



# New model for electron-impact ionisation cross sections of atoms and molecules

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## Abstract:

The "total cross sections for the ionisation and excitation of atoms and molecules by electron impact are one of the most important data sets because they are used to model plasmas for plasma processing of semiconductors, to design mercury-free fluorescent lamps, to assess the performance of ion gauges, to standardise the output of mass spectrometers, to diagnose plasmas in magnetic fusion devices, and to simulate the effects of radiation on materials. Ionization of atoms and ions by electron impact is briefly discussed theoretically. Both the major theoretical frameworks and the data archives are described. We show that the ground and metastable ionisation cross sections for light species are in good agreement with experiment when non-perturbative data are used for the near neutrals and distorted wave data are used for ions greater than a few times ionised."

**Keywords:** Ground, Metastable, Ionization, Cross.

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## Introduction

The accuracy of the standard theoretical methods to ionisation cross sections depends on the accuracy of the wave functions and the collision theory used in their calculation. Despite the fact that many theories seem to hold water at high incidence energies  $T$ , very few can be depended upon at low incident energies, particularly around the ionisation threshold [1]. Since calculating continuum wave functions for molecules suitable for ionisation cross sections is, in general, a very complex procedure, particularly for polyatomic compounds, it is difficult to apply theories that depend on them to molecules. Studies and theories, usually semiempirical, that worked well only on limited sorts of targets and/or small ranges of  $T$  [2] have been the main sources of ionisation cross sections for molecules up to now.

The non-perturbative computation of electron-impact ionisation cross sections has made great strides in recent years. It has helped round out the work made utilising distorted-wave techniques for quite some time and has resulted in complete sets of ionisation rate coefficients being developed for many systems [3]. There have been two recent reviews [4] of electron-impact ionisation. Ionization balance curves were analysed [5] to determine the effect of new data offered in these recent studies. Moreover, there are databases of electron-impact ionisation rate coefficients available online; we provide links to a few of the most popular ones below [6].

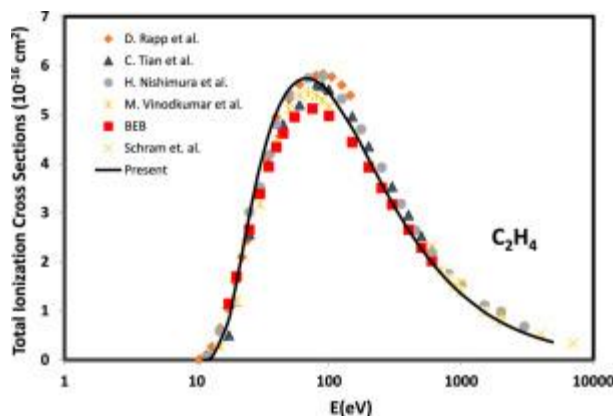


Fig 1: Ionisation cross section [1]

This collection of ionisation cross sections is grounded upon theories developed for the unique case of electron-impact ionisation. It's flexible, giving you access to atomic and molecular cross sections. The hypothesis, called the "Binary-Encounter-Bethe (BEB) model" [7], integrates the Mott cross section with the high-T behaviour of the Bethe cross section. Without needing to fit parameters, this theory provides a simple analytic expression for the ionisation cross section for any atomic or molecule orbital. The total ionisation cross section of a target may be computed by adding the individual orbital cross sections. The first three values of the four orbital constants (binding energy  $B$ , orbital kinetic energy  $U$ , electron occupancy number  $N$ , and a dipole constant  $Q$ ) are readily available from the ground-state wave function of the target atom or molecule. This formula [8] is used to determine the cross section for ionisation of a single orbit:

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

where  $t = T/B$ ,  $u = U/B$ ,  $S = 4\pi a_0^2 N (R/B)^2$ ,  $a_0 = 0.52918 \text{ \AA}$ , and  $R = 13.6057 \text{ eV}$ , and the dipole constant  $Q$  is defined in terms of the continuum dipole oscillator strength  $df/dW$ , where  $W$  is the kinetic energy of the ionized electron:

$$Q = \frac{2}{N} \int \frac{B}{B + W} \frac{df}{dW} dW. \quad (2)$$

When  $df/dW$  is unknown, one can put  $Q = 1$  as a further approximation. The constant  $n$  on the right-hand side (RHS) of Eq. (1) is used for ion targets and valence orbitals of large atoms as indicated at the end of this section. Unless noted otherwise, use  $n = 1$ .

The BEB cross section is only somewhat sensitive to the accuracy of the orbital constants used, with the exception of the very smallest  $B$  value. As for the smallest possible  $B$ , one possible ionisation energy is up and down. As much as feasible, we used an empirically established value. Otherwise, we'd have to rely on hypothetical numbers. The outer-valence group function was used to calculate the "OVGF"  $B$  values. Green's function methodology was used to calculate "CCSD" values using coupled cluster single double excitations, and "CCSD(T)" values were found using the CCSD method with the inclusion of perturbative triple excitations. It is sufficient to use the orbital constants of the Hartree-Fock or a similar

wave function. The majority of the targets in this database have threshold to T 1 keV cross sections that are accurate to within 5-20%.

## APPLICATIONS TO ATOMS AND MOLECULES

There is a comparison between the theoretical BEB and BED cross sections and experimental data for a number of atomic and molecular species. The "gross" ionisation cross section has traditionally been calculated by focusing on the total ion current rather than the number of ions. However, the most commonly used theoretical figure is the "counting" ionisation cross section, which accounts for the total number of ions generated [9]. The gross ionisation cross section will be much larger than the counting ionisation cross section if a large number of doubly charged ions are produced. Gross ionisation cross sections measured in experiments can be bound using the counting ionisation cross sections calculated from the BEB and BED models. It is possible for the ion formed after ionising an inner shell of an atom to contain several charges [9].

It is important to note that in addition to their constituent parts, molecules often give birth to molecular ions. Since the BEB and BED cross sections are just additive sums of cross sections for ejecting a single electron from an atomic or molecular orbital, the theory is constrained in its capacity to explain dissociative ionisation and the subsequent fragments. It is challenging to establish direct comparisons between theory and experiment when dealing with large molecules due to the several dissociative ionisation and fragmentation paths they possess. To keep things simple, we compared the sum of all observed partial cross sections that led to an ion with our theoretical molecular cross sections. The fact that our theory can be applied to such a wide range of molecules makes the comparisons here particularly instructive [10].

It is common practise to multiply the ionisation cross sections of individual atomic or molecular orbitals whose binding energies  $B$  exceed the double ionisation energy (roughly  $B > 40$  eV) [11] in order to estimate the production of a doubly charged ion or two singly charged molecular fragments due to inner-shell ionisation. The presence of a "Yes" in the "Dbllon" column of the atomic/molecular orbital constant table for C2F6 and C3F8 suggests that these contributions are taken into account by the BEB theory [11].

In order to (a) determine the total ionisation cross section at any incident energy  $T$ , the user may (b) download ASCII files providing orbital constants and ionisation cross sections for any atom or molecule of interest. (c) zoom into an area of the BEB cross section (unless otherwise noted), and (d) display a graph for every atom or molecule comparing the BEB model to experiments (data points for experiments, curves for theory unless otherwise noted).

Both the molecules and atoms tables provide examples of where the BEB model was used.

This database is continually updated to include the most recent atomic and molecular cross sections. As you'll see in the next section, the BEB model is only a shorthand way of referring to the BED model. For one-charged molecule ions like  $H_2^+$ ,  $n = 2$  is used on the right-hand side of Eq. (1). Further, if the Mulliken population analysis of a valence molecular orbital indicates that a specific atomic orbital with main quantum number  $n > 2$  represents the major component ( $> 50\%$ ), then this value of  $n$  is used in Eq

(1) Similar to, say, Adobe Photoshop 2 (CS2). If the primary quantum number (pqn) of the atomic orbital is greater than 3, then Eq (1). For pqn == 2, change n to 2.

**Cross Section for Differential Ionization Produced by a Single Particle (Energy Distribution of the Proton Impact):**

Using the BED model, we can write down the SDCS for the ejection of an electron from an atomic or molecular orbital at kinetic energy W as:

$$\frac{d\sigma(W, T)}{dW} = \frac{S}{B[t + (u + 1)/n]} \left\{ \frac{(N_i/N) - 2}{t + 1} \left( \frac{1}{w + 1} + \frac{1}{t - w} \right) + [2 - (N_i/N)] \left[ \frac{1}{(w + 1)^2} + \frac{1}{(t - w)^2} \right] + \frac{\ln t}{N(w + 1)} \frac{df(w)}{dw} \right\}, \quad (3)$$

where  $w = W/B$ ,  $df(w)/dw$  = the continuum dipole oscillator strength for ejecting an electron of kinetic energy W by photoionization, and  $N_i = \int_0^\infty (df/dw)dw$ . For H, He, and H<sub>2</sub>, known  $df/dw$  values have been fitted to a simple power series of  $y = B/(W + B)$ ,

$$df/dw = ay^2 + by^3 + cy^4 + dy^5 + ey^6, \quad (4)$$

In addition, the user may see the values of the coefficients a, b,... and the corresponding SDCS on the websites of specific targets, or view a table of SDCS for a certain T value and a collection of preselected values of W. The resultant d/dW is then normalised using the total ionisation cross section. Example comparisons between experiments and theory for SDCS [9] may be found online.

The BEB model for both total and differential cross sections has limitations, as do all other theories. The BEB model discussed here, for instance, is a nonrelativistic theory and should not be applied to energies  $T > 10$  keV. Please refer to [12] for a relativistic update on the BED/BEB model.

**Excitation of Atoms via Electron Impact**

Though the original Born cross sections are only trustworthy for high T [13], a scaling technique known as BE scaling may convert plane-wave Born cross sections (PWB) for electron-impact excitation of neutral atoms to very accurate cross sections at all incidence energies T. Definition of the BE scaled cross section BE:

$$\sigma_{BE}(T) = \sigma_{PWB}[T/(T + B + E)], \quad (5)$$

where E is the excitation energy.

Although the initial Coulomb Born cross sections are only trustworthy at high T [14], by simply scaling with the excitation energy E, we get very accurate cross sections at all incidence energies T. This process is known as E scaling. The E scaled cross section  $\sigma_E$  is defined as:

$$\sigma_E(T) = \sigma_{CB}[T/(T + E)]. \quad (6)$$

**Excitation-Autoionization**

Cross sections for ionising atoms and molecules may be broken down into two categories: direct ionisation and indirect ionisation. Direct ionisation is required for a bound electron to be dissipated into the environment. The BEB/BED model is used to ascertain the ionisation cross sections in a given path. It is usual for an inner-shell electron to be stimulated to an unstable valence state, "resulting in indirect ionisation (3s 3p excitation in aluminium, for example). The excited state may decay by either photon or electron emission. Excitation-autoionization describes the second mechanism (EA). In cases when the gap between the energy of the excited state and the lowest ionisation energy is minimal, EA prevails" [14]. Cross sections for significant EA (mostly electric-dipole and spin-permitted excitations) were computed using the BE and E scalings described in Section C above, and these values were included into the total ionisation cross sections for the atoms in this database.

Atomic and molecular ionisation cross sections predicted by most theoretical models suffer from two key flaws. One difficulty is that it is unusual for a single model to be applicable to both atoms and molecules. This is because it is simpler to calculate many theoretical parameters for atoms than for molecules, including the continuum wave functions. When a slow incident electron collides with a target, it's important to choose a strategy that considers the two particles as a compound system, such as by providing high coupling amplification. For most neutral atoms and molecules, the ionisation peak is between 60 eV and 150 eV, hence a theoretical model may not be accurate for these energies [15]. At low incidence electron energies, this is a crucial reason why most theories fail. This is particularly true for those relying on the perturbation approach. For high temperatures, the plane-wave Born approximation accurately predicts ionisation cross sections when valid initial and terminal wave functions are used.

Strong-coupling theories, such as the close-coupling or R-matrix method, need a large basis set to describe the system, making it difficult to cope with ionising collisions. With the exception of two novel theoretical methodologies [16], it is challenging to apply these strong coupling theories to the ionisation of atoms and molecules with intricate shell configurations.

However, the estimate of specific empirical parameters or "the explicit knowledge of the intensities of the target's continuum dipole oscillators are prerequisites for all of the proposed models that employ this combination" [17]. Some of these models use a high number of empirical parameters, some of which may be difficult to obtain. The present model uses a novel approach to determine the ratio between the low-T and high-T cross sections without resorting to any empirical parameters, and ionisation cross sections are derived in analytic forms for the entire range of T using three atomic/molecular constants per atomic/molecular orbital, which are available from atomic/molecular structure codes. Ionization cross sections may be calculated without considering the deep inner shells since their contribution is so little.

To estimate the ionisation cross sections of molecules, the "DM methodology" [17] is one of two theoretical methods that are equally flexible. The ionisation cross section of a molecule is calculated using the DM approach by adding up the ionisation cross sections of the atoms that make up the molecule. These atomic cross sections are given as absolute values in terms of (a) atomic orbital radii obtained from atomic wave function codes, (b) atomic orbital occupation numbers obtained from the Mulliken population analysis of the target molecule, and (c) atomic weighting factors fitted to known atomic ionisation cross sections [18]. The present model makes use of many fewer ab initio atomic/molecular parameters, which are also the standard for output from atomic/molecular structure codes. The WW technique [19] is very similar to the BED model presented in the next section, which

similarly requires exact data on the intensities of the target's continuum dipole oscillators. However, the WW method may provide implausible results for incident electrons with energies in the hundreds of eV, despite its efficacy for high-energy incident electrons.

### Conclusion:

However, the estimate of specific empirical parameters or the explicit knowledge of the intensities of the target's continuum dipole oscillators are prerequisites for all of the proposed models that use this combination [17]. These models often rely heavily on empirical parameters, some of which may be hard to obtain. The present model uses a novel approach to determine the ratio between the low-T and high-T cross sections without resorting to any empirical parameters; these cross sections are derived in analytic forms for the entire range of T using three atomic/molecular constants per atomic/molecular orbital, which are available from atomic/molecular structure codes. It is possible to omit the deep inner shells when computing ionisation cross sections since their contribution is so small. Only at high incident energies T do the various theories of ionisation cross sections for molecules hold water; at low T, they all but fall apart. Significant progress has been achieved in recent years toward the non-perturbative computing of electron-impact ionisation. Binary-Encounter-Bethe combines the Mott cross section and the high-T behaviour of the Bethe cross section into a single framework. In addition to providing a straightforward analytic formula for every orbital, it also allows you to easily get atomic and molecular cross sections.

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