REVIEW OF LITERATURE

In this section we describe briefly the concepts and the historical development of the DM formalism, the method of Khare and co-workers, and the BEB formalism of Kim and Rudd. We will begin with a brief discussion of the formalisms developed by Khare and co-workers and by Kim and Rudd, that in some sense have a common origin. We will subsequently review the development of the DM formalism that was developed from a different point of view.

1. Formalisms combining cross section expressions

Inelastic collisions between electrons and atoms may be divided into two broad categories: soft (or distant) collisions that occur at large impact parameters and hard (or close) collisions that occur at small impact parameters. The Mott cross section formalism, which is a generalized Rutherford cross section \[2\] taking into account electron exchange effects, describes the collision of two free electrons, thus accounting well for hard collisions. Conversely, using the first Born approximation, Bethe \[3\] derived a cross section formula for the dipole interaction involving fast incident electrons and thus accounting well for soft collisions. Attempts have been made by various authors \[4\] to combine the dipole interaction with free electron collisions in order to arrive at a “correct” ionization cross section formula that is essentially free of adjustable or fit parameters. All early attempts had only limited success because they failed to find the “correct” mixing ratio between the soft and hard collision terms. Two groups recently revisited this problem again with more success. The group of S.P. Khare and co-workers at the Meerut University in India and a collaboration between M.E. Rudd at the University of Nebraska and Y-K. Kim at NIST, as will be shown in the following sections where we will describe in detail these developments, both approaches involve approximations in deriving the corresponding expressions (cross sections) and, in addition, both approaches require certain input parameters that are not always readily available, e.g. (differential) dipole oscillator strengths.

2. The formalism of Khare and co-workers

The first successful attempt to calculate total (counting) \[5\] ionization cross sections for molecules using a combination of theories describing the two different types of collisions
mentioned above was made by Khare and co-workers in 1976 (earlier work of Khare and co-
workers on total ionization cross sections for the rare gases). This work was based on earlier 
work to (1) calculate energy-loss cross sections $d\sigma(E,w)/dw$, where $E$ is the energy of the 
incident electron and $w$ is the energy loss suffered by the incident electron in the ionizing 
collision and (2) to calculate [6] the single differential ionization cross section $d\sigma(E,\varepsilon)/d\varepsilon$ for the 
production of a secondary electron of energy $\varepsilon$, with $w = \varepsilon + E_i$ where $E_i$ refers to the ionization 
energy. The total ionization cross section $u(E)$ is then obtained by integration over all possible 
values of $\varepsilon$ from 0 to $(E-E_i)/2$. Moreover, Khare and coworkers [7-10] recently extended their 
formalism to the calculation of partial ionization cross sections of molecules (that is, the cross 
section for the production of a specific parent or fragment ion.

As summarized by these authors, according to Inokuti [35] the single differential ionization cross section $d\sigma(E, \varepsilon)/d\varepsilon$ is given in the first Born approximation by

$$
d\sigma(E, \varepsilon)/d\varepsilon = (4\pi a_0^2 R^2 / Ew) \times \left( \delta f (w, K^2 a_0^2) / \delta w \right) \times \left[ \frac{1}{\varepsilon^2} \right] \times \ln(K a_0^2)$$ (1)

where $a_0$ denotes the Bohr radius, $R$ the Rydberg energy (ionization energy $E$, of the hydrogen 
atom), $\delta f (w, K^2 a_0^2) / \delta w$ is the density of the generalized oscillator strength per unit energy range, 
and $Ka_0$ is the change in the momentum vector of the incident electron due to scattering. The 
generalized oscillator strength may be given in a complete fashion by plotting $\delta f / \delta w$ versus $\ln$ 
$[(Ka_0)^2]$ and $w/R$ (Bethe surface). Depending on the nature of the energy transfer—“hard” 
collisions are associated with a large energy transfer and “soft” (glancing) collisions with small 
energy transfer-ionizing collisions can be divided into two regimes on this Bethe surface. Eq. (1) 
is reduced to the Bethe term for soft collisions where the collisions take place primarily through 
the dipole interaction between the incident electron and the target electron

$$
d\sigma(E, \varepsilon)/d\varepsilon \bigg|_B = (4\pi a_0^2 R^2 / Ew) \times \left( \delta f (w,0) \delta w \right) \ln[CE]$$ (2)

Here $\delta f (w,0) / \delta w$ is the differential optical oscillator strength for the ionization of the molecule 
by a photon of energy $w$ and $C (w)$ is the collisional parameter. One can see that the Bethe cross
section exhibits the characteristic asymptotic energy dependence $\ln E/E$ that arises from the
dipole interaction. In the case of hard collisions, the differential cross section is given by the
Mott term that describes the collision of two free electrons

$$d\sigma(E, \varepsilon)/d\varepsilon \bigg|_M = (4\pi a_0^2 R^2 s \times (1/\varepsilon^2 - 1/(E - \varepsilon)\varepsilon + 1/(E-\varepsilon)^2)) / E$$

(3)

where $s$ is the number of electrons that participate in these hard collisions. The first term in the
bracket corresponds to the direct collision term (as used in the Rutherford cross section), the
second term represents the interference between the direct and exchange term, and the third term
accounts for the exchange effects. As expected, the Mott cross section is symmetric in terms of
the kinetic energies of the outgoing electrons, i.e. in terms of $e$ and $(E-\varepsilon)$ for the “secondary” (or
ejected) electron and the “scattered” electron, respectively.

Both Eqs. (2) and (3) are valid in the limit of high incident electron energies. To extend
the range of their validity to low incident energies, Khare and co-workers added the two cross
sections after multiplying each cross section by an arbitrary factor, $f_1$ and $f_2$, which were chosen
by the authors [8] to obtain satisfactory agreement with experimental data

$$d\sigma(E, \varepsilon)/d\varepsilon = f_1 d\sigma(E, \varepsilon)/d\varepsilon \bigg|_B + f_2 d\sigma(E, \varepsilon)/d\varepsilon \bigg|_M$$

(4)

with

$$f_1(E, \varepsilon) = [1/(1 - E_i / E)] \times (1 - \varepsilon(E - E_i) \ln[1 - C(E - E_i)] / \ln[CE])$$

(5)

$$f_2(E, \varepsilon) = [\varepsilon^3 / (\varepsilon^3 + \varepsilon^2_0)](1 - E_i / E)$$

(6)

thereby extrapolating the Bethe and Mott cross sections to low incident electron energies and
controlling the mixing of soft and hard collisions. Here $\varepsilon_0$ denotes a “mixing parameter”.

Thus, $f_1 d\sigma(E, \varepsilon)/d\varepsilon \bigg|_B$ dominates the single differential cross section for small values of $\varepsilon$ and
$f_2 d\sigma(E, \varepsilon)/d\varepsilon \bigg|_M$ dominates the single differential cross section for large values of $\varepsilon$. 
As we will see later, the total cross sections $\sigma(E)$ obtained by Khare and co-workers using this formalism after proper integration $\sigma(E) = \int \frac{d\sigma(E, \epsilon)}{d\epsilon} d\epsilon$ was found to agree reasonably well with experimental results in many cases.

By extending the approach of Khare and coworkers, Saksena et al. demonstrated recently that based on an approach by Mayol and Salvat, no a priori knowledge of the mixing parameter $c$ and the collision parameter $C$ is necessary and thus, calculations can be earned out for all molecules for which total photoionization cross section data are available.

Moreover, it is interesting to note that Khare and co-workers recently combined the features of the approach of Saksena et al. [11] and that of Kim and Rudd [12]. According to these authors they arrived at expressions for the total ionization cross section in the BED and BEB formulations (see below) that are close to the results from Kim and Rudd [12].

3. The formalism of Kim and Rudd

In 1994, Kim and Rudd [64] extended the previous approach in several ways. First, they used the binary encounter approximation (BEA) (2 for its symmetric form), where a velocity or momentum distribution is ascribed to the target particle to replace the Molt cross section. Such a momentum distribution is frequently derived from the wave function of the target particle. Thus, the symmetric form of the BEA cross section differs from the Molt cross section by an extra term incorporating the average kinetic energy $KE$ of the target electron. Kim and Rudd then combined this modified form of the Molt cross section and the Bethe cross section by requiring the ionization cross section and the corresponding stopping cross section to satisfy the high energy asymptotic behavior of the Bethe theory. After some further approximations that are described in detail in [12] the single differential ionization cross section for a particular subshell is given in what Kim and Rudd refer to as the BED model by

$$d\sigma(E, \epsilon)/d\epsilon = 4\pi a_0^2 (R/E \eta^2 \xi) / E \eta (t + u + 1) x \{([N/\zeta]-2)$$
\[
\left[\frac{1}{(w + 1)} + 1(t-w)\right] + \left[2-(N_i/\zeta)\right] \left[\frac{1}{(w +1)} + 1(t-w)^2\right] \\
+ \left[\ln (t) /\zeta(w+1)\right] [df(w)/dw]\] (7)

where \(E_j\) is the binding energy of the ejected electron, \(i\) is the number of bound electrons in that particular subshell \(j\), \(t = E/E_j\), \(w = /E_j\), \(u = KE/E_j\), \(N_i = \int [df(w)/dw]dw\), and \([df(w)/dw]\) denotes the differential oscillator strength. The total ionization cross section, which is obtained by integrating the differential cross section, is then given by the simple expression

\[
\sigma(E) = 4\pi a_0^2 \left(\frac{R}{E_j}\right)^2 \xi [(D(t)\ln(t) + [2 - (N_i/\zeta)][(t-1)/t-ln(t)/(t+1)]] (8)
\]

with \(D(t) = \xi^{-1}\int [1/(1 + w)][df(w)/dw]dw\) (9)

Integrated from 0 to \((t-1)\) according to [53] [and not to \((t-1)/2\) as given in the original reference].

The above given cross sections are for a specific subshell and the cross section \(\sigma\) for the entire target must be summed over all subshells that contribute to the ionization yield. It is clear that in addition to information on \(E_j\) and \(\zeta\), the differential oscillator strengths are needed for each subshell of the target. The average kinetic energy \(KE\) needed in the BED model is a theoretical quantity that can be obtained from quantum chemistry codes (and thus from an explicit knowledge of molecular wave functions). Average kinetic energies for subshells of some atoms and molecules are listed in [13] (the various articles by Kim, Rudd, and co-workers [14-16]). Differential oscillator strengths for specific subshells are even harder to obtain; some of these are summarized in [17] and in articles by Kim, Rudd, and co-workers.

4. The DM formalism

The formalism introduced by Deutsch and Mark [18] has a different origin from the previously discussed formalisms of Khare and co-workers and Kim and Rudd. The original concept of Deutsch and Mark [18], which was developed for the calculation of atomic ionization
cross sections, has been modified and extended several times. We begin with a brief outline of the original DM approach and the subsequent modifications that resulted in a very general formula now applicable to the single ionization of ground-state [18-19] and excited-state (metastable) atoms [20-22], the removal of a specific single outer- shell [23] and innershell electron [23] of atoms as well as to the single ionization of molecules [24], radicals, and CO$_2$ clusters, and C$_{60}$ [22,25-27] and atomic ions [25-26] as well as to the multiple ionization of atoms [28-29]. In all cases, only direct ionization processes are considered in the original DM formalism (i.e. the prompt removal of a single electron from the electron shell by the incoming electron—therefore it is not possible to distinguish between single and multiple ionization when inner-shell electron ejection occurs). Two-step ionization mechanisms such as autoionization after innershell excitation cannot be described by the DM formalism (nor by any of the other methods described above).

Thomson was the first to derive a formula for the electron-impact ionization cross section of an atom using a classical binary encounter approximation. This classical treatment was modified by several authors using different initial conditions. Gryzinski introduced the concept of a continuous velocity distribution for atomic electrons, which resulted in an expression for the ionization cross section $\sigma$ of the form

$$\sigma = \sum_{n,l} 4\pi a_0^2 \left( \frac{\zeta_n}{E_{nl}} \right)^2 \left( \frac{R}{E_{nl}} \right)^2 f(U)$$

(10)

With

$$f(U) = d \left( \frac{1}{U} \right) \left( \frac{U-1}{U+1} \right)^a \left\{ b+c \left[ 1-\left( \frac{1}{2U} \right) \right] \ln \left[ 2.7 + \left( \frac{U-1}{2} \right)^{0.5} \right] \right\}$$

(11)

and $a = 3/3$, $b = 1$, $c = 2/3$, and $d=1$

(12)

Here $\zeta_n$ is the number of electrons in the nth atomic subshell, and $E_{nl}$ refers to the ionization energy in the nth subshell, and $U$ is the reduced energy given by $U = E/E_{nl}$ where $E$ is the energy of the incident electron. However, even this improved cross section formula fails for some rather simple atoms such as neon, nitrogen, and fluorine.