16), and not by the kinetic energy of the projectile. For example, proton-impact data can be scaled to give electron-impact cross sections and vice versa, by using Eq. (38a) in the asymptotic region.

Fig. 6. Illustration of the Bethe approximation for integrated cross sections. The sum of areas I and II is the integral $G$ in Eq. (36), corresponding to the exact PWBA integrated cross section. The Bethe approximation replaces the integral by a rectangle by choosing $Q_0$ such that areas II and III are equal. The shaded areas contribute to a higher order term denoted by $C_n$ in Eq. (41).

The Bethe approximation is equivalent to an expansion of the Born cross section, Eq. (33), in powers of $1/T$. We can extend the power series by one more term, i.e.,

$$\sigma_n = \frac{4\pi a_0^2}{T/R} \left[ A_n \ln(T/R) + B_n + C_n R/T \right]$$  \hspace{1cm} (41)

Again, $C_n$ is a constant that is independent of $T$, but now it depends not only on the target property but also on the type of projectile. The shaded area in Fig. 6 contributes to $C_n$.

Furthermore, for electron-impact excitations, the electron-exchange effect and distortion of the projectile wave functions in the field of the target (i.e., departure from the plane-wave description) compete with the $C_n$ term in Eq. (41). In this sense, the original work by Bethe, in which he evaluated $A_n$ and $B_n$ for the
hydrogen atom, extracted all the essential physics contained in the FWBA.

For a forbidden transition, $A_n = 0$ and $B_n$ is obtained from the integration of the COS (e.g., Fig. 3) from $Q = 0$ to $\omega$. Values of the Bethe parameters for some Li-like ions are presented in Table I.

2. The Fano Plot and Line Strength

Asymptotic behavior of an integrated cross section can be seen clearly by plotting

$$ Y = \sigma T/4\pi a^2 \frac{2}{n} \left( \frac{Z}{R} \right) $$

as a function of

$$ X = \ln(T/R) $$

(42)

Then, at high $T$, $Y$ will approach a straight line with slope $A_n$ and the $Y$ intercept $B_n$. For low $T$, the straight line will curve as the $C_n$ term in Eq. (41) and other effects not included in the FWBA, become important.

The $X$-$Y$ plot is known as the Fano plot. This is a very powerful tool in investigating systematics of both theoretical and experimental data. For instance, electron-impact data on a discrete transition can be put into a Fano plot (even if they are relative cross sections!) and be examined for consistency by checking:

a) how smoothly do the data points approach a straight line as $T$ increases; and

b) the slope against the value of $A_n = f_n R_n E_n$ derived from photoabsorption data, if they are available. This is another example of using photon data for a consistency check on electron-impact data. For a forbidden transition, the slope vanishes; i.e., the Fano plot approaches a horizontal line at high $T$.

An example of the Fano plot is presented in Fig. 7 for the $2^1$ excitation of He.

Sometimes the collision strength, a quantity proportional to $Y$, is used:

Table I. Bethe parameters for the excitation of Li-like ions by electron impact. Theoretical data are evaluated from the Hartree-Fock wave functions. Entries in parentheses in columns 3 and 4 are based on experimental energies and $f_n$ values recommended in Ref. 16.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Excited state</th>
<th>$E_n/R_n$</th>
<th>$A_n$</th>
<th>$B_n$</th>
<th>$C_n$</th>
</tr>
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<tr>
<td>Li</td>
<td>$2^2p$</td>
<td>0.1353</td>
<td>5.658</td>
<td>17.330</td>
<td>-0.226</td>
</tr>
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<td></td>
<td></td>
<td>(0.1359)</td>
<td></td>
<td>(5.54)</td>
<td></td>
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<td></td>
<td>$3^2s$</td>
<td>0.2490</td>
<td></td>
<td>0.578</td>
<td>-0.0797</td>
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<td></td>
<td>$3^2p$</td>
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<td>0.0121</td>
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<td>0.0223</td>
</tr>
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<td></td>
<td></td>
<td>(0.2819)</td>
<td></td>
<td>(0.020)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$3^2d$</td>
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</tr>
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<td>C$^{3+}$</td>
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<td>0.493</td>
<td>1.271</td>
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<td>(0.5883)</td>
<td></td>
<td>(0.486)</td>
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<td></td>
<td>(2.917)</td>
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<td>(0.0675)</td>
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<td></td>
<td>$3^2p$</td>
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<td>N$^{4+}$</td>
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<td>(0.7348)</td>
<td></td>
<td>(0.320)</td>
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<td>$3^2s$</td>
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<td></td>
<td>0.0408</td>
<td>-0.105</td>
</tr>
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<td></td>
<td>(4.354)</td>
<td></td>
<td>(0.0535)</td>
<td></td>
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<tr>
<td></td>
<td>$3^2p$</td>
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<td>0.0540</td>
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<td></td>
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<td>(4.354)</td>
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<td>(0.0535)</td>
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</tr>
<tr>
<td></td>
<td>$3^2d$</td>
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<td></td>
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<td>Ne$^{7+}$</td>
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<td>0.324</td>
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<td>(1.178)</td>
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<td>(0.133)</td>
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<td></td>
<td>(0.0283)</td>
<td></td>
</tr>
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<td></td>
<td>$3^2p$</td>
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<td>0.0288</td>
<td>0.0903</td>
<td>0.212</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(10.34)</td>
<td></td>
<td>(0.0283)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$3^2d$</td>
<td>10.45</td>
<td></td>
<td>0.0498</td>
<td>-0.283</td>
</tr>
<tr>
<td>Ar$^{15+}$</td>
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<td>2.363</td>
<td>0.0112</td>
<td>0.0272</td>
<td>-0.0126</td>
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<td></td>
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<td>0.0505</td>
<td>-0.0278</td>
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<tr>
<td></td>
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<td>47.89</td>
<td>0.101</td>
<td>0.0183</td>
<td>-0.0231</td>
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<td>Fe$^{23+}$</td>
<td>$2^2p_1/2$</td>
<td>36.24</td>
<td>0.0495</td>
<td>0.0118</td>
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<tr>
<td></td>
<td>$2^2p_3/2$</td>
<td>47.89</td>
<td>0.101</td>
<td>0.0183</td>
<td>-0.0231</td>
</tr>
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Fig. 7. Integrated cross section for the $^1S \rightarrow ^1P$ excitation of He. The solid straight line is the Bethe asymptotic cross section [Eq. (38)], and the broken curves marked $e$ and $\infty$ are the Bethe cross section with the projectile dependent term [Eq. (41)], the former for electrons and the latter for heavy particles such as protons and $\alpha$ particles. The Bethe parameters were computed from highly correlated wave functions (Ref. 6). The triangles are experimental data by Vriens et al. (Ref. 10), and other symbols represent electron-impact experimental data by other investigators. See Ref. 6 for details. (From Ref. 6.)

$$S_n = \frac{\sigma_n T_n}{n_a} = \frac{4}{3} \omega_i^2 Y,$$

where $\omega_i$ is the multiplicity of the initial state of the target.

3. Comparison of the PWBA, CBA, and DWBA on Discrete Excitations

At high incident energies, the PWBA is expected to be valid, and hence the CBA and DWBA results are expected to merge toward those from PWBA. In this type of comparison, however, it is important that all theoretical data be evaluated using identical wave functions;

otherwise differences in wave functions may mask the effects of differences in theoretical models.

Major departures from the PWBA results occur for low $T$. The leading causes for the departures are:

(a) for target ions, difference in the threshold behavior of the cross sections;

(b) distortion of the projectile wave function;

(c) electron-exchange effect between the incident and bound electrons in the target atom; and

(d) polarization of the target charge distribution during the collision due to the presence of the incident electron.

The first two causes can be corrected by the use of a Coulomb or distorted wave for the projectile, i.e., by the CBA or DWBA.

The third cause is usually corrected by requiring antisymmetrization of the projectile with the bound electrons. The same procedure is sometimes used in the PWBA—known as the Born-Oppenheimer approximation—but the results have been unsatisfactory. It is rare that the Born-Oppenheimer approximation brings genuine improvements to the PWBA results.

The exchange effect is intrinsically a strong interaction between the projectile and the affected bound electrons, which is likely to modify both the projectile and the bound-state wave functions. Any treatment of the exchange effect that leaves the bound-state description unchanged is likely to be incomplete.

The fourth cause cannot be handled within the framework of the first order perturbation theory at all. In a simplified picture, the target must be considered as a linear combination of many of its excited states during the collision, which is the basic premise of the strong coupling methods such as the close-coupling and R-matrix theories.

In Fig. 8 we compare the PWBA, CBA, and DWBA (with exchange) cross sections with experimental data for the $^2P$ excitation of $C^3+$ by electron impact. As expected, the PWBA data agree better with other theories at high incident energies, and the DWBA results agree...
Zn isoelectronic sequences belong to this category. Also, highly charged ions exhibit relativistic effects through changes in energy levels, coupling schemes and orbital sizes. Correlation and relativistic effects in collision cross sections will be discussed in more detail later.

III. Ionization by Electron-Impact

Although the ionization process has been studied experimentally from the early days of modern physics—e.g., discharge in gases, production of x rays, Geiger counters—we have only a limited success in predicting ionization cross sections from theory.

An obvious departure from discrete excitations is that two electrons that emerge after an ionizing collision (scattered and ejected) are indistinguishable. The faster one of the two is referred to as the "primary" electron and the slower one as the "secondary" electron. This is strictly an operational definition. Such a distinction becomes ambiguous when many electrons are ejected simultaneously during or immediately after a collision. For instance, multiple ionization makes substantial contributions (through the decay of inner-shell holes) to the total ionization cross section of alkali-like ions, for which inner-shell electrons outnumber valence electrons by a large margin.

A comprehensive theory of ionization can provide detailed information for both primary and secondary electrons, i.e., ionization cross sections differential in

(a) incident energy $T$,
(b) energy loss $E$, of the primary electron,
(c) scattering angles of the primary electron $\Theta_p$ and $\phi_p$,
(d) kinetic energy of the secondary electron $W$, and
(e) scattering angles of the secondary electron $\Theta_s$ and $\phi_s$.

If only one electron is ejected, $E$ and $W$ uniquely identify the shell from which the electron was ejected. Also, one can choose the reference plane to be that defined by the initial and final momenta of the primary electron, i.e., set $\phi_p = 0$. 

Fig. 8. Integrated cross section for the $2S^2 - 2P^2$ excitation of C$^{3+}$. The solid curve is the PWBA result calculated by the present author from the Hartree-Fock wave functions, the broken and dashed curves are the CBA and DWBA results calculated by Mann (Ref. 18), also from the Hartree-Fock wave functions. The triangles are the results of a 5-state close-coupling calculation by Gau and Henry (Ref. 20). The circles with error bars are the experimental data by Taylor et al. (Ref. 19). The PWBA cross section vanishes at the threshold, whereas all other theoretical results are finite as they should be.

slightly better with the experiment near the threshold than those from the CBA. Because of the finite energy resolution of experiments, theoretical data near the threshold should be folded with experimental resolution when comparing with the experiment.

The DWBA results without exchange (not shown in Fig. 8)—i.e., without antisymmetrization of the total wave function $\Psi_0$—are very close to those of the CBA in Fig. 8. The antisymmetrization reduces cross sections for all incident energies. The scatter in the experimental data is too large to draw any conclusion on asymptotic behavior.

For ions with complicated electronic structure, use of correlated wave functions may be at least as important as, if not more than, the use of advanced collision theory. Ions of the Be, Mg, and
In the literature, ionization cross sections which specify $T$, $E$, $\Omega_p$ ($\phi_p$ and $\phi_p$), $W$, and $\Omega_S$ ($\Omega_0$ and $\phi_0$) are known as the "triple" differential cross sections, denoted by $d^3\sigma/d\Omega_p d\Omega_S dW$. Those which specify only $T$, $W$, and $\Omega_S$ are called "double" differential cross sections, $d^2\sigma/d\Omega_S dW$. A double differential cross section is obtained from corresponding triple differential cross section by integrating over $\Omega_p$ and summing over all $E$ that produce secondary electrons of kinetic energy $W$, e.g., secondaries from different shells. The "single" differential cross section, $d\sigma/dW$, is derived from the double differential cross section by integrating over $\Omega_S$. Finally, the total ionization cross section, $\sigma_{ion}$, is obtained by integrating $d\sigma/dW$ over $W$. One can also define cross sections which are double and single differential in the primary electron variables by integrating the triple differential cross section over $\Omega_p$ and $\Omega_S$, respectively. For a theoretical treatment, integration over $\Omega_S$ often leads to simpler expressions. In this section, we shall concentrate on the systematics of the secondary electrons and the total ionization cross section, after a brief discussion of triple differential cross sections.

**A. Triple Differential Cross Sections**

In principle, triple differential cross sections provide the most complete and stringent comparison of theory and experiment. However, possible combinations of variables are so numerous that meaningful and feasible combinations must be selected judiciously.

1. General Comments

For fast primary electrons, the angular distribution is sharply peaked in the forward direction. Most of them emerge in the forward cone of $\phi_p \approx 20^\circ$. For this reason, it is impractical to measure triple differential cross sections for large scattering angles of fast primary electrons.\(^{21,22}\) Even under favorable experimental conditions, a coincidence counting rate of one per second is common. Unfortunately, theorists have failed so far to provide guidance to experimentalists identifying most significant combinations of variables and targets. This is one of the challenging tasks left for theorists. Some experimental features observed in triple differential cross sections are:

(a) The angular distribution of secondary electrons shows two peaks, one in the forward hemisphere referred to as the binary peak, and the other in the backward direction, which is called the recoil peak;

(b) the binary peak occurs at an angle slightly larger than the momentum transfer direction, presumably from mutual repulsion of the two outgoing electrons;

(c) the binary peak sometimes splits into two lobes, suggesting the existence of a node; and

(d) the recoil peak is small compared to the binary peak in most cases, particularly for fast secondaries, but they may become comparable in magnitude for slow secondaries.

No theory has yet accounted for all the features mentioned above, even qualitatively. For instance, the second feature mentioned above could be explained properly only if the theory includes interaction between the two outgoing electrons in the computation of wave function for the secondary electron. The PWBA predicts both binary and recoil peaks to be symmetric around the momentum transfer direction. Symmetry of the collision process is such that the secondary-electron angular distribution must be symmetric with respect to the collision plane ($\phi_p = 0$), but not necessarily with respect to $\phi_1$, $\phi_2$, or $\phi$. Also, correct shape of the recoil peak would be difficult to predict from any theory that does not incorporate electron-exchange properly.

2. Zero-Angle Scattering of Fast Primary Electrons—Poor Man's Synchrotron Light Source

An ingenious method of simulating a high-energy (VUV to soft x-ray) photon source, similar to those available from electron synchrotrons, has been developed and extensively used by van der Wiel and co-workers.\(^{23,24}\) The method is based on the "photon connection" mentioned earlier for the inelastic scattering of fast electrons.

In the PWBA, $df(Q)/dE$ reduces to continuum dipole oscillator strength $df/dE$ at $Q = 0$. When primary electron energy is much higher than energy loss, i.e., $E/T < 1$, $Q_{min}$ at $\phi_p = 0$ becomes sufficiently small so that the GOS can be replaced by the dipole limit, $df/dE$. Then, using the PWBA formula, Eq. (32), one can deduce

(a) $df/dE$, where $E$ corresponds to photon energy $h\nu$, by measuring the primary-electron energy loss cross section at $\phi_p = 0$; or

(b) $d^2f(\phi_0)/dE d\phi_0$, angular distribution of photoelectrons, by measuring the angular distribution of secondary electrons in coincidence with the primary electrons that lost its kinetic energy by $E$ and emerge at $\phi = 0$.\(^{20}\)
Apparatus for this type of experiment is cheaper, simpler, and easier to operate than an electron synchrotron. This is why it is called a "poor man's synchrotron." Such an apparatus provides a continuous range of $E = hv$ as long as $E/T$ remains small. Also, it can, in principle, provide information on the ionization yield; i.e., the ratio between photoionization ($\int \left[ \frac{d^2\sigma}{d\Omega_d dE_d} \right] d\Omega_d$) and photoabsorption ($\frac{d\sigma}{dE}$).

Disadvantages of this method are in the energy resolution and its dependence on the Born theory to relate electron-impact data to photon data. Good energy resolution, however, is important only when the cross section depends sharply on the photon energy such as near a resonance. For a routine survey of photoionization cross sections, this method offers many advantages. Primary energy must be kept high to insure the validity of the FWBA. Moreover, when $\theta_{\text{min}} \approx 0.01$, the GOS may not be close to its dipole limit yet. (See Fig. 4, for example.) In such a case, the angular distribution ($\theta_0 < 5^\circ$) of the primary electron should be measured and converted into the GOS to assure proper convergence to the dipole limit.

B. Secondary Electrons

Detailed information on angular energy distributions of secondary electrons is needed not only to verify various theories but also as vital input to plasma modeling in fusion research, energy deposition modeling in radiation research, and in the study of upper atmosphere. More experimental data on secondary electrons are available, though not abundant, than those on primary electrons in ionizing collisions. Theoretical studies have progressed beyond the FWBA, although many qualitative aspects have been identified to analyze experimental data and extrapolate them to variable ranges not covered by the experiments.

1. Angular Distribution of Secondary Electrons

From energy-momentum conservation one can easily show that, when an electron of kinetic energy $T$ collides with another at rest, the struck electron will be ejected with kinetic energy $E$ in the direction given by

$$\cos \theta_b = \frac{E}{T}$$

where $\theta_b$ is measured from the direction of the incident momentum.

Although Eq. (45) was derived for a free target electron (without exchange effect), we can still use it for bound electrons as a qualitative guide by interpreting $E$ as the energy loss of the primary electron; i.e., the kinetic energy $W$ of the secondary electron plus its binding energy, $B$:

$$E = W + B$$

Of course, for a multi-shell target, it is difficult to determine $E$ when only $W$ is measured—a common situation for most experiments on secondary electrons. In this case, we must sum over all energy losses consistent with the energy conservation law; i.e., sum over all inner shells that could have produced a secondary electron of kinetic energy $W$. For example, for a multi-shell atom,

$$\frac{d^2\sigma}{d\Omega dE} = \sum_j \frac{d^2\sigma}{d\Omega_j dE}$$

with

$$E_j = W + B_j$$

where $B_j$ is the binding energy of the $j$th orbital.

For a free electron, the secondary electron peak will be sharp; it can be ejected only in the direction of $\theta_b$. A bound electron, however, has its own momentum distribution while in a bound orbit, and when ejected, its angular distribution is broadened around the "binary" peak at $\theta_b$. One can simply use addition of the ejected electron momentum with its average orbital momentum to provide the width of the binary peak:

$$\tan \Delta \theta_b = \sqrt{E/U}$$

where $U$ is the orbital kinetic energy of the ejected electron. In Table II, we list average orbital kinetic energies and binding energies of rare gases and some diatomic molecules. The orbital kinetic energies are larger in magnitude than the binding energies for nonhydrogenic atoms, particularly for outer orbitals with many radial nodes. Note that the virial theorem holds only for the total potential and kinetic energies, but not for each orbital. Radial nodes reduce the probability of finding an electron near the nodes; this implies that the electron is moving fast near the nodes, raising its average kinetic energy.
Although there are sizable differences in detail among the measured angular distributions of secondary electrons in the literature, all of them exhibit binary peaks, whenever they are discernible, in the vicinity of \( \Theta_s \) given by Eq. (45).

Another important point is the asymptotic behavior of the angular distribution at high incident energy, \( T \). For a given energy \( W \) and angle \( \Theta_s \) of a secondary electron, the same asymptotic behavior (as \( T \) increases) as that discussed for the integrated cross section (Eq. (38)) applies to the doubly differential cross section. It can be shown, analogous to Eq. (38), that

\[
\frac{d^2\sigma}{d\Omega_s dW} = \frac{4\pi a_0^2}{T} [A(W,\Theta_s)\ln(T/R) + B(W,\Theta_s) + ...] ,
\]

where

\[
A(W,\Theta_s) = \sum_j \frac{R}{E_j} \left[ 1 - \beta(E_j) P_2(\cos \Theta_s)/2 \right]
\]

with the summation over all binding energies \( E_j \) of the target (provided that \( T > E_j \)). \( E_j \) is defined by Eq. (48). The RHS of Eq. (51) is simply a summation over the photoelectron angular distribution divided by the photon energy, \( E_j \), where \( \beta \) is known as the asymmetry parameter and \( P_2 \) is the Legendre polynomial of the second order. Again, this is one of the photon connections. A large body of data exists on the photoelectron angular distribution in the literature.

Moreover, since \( P_2(\cos \Theta_s) \) is an even function of \( \cos \Theta_s \), \( A(W,\Theta_s) \) should be symmetric with respect to \( 90^\circ \), i.e.,

\[
A(W,90^\circ - \Theta) = A(W,90^\circ + \Theta)
\]

for all angles \( \Theta \leq 90^\circ \). This symmetry can be used in checking consistency of experimental angular distribution if data exist for high values of \( T \) so that one can plot the Fano plots for a given \( W \) but at two supplementary angles. Then, at high \( T \), the data points for the two angles should become parallel; i.e., they exhibit same slope, although their heights—the \( B(W,\Theta_s) \) term in Eq. (50)—are different for the two angles. Electron-impact data on \( N_2 \) in Fig. 9 clearly show expected symmetry [Eq. (52)] in slope.

Some investigators reported a sharp forward peak (\( \Theta_s \leq 15^\circ \)) in the angular distribution. Although it is tempting to associate
the peak with exchange effects, it is more likely that the peak is an experimental artifact.

2. Energy Distribution of Secondary Electrons

Although the extreme forward and backward angles pose severe difficulties in measuring the angular distribution of secondary electrons, the energy distribution $d\sigma/dW$ (obtained by integrating $d^2\sigma/dWd\Omega$ over $\Omega$) is insensitive to these angles because of the

$$\sin\theta\sin\phi = 2\pi \sin\theta_0 d\theta_0.$$  

On the other hand, experimental results are sensitive to the secondary electron energy, and most data in the literature show signs of difficulties for slow secondaries, as we shall see presently.

A powerful method of analyzing experimental data on energy distributions is to use the Platzman plot in which the ratio of measured cross section to the Rutherford cross section is plotted as a function of the energy loss of the primary electron. For a multi-shell atom, one can still use the lowest binding energy to determine the energy loss; this amounts to an assumption that all secondaries come from the valence shell. In atomic ions, this assumption will not cause any problem because the cross sections are much larger for valence electrons than inner ones. (For molecules, some refinements are necessary because, in general, there are several valence molecular orbitals and corresponding ionization potentials.)

The basic idea of the Platzman plot is that the ratio

$$Y = \frac{(d\sigma/dW)_{\text{observed}}}{(d\sigma/dW)_{\text{Rutherford}}}$$

is equivalent to the effective number of free electrons participating in the ionizing collision, because the Rutherford cross section

$$\frac{d\sigma}{dW}_{\text{Ruth.}} = \frac{4\pi a_0^2}{T} \left( \frac{R}{W} \right)^2$$

is exact if the target electron is unbound and at rest. (We disregard the indistinguishability of the two electrons for a moment.) In reality, Eq. (54) will diverge for a secondary electron with $W = 0$. To avoid the divergence, we use [see Eq. (46)]

$$E \equiv E_1 = W + B_1,$$

where $B_1$ is the lowest ionization potential. With this approximation,

$$Y = \frac{d\sigma}{dW} \frac{T}{4\pi a_0^2} \left( \frac{E}{R} \right)^2$$

is the (dimensionless) ordinate of the Platzman plot. As the abscissa, one can use either $E/R$ or $R/E$. A plot with $E/R$ as the abscissa
is convenient in studying the cross section for fast secondaries. A plot with \( R/E \) as the abscissa is better suited to elucidate details for slow secondaries, and also it has an advantage that the area under the curve gives the total ionization cross section:

\[
\sigma_{\text{ion}} \equiv \int_{0}^{W_{\text{max}}} (d\sigma/dW) dW 
\]

\[
\sigma_{\text{ion}} = \frac{4\pi a_0^2}{T/R} \int_{R/E_{\text{max}}}^{R/E_1} \frac{R}{Y_d(R/E)} dY_d(R/E), \tag{56b}
\]

where, according to the definition of the secondary electrons,

\[
W_{\text{max}} = (T - B_2)/2, \tag{57a}
\]

and

\[
E_{\text{max}} = W_{\text{max}} + B_1. \tag{57b}
\]

For high incident energies, again we can use the photon connection. Upon integration of the doubly differential cross section, Eq. (50), over \( N_\alpha \), we get

\[
\frac{d\sigma}{dW} = \frac{4\pi a_0^2}{T} \left( \frac{R}{E} \frac{df}{d\varepsilon} \ln(T/R) + B(W) + \ldots \right). \tag{58}
\]

and accordingly,

\[
Y = E(df/d\varepsilon)\ln(T/R) + (E/R)^2 B(W) + \ldots. \tag{59}
\]

We expect to see the following trends in the Platzman plot when the incident energy is high:

(a) When photoionization cross section is significant—for slow secondary electrons in general—the shape of the Platzman plot should resemble that of the photoionization, or the first term on the RHS of Eq. (59);

(b) For fast secondaries such that binding energy can be ignored, \( W \gg B_1 \), \( Y \) should approach effective number of free electrons participating in the ionization, i.e., the total number of valence electrons;

(c) Near \( W_{\text{max}} \) [Eq. (57a)], where the exchange effect is strong, the shape of the Platzman plot should resemble that of the Mott cross section instead of the Rutherford cross section; and

(d) Auger electrons appear as additional peaks superposed on the above features.

In Fig. 10, we present the Platzman plot for the energy distribution of secondary electrons from Ar produced by 500 eV incident electrons. The shape of measured secondary electron spectra clearly resembles that of photoelectrons except for the peak near \( W = 200 \) eV. The peak actually consists of several closely spaced LMM Auger peaks. Steps in the solid curves in Fig. 10 represent a new threshold for ionizing 2p electrons. The curve marked M is based on the Mott cross section\(^{39}\)—collision of two unbound electrons with exchange. As in the case of the Rutherford cross section, we introduced the binding energy into the Mott cross section to

(e) avoid divergence for \( W = 0 \) and

(f) preserve the symmetry in cross section between the two outgoing electrons.

The modified Mott cross section is:

\[
\left( \frac{d\sigma}{dW} \right)_{\text{Mott}} = \frac{4\pi a_0^2}{T} \sum_j N_j \left[ \frac{1}{E_j^2} + \frac{1}{(T-W)^2} - \frac{1}{E_j(T-W)} \right], \tag{60}
\]

where \( N_j \) is the occupation number of the \( j \)th orbital, and the summation is over all orbitals that satisfy \( B_j \leq T \). The curve marked BM in Fig. 10 is based on the binary encounter theory with exchange corrections. It is clear that the binary encounter theory cannot reproduce the delicate shape of the secondary electron spectra.

The dip in Fig. 10 at \( E/R \approx 3.5 \) is the Cooper minimum, where a leading term in the dipole matrix element for ionization vanishes. Note that the secondary electron cross section reduces to the Mott cross section at the Cooper minimum; the Mott cross section does not include dipole interaction.
Fig. 10. Energy distribution of electrons ejected from Ar: (a) by electron impact, and (b) by photoionization. In (a), the circles are experimental data by Opal et al. (Ref. 25), the square is by Grissom et al. (Ref. 40), and the triangle is the PWBA cross section extrapolated from discrete excitations (Ref. 41). The curves marked BM and M are Binary-Mott and Mott cross sections, respectively. The circles in (b) are photoionization cross sections compiled by Berkowitz (Ref. 34). The abscissa in (a) is the sum of secondary-electron energy W and the lowest ionization potential, and that in (b) is the photon energy. (From Ref. 33.)

An independent measurement of the cross section for the production of zero-kinetic energy secondary electrons by Grissom et al. (Ref. 40) and a theoretical estimate of the same cross section by extrapolation of bound-state excitation cross sections (Ref. 41) all support the close relationship between photoionization and secondary electron spectra.

An example of the Platzman plot with R/E abscissa is given in Fig. 11. Again, there is a striking resemblance between the shape

Fig. 11. Platzman plot of secondary electrons ejected from Ne: (a) by electron and photon impact, and (b) by photoionization. In (a), the circles are the experimental data by Opal et al. (Ref. 25). The curve marked R is the Rutherford cross section [Eq. (60) without the last two terms in the brackets], M is the Mott cross section [Eq. (60)], e− is the theoretical cross section for electron impact (T = 500 eV) that is consistent with known σIon, and p is the corresponding one for proton impact. The square is the experimental value by Grissom et al. (Ref. 40) and the triangle is the PWBA cross section extrapolated from discrete excitation (Ref. 41). The arrow marked KLL is the KLL Auger peak. The shaded area represents the difference between cross sections for electron and proton impact. In (b), the circles are photoionization data compiled by Berkowitz (Ref. 34). (From Ref. 33.)
of the secondary electron spectra and that of the photoelectrons. In addition, the electron impact data should be renormalized to the dot-dash curve marked "e-" so that the area under the curve matches the known total ionization cross section.

The dot-dashed curve marked "p" in Fig. 11 is an estimated cross section for electrons ejected by 0.918 MeV protons, which has the same speed as 500 eV electrons. The shaded area in Fig. 11, which represents the difference between electron- and proton-impact ionization cross sections, results mainly from the fact that the maximum energy of the electrons ejected by proton is not restricted by Eq. (57a). This is another example of using electron-impact data to infer proton-impact cross sections. Secondary electrons ejected by fast protons exhibit all the characteristics of electron-impact data except for those attributed to electron exchange effects. \(^{42,43}\)

Spectra of very slow secondary electrons (\(W < 5 \text{ eV}\)) are often difficult to measure. One can extrapolate the missing part, however, by comparison with the shape of corresponding photoelectron spectra, which are easier to measure. Extrapolation to fast secondaries can also be carried out with the help of the photoionization spectra and the Mott cross section, Eq. (60), as is done in Figs. 10 and 11. Clearly, the area under the Platzman plot with \(R/E\) abscissa (Fig. 11) which is proportional to \(g_{\text{ion}}\), is more sensitive to the extrapolation for slow secondaries than that for fast secondaries. In fact, 50-70% of the total ionization cross section comes from the production of secondary electrons whose kinetic energies are less than the lowest ionization potential of the target.

For a fixed value of \(W\), \(d\sigma/dW\) is expected to show the familiar asymptotic behavior [Eq. (41)] as \(T\) increases. In fact, one can combine the Platzman plot and the Fano plot as a three-dimensional plot by using \(Y\) defined by Eq. (56) as the \(Z\) axis, \(\ln(T/R)\) as the \(Y\) axis, and \(R/E\) as the \(X\) axis. Then the curve on a plane parallel to the \(X-Y\) plane is a Fano plot exhibiting the \(T\) dependence of \(d\sigma/dW\) for a given \(W\) or \(E\), approaching a straight line with the slope \(E(d\sigma/dE)\). On the other hand, the curve on a plane parallel to the \(X-Z\) plane is a Platzman plot with the area under the curve equal to \(g_{\text{ion}}T/4\pi q_{0} R\). When \(g_{\text{ion}}\) and \(d\sigma/dE\) are well known, details of the three-dimensional plot can be determined to a remarkable degree by satisfying constraints imposed on \(d\sigma/dW\) by the values of \(g_{\text{ion}}\) and \(d\sigma/dE\). The energy distribution of secondary electrons ejected from He by electron impact determined by the three-dimensional plot is presented in Fig. 12. An advantage of the cross sections determined in this way is its versatility in covering continuous ranges of \(T\) and \(W\), particularly for high \(T\). The shaded area in Fig. 12 represents the contribution to \(g_{\text{ion}}\) by secondary electrons with \(W < 24.6 \text{ eV}\), the first ionization potential of He.

For highly stripped ions, \(d\sigma/dW\) should resemble at high \(T\) the shape of the hydrogenic \(d\sigma/dE\), calculated from appropriate initial state, not necessarily \(1s\), interlaced with many autoionizing peaks. Well isolated autoionizing peaks appear as narrow peaks in the Platzman plots such as in Figs. 11 and 12, and hence contribute little
to total ionization. For instance, experimental data on $\frac{d\sigma}{dW}$ of He show a small peak for the $2s2p^1P$ excitation at the place marked in Fig. 12, but the area of the autoionizing peak is insignificant. If there are a large number of autoionizing peaks concentrated near the threshold and all of them produce slow secondary electrons ($W \lesssim 10$ eV), then it is obvious from the properties of the Platzman plot that such peaks will add significantly to the total ionization cross section. When an unusually large number of autoionization peaks occurs right above the ionization threshold, the Platzman plot is an effective way to estimate the contribution of such peaks to $\sigma_{\text{Ion}}$.

In summary, we note that the Platzman plot is not tied to any particular theory, and it can be used with experimental data (absolute or relative) for any $T$. The plot is especially useful:

- (g) in extrapolating $\frac{d\sigma}{dW}$ to slow secondaries by comparing the shape with that of photoionization;
- (h) in identifying Auger and autoionization peaks when their energies are known;
- (i) in extrapolating $\frac{d\sigma}{dW}$ to fast secondaries to match the shape and order of magnitude to those of the Mott cross section;
- (j) in identifying similarities and dissimilarities between electron- and proton-impact $\frac{d\sigma}{dW}$; and finally,
- (k) in checking consistency with $\sigma_{\text{Ion}}$ if it is known, or in integrating $\frac{d\sigma}{dW}$ to obtain $\sigma_{\text{Ion}}$.

Comparisons (g) and (j) are meaningful only when $T$ is sufficiently high ($\gtrsim 500$ eV for ionization of neutral atoms and molecules). However, even at lower $T$, many systematic problems in experiments—i.e., poor transmission of slow secondaries—can be detected simply by putting experimental data into the Fano and/or Platzman plot. As an illustration, in Fig. 13, $\frac{d\sigma}{dW}$ of He with 200 eV incident electrons measured by Opal et al., 25 DuBois and Rudd, 27, and by Shyn and Sharp 28 are compared with the theoretical cross section determined by the three-dimensional analysis. 33 We find that the shape of the Opal data is in best agreement with theoretical shape, but their data require renormalization by $\sim 20\%$. The DuBois data show a clear sign of missing some slow secondaries; the Shyn data also show a similar trend for $W \lesssim 5$ eV. The small peak near $W = 32$ eV in the data by

Fig. 13. Comparison of energy distributions for secondary electrons from He: (a) by electron impact, and (b) by photoionization. In (a), the solid curve is the recommended cross section from Fig. 12, the circles are the experimental data by Opal et al. (Ref. 25), the squares are those by Shyn and Sharp (Ref. 28), and the triangles are those by DuBois and Rudd (Ref. 27). In (b), the solid curve is the photoionization cross section compiled by Berkowitz (Ref. 34). Note the small peak of electrons from the $2s2p^1P$ state in the data by Opal et al. near $W = 35$ eV.

Opal et al. represents the autoionization of the $2s2p^1P$ state.

C. Total Ionization Cross Section

Reliability of theoretical ionization cross sections depends mainly on the collision theory and the continuum wave function for
the ejected electron. Preceding discussions on the energy distribution of secondary electrons clearly indicate that slow secondaries contribute most to ionization cross sections. Hence, it is important to describe slow secondaries well in computing ionization cross sections. Wave functions for slow secondaries are more sensitive to effective screening, correlation effects, interaction with the primary electron, excited ion states, etc. than those for fast secondaries. At present, perturbation theories mentioned in Section II and their variants are the only practical methods for calculating ionization cross sections. Among these methods, as usual, the PWBA has been the most popular one. Since the two electrons that emerge after a collision are indistinguishable, the electron exchange effect should be treated properly. In addition, for a nonhydrogenic atom or ion, choice of wave functions introduces more complexity. As a result, there are many versions of PWBA, e.g., with or without exchange, with or without correlation in the initial and/or final state of the target, etc. All these variants of the PWBA, however, have one goal in common: How to reduce the theoretical ionization cross section near its peak, and attain better agreement with experiment for intermediate and low primary energies.

1. Ionization Cross Section for Fast Incident Electrons

Most modifications to the PWBA affect ionization cross sections only slightly for high T. As we have seen already, the dipole term becomes the leading part of the PWBA cross sections at high T, and the Fano plot is effective in investigating the asymptotic behavior of ionization cross sections. Again, \( \sigma_{\text{ion}} \) in the PWBA can be expressed in the Bethe form for high T:

\[
\sigma_{\text{ion}} = \frac{4\pi a_0^2 z}{T/R} \left[ A_{\text{ion}} \ln(T/R) + B_{\text{ion}} + C_{\text{ion}} \frac{R}{T} \right],
\]

(61)

where

\[
A_{\text{ion}} = \int_{B_1}^{\infty} (R/E)(d\bar{f}/dE) dE,
\]

(62)

and \( B_{\text{ion}} \) and \( C_{\text{ion}} \) are constants independent of T.

It is possible to evaluate \( A_{\text{ion}} \) from photoionization data in principle, but direct computation of \( B_{\text{ion}} \) and \( C_{\text{ion}} \) is impractical. Instead, one can use sum rules to sum Bethe parameters for all inelastic scattering and subtract those for all discrete transitions. Then the remainder corresponds to the Bethe parameters for total ionization plus decay of inner-shell excited states through nonionizing channels (e.g., through fluorescence). For atoms of low nuclear charge, the Auger process is the dominant mode for the decay of inner-shell excited states, and hence the difference between the cross section for total inelastic scattering, \( \sigma_{\text{tot}} \), and that for the total discrete excitation, \( \sigma_{\text{exc}} \), is practically the total ionization cross section.

The sum rule method is preferable because:

(a) The Bethe parameters for the total inelastic scattering depend on the ground-state wave function of the target and a complete information on its continuum dipole oscillator strength, which can be obtained either from photoionization experiments or by direct computation—an easier task than a direct computation of the ionization cross section itself;

(b) Reliable Bethe parameters for discrete excitations can be calculated for low-lying states by using accurate bound-state wave functions; and

(c) Those for the Rydberg states can be extrapolated by the quantum defect method.

In many cases, the continuum oscillator strengths are known in sufficient detail and accuracy to determine \( A_{\text{ion}} \) through Eq. (62). Hence, by using the sum rule method, we can avoid all difficulties and uncertainties associated with continuum wave functions in direct computation of \( \sigma_{\text{ion}} \).

One simple but effective method of calculating exchange corrections to \( \sigma_{\text{ion}} \) is to use the Mott cross section, Eq. (60). In Eq. (60), the first term in the brackets arises from direct (Coulomb) interaction, the second term from the exchange interaction, and the third term represents the interference between the direct and exchange interactions. Hence, the exchange correction to \( \sigma_{\text{ion}} \) is obtained by integrating the second and third terms in Eq. (60) over the allowed ranges of \( E_j \).
\[
\sigma_{\text{exch}} = \frac{4\pi a_0^2 R^2}{T} \sum_j N_j \int_{B_j} \left[ \frac{1}{(T-E_j+B_j)^2} - \frac{1}{E_j(T-E_j+B_j)} \right] dE_j
\]

For the asymptotic region where \(B_j \ll T\), Eq. (60) is simplified further:

\[
\sigma_{\text{exch}} = \frac{4\pi a_0^2 R^2}{(T/R)^2} \sum_j N_j \left[ 1 + \ln(B_j/T) \right].
\]

(63a)

Details of the sum-rule method is given elsewhere. We simply note that in the sum-rule method, the first Bethe parameter, \(A_{\text{ion}}\) in Eq. (61), is more reliable than the second one, \(B_{\text{ion}}\). The value of \(A_{\text{ion}}\) is calculated directly from bound-state wave functions alone whereas \(B_{\text{ion}}\) requires a weighted sum of all continuum dipole oscillator strengths, which is sensitive to the reliability of the dipole data, either experimental or theoretical. Also, since the Bethe cross section is an asymptotic formula, it should not be used at low incident energies.

We present typical results (\(H^-, \text{He}, \text{and Li}^+\)) in Figs. 14-16. The utility of the Fano plot is clearly demonstrated in Fig. 14, where the data by Tisone and Branscomb\(^{45}\) exhibit irregular asymptotic behavior. The Bethe parameters for ionization for light atoms and ions are presented in Table III.

When the target has inner-shell structure, a direct calculation requires shell-by-shell summation of the ionization cross section. Furthermore, as the incident energy is increased, more partial waves are required escalating numerical complexity. The sum-rule method does avoid this problem and includes all inner-shell events automatically by definition:

\[
\sigma_{\text{ion}} = \sigma_{\text{tot}} - \sigma_{\text{exc}}.
\]

(64)

On the other hand, the sum-rule method does not provide any information on individual inner-shell events. A combination of direct calculation for low and intermediate \(T\) and the sum-rule cross section for high \(T\) is the most effective way to determine an ionization cross section for a wide range of \(T\). As will be shown later, the Bethe cross section can also be extended to relativistic range of \(T (\xi, 10 \text{ keV})\) in a trivial manner.

2. Ionization cross sections at intermediate and low incident energies

To describe ionizing events, it is necessary to determine continuum wave functions for three electrons; incident, scattered, and
Fig. 15. Fano plot for the total ionization of He. The curve labeled (d) is the Bethe cross section [Eq. (61)] with Cion for heavy projectiles, and the circles are proton-impact experimental data by Hooper et al. (Ref. 48). Other curves are for electron impact, and their labels are the same as those used in Fig. 14. The squares are electron-impact data measured by Smith (Ref. 49), and the triangles are those by Schram et al. (Ref. 50). (From Ref. 44.)

ejected. Even within the FWBA, in which plane waves are used for the first two wave functions, different options for the third wave function, e.g., Coulomb wave, distorted wave, etc. exist. For highly stripped ions, it is obvious that plane waves for slow incident electrons would be a poor choice. On the other hand, the wave function for the electron ejected from a highly stripped ion may not differ much from a Coulomb wave. One of the requirements that should be satisfied is the orthogonality between the continuum wave function for the ejected electron and its bound-state wave function. For this purpose, it is preferable to calculate all distorted waves in the potential of the initial state of the target; or for Coulomb waves, use the same screened charge throughout the calculation.

Coulomb functions have been used often in the computation of ionization cross sections of ions, but the use of distorted waves for all three continuum wave functions is relatively new. An urgent need for the ionization cross sections of impurity ions in Tokamak plasma has stimulated the atomic physics community and some theoretical and experimental data on multiply charged ions are available now. We compare theory and experiment on the ionization of C^{3+}, N^{4+}, and O^{5+} in Figs. 17-19, respectively. Recent
Table III. Bethe cross sections for ionization. The Bethe formula is given by

\[ \sigma_{\text{ion}} = \frac{4\pi a_0^2}{T/R} \left[ A_{\text{ion}} \ln(T/R) + B_{\text{ion}} + C_{\text{ion}} R/T \right] + \sigma_{\text{exch}}, \]

\[ \sigma_{\text{exch}} = \frac{4\pi a_0^2}{(T/R)^2} \sum_{j} \left[ 1 + \ln(B_j/T) \right], \]

where \( N_j \) and \( B_j \) are the number of electrons and binding energies of the \( j \)th orbital, respectively. The Bethe parameters, \( A_{\text{ion}}, B_{\text{ion}}, \) and \( C_{\text{ion}} \) are dimensionless.

<table>
<thead>
<tr>
<th>Atom</th>
<th>( A_{\text{ion}} )</th>
<th>( B_{\text{ion}} )</th>
<th>( C_{\text{ion}} )</th>
<th>( B_j ) (eV)</th>
<th>( N_j )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.2834</td>
<td>1.2566</td>
<td>-2.6294</td>
<td>R = 13.606</td>
<td>1</td>
</tr>
<tr>
<td>H-like ions</td>
<td>0.2834/z²</td>
<td>84.241/z²</td>
<td>-2.6294</td>
<td>( z^2R )</td>
<td>1</td>
</tr>
<tr>
<td>H⁻</td>
<td>7.484</td>
<td>25.11</td>
<td>-5.545</td>
<td>0.7552</td>
<td>2</td>
</tr>
<tr>
<td>He</td>
<td>0.489</td>
<td>0.714</td>
<td>-5.519</td>
<td>24.59</td>
<td>2</td>
</tr>
<tr>
<td>Li⁺</td>
<td>0.1445</td>
<td>0.137</td>
<td>-5.439</td>
<td>75.64</td>
<td>2</td>
</tr>
<tr>
<td>Li</td>
<td>0.536</td>
<td>2.783</td>
<td>-7.728</td>
<td>5.392(2s)</td>
<td>1</td>
</tr>
<tr>
<td>Li⁺</td>
<td>0.107</td>
<td>0.0498</td>
<td>-7.927</td>
<td>64.49(2s)</td>
<td>2</td>
</tr>
<tr>
<td>C³⁺</td>
<td>0.0750</td>
<td>-0.0077</td>
<td>-7.951</td>
<td>521.2(1s)</td>
<td>2</td>
</tr>
<tr>
<td>N⁴⁺</td>
<td>0.0554</td>
<td>-0.0385</td>
<td>-7.968</td>
<td>138.1(2s)</td>
<td>1</td>
</tr>
<tr>
<td>O⁵⁺</td>
<td></td>
<td></td>
<td></td>
<td>702.9(1s)</td>
<td>2</td>
</tr>
</tbody>
</table>

The Bethe formula should be used only for high incident electron energies, beyond the peak in \( \sigma_{\text{ion}} \).

The binding energies of the valence orbitals are experimental ones, and those for the inner orbitals are from the Hartree-Fock orbital energies.

The DWBA results by Younger \(^5^4\) agree closely with CBA results \(^5^5,5^6\) from the threshold to 2.25 times the threshold. The CBA results in Figs. 17-19 do not include the ionization of 1s electrons, and hence their high T results do not agree with experiment. The sum-rule results agree well with experiment in the slopes of the asymptotic cross sections, but the heights disagree. As was mentioned, the sum-rule method requires accurate df/dE to determine the height of the Fano plot. For the Li-like ions, df/dE based on the Hartree-Slater potential was used in the sum-rule cross section.
In the past, both experimental and theoretical studies of electron-neutral atom collisions have been centered on atoms with simple electronic configurations such as rare gases and alkali-atoms. With the recent advances in experimental techniques, targets with more complex shell structure can be studied. This will also provide a new challenge to theorists. For ions of low ionicity and neutral atoms, electron correlation becomes important. Theorists have not yet found any convenient and effective method to account for the final-state correlation in ionizing collisions. For highly stripped ions, the decay of inner-shell hole states must be studied carefully, because most of them decay through fluorescence as the nuclear charge increases. Finally, the subject of multiple ionization has not been studied well. Again, experimental data on multiple ionization will stimulate the development of comprehensive theory.

IV. RELATIVISTIC AND CORRELATION EFFECTS

So far, we have used nonrelativistic collision theory, but relativistic kinematics begin to affect collision cross sections for $T \gtrsim 10$ keV. In fact, most electron-impact cross sections begin to rise beyond $T \gtrsim 1.5$ MeV, known as the relativistic rise. In addition, inner-shell electrons of medium to heavy atoms are affected by relativistic structure effects that change binding energies, orbital sizes, and coupling schemes.

For light atoms, the electron correlation effect can be studied independent of the relativistic structure effect. For heavy atoms, however, the correlation and relativistic effects affect each other.
because changes in the coupling scheme also alter configurations that are strongly correlated.

The relativistic kinematics is well understood, but the correlation and relativistic structure effects in collision are new subjects.

1. Relativistic kinematics

Fortunately, the collision of high energy electrons can be handled well within the PWBA.\textsuperscript{59,60} For instance, the relativistic form of the Mott cross section for the collision of two free electrons is known as the Möller cross section.\textsuperscript{61} In our notation, the Möller formula that replaces the Mott formula [Eq. (60)] is given by\textsuperscript{33}

\[
\frac{d\sigma}{dW} = \frac{4\alpha^2}{\beta^2} \sum_{J} N_{J} \left[ \frac{1}{E_J^2} + \frac{1}{(T-W)^2} + \frac{4}{4(R+\alpha^2T/2)^2} \right] \left( \frac{1}{(1+\alpha^2T/2R)} - \frac{1}{(1+\alpha^2T/2R)^2} \right) \tag{65}
\]

where \(\alpha\) is the fine structure constant, and \(\beta = v/c\), with the speed of light \(c\). At the maximum secondary electron energies [Eq. (57a)] the Möller cross sections are 3% and 54% larger than the Mott cross sections for incident electrons of 100 keV and 1 MeV, respectively.

Bethe\textsuperscript{59} and Fano\textsuperscript{60} have shown that the relativistic kinematics raises the angular distribution of primary electrons in the extreme forward direction. Consequently, only dipole-allowed transitions are affected by the relativistic kinematics. The net change in the integrated cross sections (\(\sigma_{\text{n}}\) and \(\sigma_{\text{ion}}\)) is to rewrite the Bethe format [Eqs. (38) and (61)] to

\[
\sigma_n = \frac{4\alpha^2}{\beta^2} \sum_{J} A_n \left[ \ln \left( \frac{\beta^2}{1-\beta^2} \right) - \beta^2 \right] + B' \tag{66}
\]

and

\[
\sigma_{\text{ion}} = \frac{4\alpha^2}{\beta^2} \sum_{J} A_{\text{ion}} \left[ \ln \left( \frac{\beta^2}{1-\beta^2} \right) - \beta^2 \right] + B' \tag{67}
\]

where

\[
B' = A \ln(2mc^2/R) + B \tag{68}
\]

The term in the square brackets in Eqs. (66) and (67) result from the combination of the relativistic expression for \(Q_{\text{min}}\), Eq. (34), and the contribution from the small component of the relativistic wave functions of the target.

One can readily see from Eqs. (66) and (67) that the extension of the nonrelativistic Bethe cross sections to relativistic incident energies is a trivial task once the values of the Bethe parameters are known. Also, the Fano plot should use \(\beta^2/4\alpha^2 \ln(\beta^2/(1-\beta^2))\) as the ordinate and \(\beta^2/(1-\beta^2)\) as the abscissa; then the asymptotic cross section should follow a straight line with the slope, \(A\). An example of the relativistic Fano plot for the ionization of He by relativistic electrons and positrons is presented in Fig. 20. As expected from the PWBA, the sign of the charge of the incident particle does not matter at high incident energies. The experiment\textsuperscript{62} was done with a small amount of \(H_2\) mixed with He so that all He atoms in discrete excited states ionized \(H_2\) molecules. All ions, both of He and \(H_2\), were detected by a Geiger counter. Hence, the experiment measured the total inelastic scattering cross section, \(Q_{\text{tot}}\), and it is in excellent agreement with the Bethe cross section\textsuperscript{63} calculated from correlated wave functions.

2. Electron correlation

The correlation effect between the incident and bound electrons should be treated in the framework of a collision theory. We consider here only the correlation among the bound electrons themselves. Qualitatively, we know what class of atoms and ions are subject to strongly correlated structure effects. For instance, the Be-like ions are known to have strong correlation effects,\textsuperscript{64} and all group II atoms (Be, Mg, Ca, Sr, Ba, Ra, Zn, Cd, and Hg) and ions of the same electronic configurations are also affected seriously by the correlation effect.\textsuperscript{65,66} In addition, atoms and ions with d shells (e.g., transition metals) show strong mixing of configurations. In fact, only alkali-like configurations (Li, Na, etc.) can be treated without elaborate configuration mixing to describe the target.

Details such as angular distributions are more susceptible to the correlation effect because they are likely to be the results of strong interference among various partial waves or interaction
channels. Optically forbidden transitions could be coupled to allowed transitions through configuration mixing (e.g., 1s2p 3P1 level mixed with 1s2p 1P1), and consequently have unexpectedly large cross sections at high incident energies. For allowed transitions, cross sections decrease in most cases when correlated wave functions are used. The correlation effect in the dipole oscillator strength of an allowed transition serves as a reliable indicator of the correlation effect in electron-impact cross sections.

In Fig. 21, two DWBA calculations by Mann [67] on the 3s 3P 2p + 3s3p 2D excitation of S3+ (Al-like) are presented. The two calculations use wave functions of different configuration composition both for the initial and final states. The admixture of the 3s23d in the final state is the most important correlation effect in this case. Since the correlation effect could affect either or both of the initial and final states, it is difficult to anticipate the net result of the correlation effect without using reliable wave functions. For heavy atoms, it is necessary to use relativistic correlated wave functions.

Fig. 20. Fano plot for the total inelastic scattering of He. The solid line is the relativistic Bethe cross section [Eq. (67)] from Ref. 63, the solid and open circles are experimental data by Rieke and Prepejchal (Ref. 62), and the squares are those by G. W. McClure [Phys. Rev. 90, 796 (1953)]. (From Ref. 63.)

Fig. 21. Fano plot for the 3s 3p 2P + 3s3p 2D excitation of S3+ by electron impact. The labels n x m denote configurations for the initial target state, and m configurations for the final target state used in the DWBA calculations by Mann (Ref. 67).
functions even for those transitions that involve valence electrons, particularly if they are from s or p shells.

V. THEORY OF SLOW COLLISIONS

For slow projectiles, the collision time is long enough for the charge distribution of the target to be polarized by the projectile, and in turn the altered charge distribution distorts the projectile wave function. Hence, the first-order perturbation treatment of the interaction Hamiltonian as we did in various versions of the Born approximation becomes inadequate for slow collisions.

An obvious approach to correct this deficiency is to try higher-order perturbation theory, i.e., the interaction Hamiltonian appears in the scattering matrix element more than once. The second Born and Glauber approximations belong to this category.

Another approach is to describe the projectile and the target electrons on equal footing, i.e., abandon the simple product-type wave function, Eq. (7), and use a linear combination of product-type wave functions that include many real and/or virtual excited states of the target and corresponding continuum functions for the projectile. The close-coupling and R-matrix theories are typical examples.

Each theoretical method mentioned above merits full exposition, and for details the reader should consult excellent and extensive reviews available in the literature. In this lecture, we shall concentrate

(a) on basic ideas of these methods without mathematical details and

(b) on the advantages and disadvantages of the methods for slow collisions as compared to the simpler methods discussed so far.

1. Second Born Approximation

The second Born approximation extends the first Born approximation by summing over all intermediate excitations as in any second-order perturbation theory. The transition matrix element in Eq. (11) is replaced by an expression that involves summation over all excited states (including continuum) of the target as well as the integration of corresponding intermediate momenta of the scattered electron, with an energy dependent denominator as usual. A simplified picture

of this process is that the target is first excited to one of the infinitely many intermediate states and then returns to the final state specified. For instance, the 1s \rightarrow 2s excitation of H by electron impact is, in the second Born approximation, treated as the sum of all two-step processes of the type 1s \rightarrow n\ell \rightarrow 2s. Of these, 1s \rightarrow 2p \rightarrow 2s is the most important correction to the direct, first order process 1s \rightarrow 2s. One can easily see that this is no simple task to perform, even with the help of high-speed computers. Furthermore, the perturbation treatment can be extended further to higher orders, and there is no proof that the perturbation series will converge. Some prototype calculations exist on the scattering by H, usually with additional shortcuts. The examples are insufficient to draw any conclusions on the utility of the method for targets of more complex electronic structure, and also on ionizing collisions. Because of its perturbative approach, the second Born approximation is not expected to be reliable for very slow collisions (e.g., threshold region). Also, the incident electron is always treated differently from the bound electrons in such a way that it is difficult to treat resonances which are the most prominent features in the scattering of slow electrons.

2. Glauber Approximation

The Glauber approximation is equivalent to an infinite order perturbation with the perturbation series summed over a particular way—H \rightarrow g appears in an exponential form—so that the scattered electron paths close to the incident momentum, i.e., small-angle scattering, are emphasized. This method reduces to the PWBA in the limit of high incident energy. One drawback of this method is that the interaction matrix element contains five-dimensional integration. For small atoms and ions, analytic Roothaan-type wave functions can be used, and the five-fold integration can be reduced to one-dimensional integration which can be carried out numerically. The Glauber results are available for the electron-impact excitation and ionization of several light atoms and ions. The theoretical results are in better agreement with experiment than the PWBA results for intermediate projectile energies ($T < 500$ eV). The difficulties associated with the five-fold integration, however, force the theory to depend on analytic target wave functions only—severe, if not fatal, restriction for ionizing collisions. Also, the Glauber theory is inherently a high-energy approximation, and as is the case of the second Born approximation, the incident electron is treated differently from the bound electrons. This makes the study of near-threshold resonances difficult. Because small-
angle scattering is emphasized in the Glauber approximation, the theoretical results on dipole-allowed transitions are more reliable than those on forbidden transitions because the former peak sharply in the forward direction.

3. Close-Coupling Approximation

In this method the incident electron is treated on the same footing as the bound electrons, i.e., the total wave function for the colliding system is given by, instead of Eq. (7),

\[ \Psi_{(1,2,\ldots,N, N+1)} = A \sum_{n} \psi_{(1,2,\ldots,N)} \phi_{n}(N+1) \]  

(69)

where 1, 2, etc. stand for the set of variables and quantum numbers to identify bound and incident electrons, \( A \) is the antisymmetrization operation, \( \psi_n \) is a target wave function representing one of the initial and excited states, and \( \phi_n \) is the corresponding wave function for the scattered electron. The target wave functions \( \psi_n \) are considered known, and \( \phi_n \) is determined by substituting Eq. (69) into the Schrödinger equation. The asymptotic \((r \to \infty)\) form of \( \phi_n \) provides the cross section for exciting the target to state \( n \). Well-designed computer programs based on this method are available.\(^{71}\) The close-coupling approximation is most appropriate for very slow collisions, particularly for detailed study of threshold behavior and resonances. Since the polarization of the target is described by \( \psi_n \) in Eq. (69) and they remain fixed during the solution of the Schrödinger equation, the effectiveness of the method depends critically on the number of target wave functions, \( \psi_n \), included in Eq. (69). In particular, the results are sensitive to \( \psi_n \) whose excitation energies are higher than the incident electron energy. On the other hand, the distortion of the projectile wave function is represented very well by the close-coupling method. In reality, one must truncate the expansion, Eq. (69), to a modest length, and this restricts the application of the close-coupling method to low and modest incident energies. Sometimes pseudo-state wave functions—those with no real corresponding states of the target—are used in the expansion to reduce its length, but there are no general principles to guide the choice of such pseudo-state wave functions. Also, pseudo-state wave functions could produce fictitious resonances. The calculation by Gau and Henry (Ref. 20), which included five states of C\(^{3+}\) (Li-like), is compared to other theoretical results and experimental data in Fig. 7. It is difficult at present to handle ionization in the framework of the close-coupling approximation. For ionizing collisions, two continuum orbitals must be included in Eq. (69), and the joint asymptotic behavior of the two unbound electrons must be determined to obtain ionization cross sections. Such asymptotic behavior is not well understood theoretically. On the other hand, the exchange effect—between bound and incident electrons—is built in the formulation by the antisymmetrization operator in Eq. (69).

To simplify computational procedure, one can reduce the number of product functions in Eq. (69) and substitute some \((N+1)\)-electron bound-state functions, \( \phi(1,2,\ldots,N,N+1) \), to represent the correlation between the projectile and the target electrons:

\[ \Psi_{(1,2,\ldots,N+1)} = \sum_{n} a_{n} \psi_{(1,2,\ldots,N)} \phi_{n}(N+1) + \sum_{m} b_{m} \phi_{(1,2,\ldots,N+1)}. \]  

(70)

One can select \( \phi_n \) and \( \phi_m \) from simpler, uncoupled calculations, and then determine coupling constants \( a_n \) and \( b_m \) by applying the Hulthén-Kohn variational principle. This process leads to a set of coupled linear equations for \( a_n \) and \( b_m \), an eminently simpler computational problem than solving Eq. (69) directly for \( \phi_n \). This procedure is called linear algebraic method, analogous to the configuration interaction method for bound states. A more sophisticated approach keeps only \( b_m \) as a variational constant (i.e., \( m = 1 \)) and solves resulting variational equations for \( \phi_n \) and \( b_m \). Here, the computational procedure becomes more involved than just solving for \( a_n \) and \( b_m \), but better results are expected because more flexibility is allowed for \( \phi_n \), from which actual cross sections are derived by taking their asymptotic forms. Note that both in Eqs. (69) and (70), functions \( \psi_n \), \( \phi_n \), and \( \phi_m \) are solved in coupled equations for all electrons in all the configuration space, particularly for \( r = 0 \) to \( \infty \) with full electron exchange effect, which may not be significant at large \( r \).

4. R-Matrix Method

In the R-matrix method, the configuration space for the projectile is divided into two regions: an internal region near the target where it is difficult to distinguish the incident electron from those bound to the target, and an external region where the projectile electron (before and after the collision) interacts with the target only through long-range Coulomb interaction and is distinguishable from the bound electrons, i.e., exchange interaction is negligible. In the internal region, the total wave function for the colliding system has the same form as in the close-coupling
approximation, Eq. (69). In the external region, however, the total wave function is characterized only by the asymptotic behavior of the projectile to simplify the task of solving the Schrödinger equation. The solution in the two regions are then joined together at the boundary—usually a sphere enclosing most of the target charge distribution. The boundary conditions that the external solutions must satisfy on the sphere are the elements of the R matrix.

Burke and co-workers \(^ {2,74} \) have been the moving force in developing and applying the R-matrix method to ions, atoms, and molecules. In principle, the R-matrix method can pack more target wave functions in the expansion, Eq. (69), in the internal region than the close-coupling method. As in the case of the close-coupling method, the R-matrix method is well suited to the study of slow collisions near the threshold. The R-matrix calculations on the collision strengths averaged over the Maxwellian distribution of plasma electrons could sometimes show drastic (up to a factor of 6) departure from those calculated by the DWBA or even by the R-matrix method with only a few bound-state functions in Eq. (69).\(^ {76} \) As in the case of the close-coupling method, computer programs are available for the R-matrix calculations, but both methods are still too cumbersome to calculate cross sections to highly-excited states, including ionization.

VI. CONCLUSIONS

It is clear from the discussions presented so far that there is no single theory that describes electron-atom and electron-ion collisions satisfactorily for all incident energies. We must therefore make compromises between accuracy and expediency. For instance, a brute force extension of the DWBA calculations to high incident energies (\( T > 1 \text{ keV} \)) would be costly and even wasteful; the PWBA with appropriate high-energy exchange corrections (Mott, Ochshur) would be sufficient and quicker. On the other hand, perturbative calculations near the threshold should be verified by strong-coupling methods such as the close-coupling and R-matrix methods, in particular on the effects of resonances near the threshold.

Unfortunately, we do not have much choice for ionization cross sections. There are no strong-coupling theories that can handle ionizing collisions at present, and we must bear with the perturbative theories. For many applications, cross sections must be known for all incident energies. In such cases, particularly those involving dipole-allowed excitations for which their cross sections remain high even at high incident energies, accurate asymptotic

![Fig. 22](image)

Qualitative illustration of importance of correlation, scaling, and relativistic effects in atomic and collision properties. Scaling of collision properties should be studied along iso-electronic sequences. Properties of ions with low ionicity, Z - N, will be dominated by the correlation effect for light ions and both by the correlation and relativistic effects for medium and heavy ions.

Values in the form of the Bethe parameters simplify the task of presenting the cross sections. Also, the Bethe cross section format serves as a reliable anchor with which the results of other theories at lower incident energies can be fitted into compact, analytic forms for simplicity and convenience.

Furthermore, for practical applications, knowledge on the scaling of collisional properties as functions of nuclear charge along iso-electronic sequences will be of great help. Most of the existing knowledge on the scaling is based on hydrogenic properties, but they are certainly altered by screening and the correlation effects in many-electron ions.\(^ {12} \) Scaling of collision properties are basically determined by the scaling of target ionic properties along
isoelectronic sequences. No clear scaling properties will be discernible for the first few members of an isoelectronic sequence; correlation effects will be more important here. For heavy atoms, relativistic effects are at least as important as, if not more than, the correlation effect both in atomic and collision properties. In Fig. 22, we qualitatively illustrate the relative importance of correlation, scaling, and relativistic effects for ions with various nuclear charges and ionocities.

In my opinion, the most pressing task for theorists in electron-atom collisions is the development of a method that allows for electron correlation effects in the final state in ionizing collisions—even on the level of a perturbation theory.

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