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An overview of the BEB method for electron-impact ionization of atoms and molecules

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An accurate and simple method for the calculation of electron-impact ionization cross sections of atoms and molecules was developed by Kim and Rudd in 1994. Since then, many articles by Kim and coworkers have demonstrated the validity of the technique and have applied it to various atomic and molecular systems. The method is particularly useful for computational modeling, where numerous cross sections are needed. This paper presents the basic formulas and method of calculation, shows applications to some neutral atoms, and describes the NIST website where results of recent calculations are available. The limitations of the method as well as the advantages are outlined. Published in 2005 by John Wiley & Sons, Ltd.

KEYWORDS: electron impact; ionization; cross section; BEB; atoms; molecules

INTRODUCTION

The Binary-Encounter-Bethe (BEB) model for calculating electron-impact ionization cross sections was developed by Kim and Rudd in 1994.[1] This model has been shown to be remarkably accurate for ionization of atoms, ions, and molecules. Since its first publication, Kim and colleagues have applied it to many atoms and ions and over 100 molecules. In addition to H and He,[1] ionization of neutral C, N, and O[2] as well as B, Al, Ga, and In has been treated.[3] Applications to molecules have been published for small and large molecules.[4–6] A review article for plasma modeling has discussed the method. All these results are presented on the National Institute of Standards and Technology (NIST) website.[7]

The BEB model provides a simple and easy-to-use formula for the ionization cross section. There are no arbitrary parameters or fitting constants. Rather, only the binding energies and kinetic energies of the orbitals of the target are required. These energies can be obtained from an electronic structure computer program, such as a Hartree–Fock or Dirac–Fock wave function program. If there are several valence orbital electrons in the target atom or molecule, then configuration mixing may be required. Once the orbital energies are obtained, the formula will provide the ionization cross section at any incident electron energy. The original BEB model was slightly modified for application to atomic and molecular ions.[8]

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BEB CROSS SECTION

The BEB cross section for the ionization of N electrons in an atomic or molecular orbital with binding energy B and orbital kinetic energy U by an incoming electron of energy T is

$$\sigma_{\mathrm{BEB}} = \frac{S}{t+u+1}\left[\frac{\ln t}{2}\left(1-\frac{1}{t^2}\right)+1-\frac{1}{t}-\frac{\ln t}{t+1}\right] \qquad (1)$$

where $t = T/B$ and $u = U/B$ are normalized incident and kinetic energies, and $S = 4\pi a_0^2 N(R/B)^2$. In this expression, a_0 is the Bohr radius (0.529 Å) and R is the Rydberg energy (13.6 eV). The total cross section (i.e. the counting ionization cross section) for the target atom or molecule is the sum over all occupied orbitals ($\sigma_{\mathrm{Total}} = \sigma_{1s} + \sigma_{2s} + \sigma_{2p} + \cdots$) of the values given by this formula. The formula depends only on the initial state of the target.

The formula arises from a melding of two theories: the Mott theory for collision of two free electrons and the Bethe theory for the dipole interaction between the incident and target electrons at high incident electron energy. The Mott theory accounts for hard collisions with small impact parameters. The Bethe theory based on the first Born approximation works well for soft collisions with large impact parameters. At high incident energies, the Born approximation is valid, and the BEB formula reduces to the plane wave Born cross section. The details of the development of the formula are given in the original paper by Kim and Rudd.[1]

The formula for the more detailed Binary-Encounter-Dipole (BED) model is

$$\sigma_{\mathrm{BED}}(t) = \frac{S}{t+u+1}\left[D(t)\ln t + \left(2-\frac{N_i}{N}\right)\left(1-\frac{1}{t}-\frac{\ln t}{t+1}\right)\right] \qquad (2)$$

where, as before, the cross section is for each orbital, and the total cross section for the target is the sum over all occupied orbitals. In this BED formula, the $D(t)$ and N_i depend on the differential oscillator strength for ionization from the initial state to the continuum:

$$D(t) \equiv \frac{1}{N}\int_0^{(t-1)/2} \frac{1}{w+1}\frac{df(w)}{dw}dw$$
$$N_i \equiv \int_0^{\infty} \frac{df}{dw}dw \quad (3)$$

where $w = W/B$, and W is the kinetic energy of the ejected electron. When the differential oscillator strength df/dw is known, from experiment or theory, the BED formula should be more accurate than the BEB formula. The BEB formula is obtained by assuming hydrogen-like df/dw.

The denominator in front of the BED and BEB formulas, $t + u + 1$, plays the role of an average flux of the incident electrons during the scattering process. The effect of the denominator is to substantially reduce the cross section near the ionization threshold, and it is a large reason for the success of the BED and BEB models.

When the target system is relatively large, with occupied orbitals having high principal quantum numbers $n \geq 3$, the reduction of the cross section by the denominator $t + u + 1$ is too great because the magnitude of the orbital kinetic energy, $u = U/B$ becomes too large. Accordingly, we have found it best to replace $(u + 1)$ by $(u + 1)/n$. The BEB cross section for ionization of orbitals with $n \geq 3$ then becomes

$$\sigma_{\mathrm{BEB}} = \frac{S}{t+(u+1)/n}\left[\frac{\ln t}{2}\left(1-\frac{1}{t^2}\right)+1-\frac{1}{t}-\frac{\ln t}{t+1}\right], \quad n \geq 3 \quad (4)$$

The BEB model does not provide cross sections differential in energy loss or angle of scattering. Also, the BED expression, given above, is for the total cross section only. The BED model can, however, provide energy distribution of ejected electrons (see Ref. 1). Neither the BED nor the BEB model can describe resonances that often occur near threshold. Rather, the models give some average over the resonances. This does not pose a problem in modeling applications of gases, plasma, and materials where the resonances are smeared out by the velocity distribution of the electrons.

In molecular applications, the models cannot account for neutral dissociation of the target molecule. They assume that all interactions lead to ionization of the parent molecule.

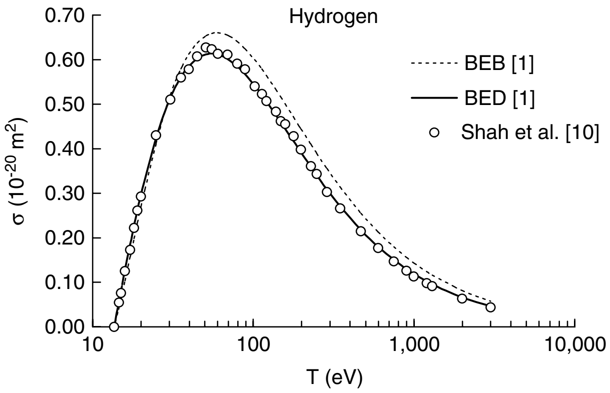

Figure 1. Hydrogen ionization. The experimental results of Shah *et al.*[10] are shown.

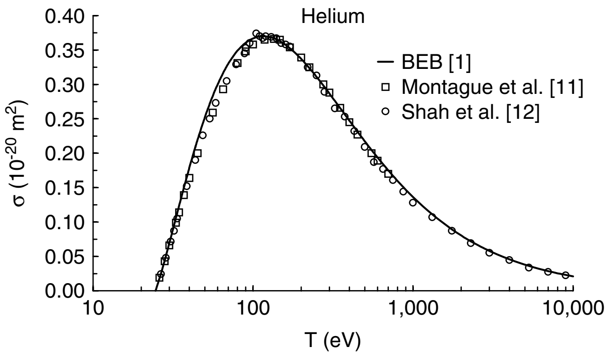

Figure 2. Helium ionization. The experimental results of Montague *et al.*[11] and Shah *et al.*[12] are shown.

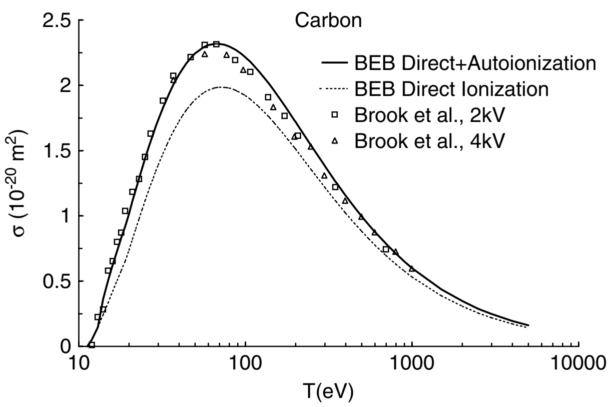

Figure 3. Carbon ionization. Autoionization contributes visibly to the total ionization and is calculated here using the scaled plane wave Born technique referred to in the text. Experimental results of Brook *et al.*[13] are shown.

RESULTS FOR SOME ATOMS

To illustrate the accuracy of the BEB model for neutral atoms, cross sections are shown for H, He, C, and Al in Figs 1–4. Applications to molecules and ions are given in references cited in the Introduction and on the website.

With some targets, excitation to energy levels above the ground-state ionization limit followed by autoionization contributes to the total ionization cross section. Autoionization can be expected to contribute significantly, whenever the excited levels involve excitation of an inner shell of the target with the same principal quantum number n as the valence orbital and when there is an allowed dipole transition from the initial state. This excitation-autoionization is a particularly large contribution in aluminum where excitation from the $3s^2\,3p$ ground state to $3s\,3p^2$ excited states above the ionization limit are strong. Similarly, excitation-autoionization is noticeable in carbon. We calculate the excitation-autoionization by scaling plane wave Born excitation cross sections using the scaling technique described by Kim.[9]

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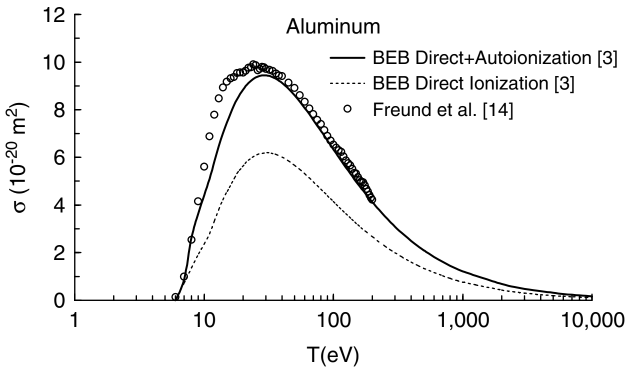

Figure 4. Aluminum ionization. Autoionization nearly doubles the total ionization cross section and is calculated using the scaled plane wave Born technique referred to in the text. Experimental results of Freund *et al*.[14] are shown.

WEBSITE

The database of the cross sections calculated and published so far by Kim and collaborators is available on the NIST website http://physics.nist.gov/ionxsec. The website presents an opening page with a link to introductory information and links to a Table of Atoms and a Table of Molecules. The atom and molecule tables allow the user to find cross sections for the atoms and molecules included in the database. The introductory page describes the elements of the BEB and BED theory and gives access to the theoretical and experimental reference included in the database. The cross-section pages for each atom or molecule show a plot of the cross section compared with experiment and other theoretical results, references for the data in the plots, and a table of the numbers in the plots. There is also a link that calculates the BEB cross section for any particular energy requested by the user.

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