



A model potential for computing total ionization cross sections of atoms and molecules by electron impact

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Abstract. We propose a model potential for computing total ionization cross sections for atoms and molecules by electron impact. The potential is obtained by a fitting procedure using the Binary–Encounter–Bethe model cross sections as a starting point. We present total ionization cross section for hydrogen, carbon, nitrogen and oxygen atoms and for hydrogen, nitrogen, water, methane and benzene molecules. The results obtained with our model potential are compared with results obtained with the Binary–Encounter–Bethe model and with the first Born approximation, and agreement is quite good. Our results show that this potential could be used to account for the ionization channel in an electron–molecule collision calculation.

1 Introduction

Several processes can occur in electron–molecule collisions, such as: (i) elastic scattering, (ii) electronic, rotational and vibrational excitations, (iii) ionization and (iv) dissociative electron attachment. Some of these processes can cause permanent physicochemical transformations in atoms or molecules and understanding how they occur is essential for applications of low-energy electron scattering by atomic and molecular targets in different areas. These processes are present in discharge environments such as atmospheric discharges [1,2], nanomaterials fabrication [3,4], biofuel production [5–8] and combustion chambers [9]. In biology and radiotherapy, secondary low-energy electrons are generated by the interaction of the ionizing radiation with the organic material [10,11]. These electrons, typically with kinetic energy from 0 to 20 eV, are capable of causing damage to the genetic material through the single- and double-strand breaks of DNA [12]. In addition, it was verified that the damage caused is local [13] and triggered by the formation of a transient negative ion.

Many challenges are encountered in the study of electron scattering by atoms and molecules. Among them, the convergence of multichannel coupling is hard to achieve due to the large number of open electronic excitation channels, which can be of valence or Rydberg character and the ionization channel, which is difficult to implement due to the infinite number of the possible continuum states. To illustrate the problem, let

us consider one of the simplest problems: the hydrogen atom. We know that the energy spectrum of H is proportional to $1/n^2$ (where $n = 1, 2, \dots$), and there are infinite discrete states up to the ionization threshold of ~ 13.6 eV. Above the ionization threshold, there are also infinite continuum ionization states. This also occurs, in a similar way, in multielectronic atoms and molecules, but in different energy ranges. Besides, there are multiple ionization thresholds, which are somehow impossible to treat analytically. In the case of electron scattering, the ionization problem of one incoming electron and two outgoing free electrons in a field of an ionized target is complex, since the wave function of the $N + 1$ -electron problem needs to be antisymmetric and needs to describe the polarization of the target, the multichannel coupling, along with the asymptotic condition (two electrons in a coulombic field).

Over the years, theoreticians have been trying to describe experimental cross sections through their ab initio and/or model potential methods. Here, we highlight the Complex–Kohn method [19,20], the R-Matrix method [17,18], the Convergent Close Coupling (CCC) approximation [16] and the Schwinger multichannel method (SMC) [21–23], which are all ab initio. In some cases, however, the theory does not agree well with the experiment. In a recent review, Brunger reported the common errors found in the calculated cross sections [24]. One way that can be improved is the treatment of the ionization effects.

An alternative to treat the ionization problem is the use of the Binary–Encounter–Bethe (BEB) model [25,26], a convenient and simple model to calculate total

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ionization cross section (TICS) by electron impact. The total ionization cross sections obtained with the BEB model agree with the experimental data within 5–15% for different molecules, and for electron-impact energies ranging from the first ionization threshold to several keV [27–29]. Recently, we have applied the BEB model to the para-benzoquinone (pBQ) molecule and confirmed its accuracy. Also, Graves et al. [30] employed the BEB model along with pseudopotentials (of effective core potentials) for a series of molecules with heavy atoms and obtained results in good agreement with previous theoretical and experimental results.

To account for the ionization channel in the Schwinger multichannel method, we propose the inclusion of model potential constructed considering the results obtained with the BEB model. We have developed a model potential for ionization to compete with the flux probability along with the elastic and inelastic channels. The implementation of this potential will enable the SMC method to treat the electronic excitation (bound state problem) within an ab initio fashion, but considering the ionization channels through this model potential.

The remainder of this paper is organized as follows. In Sect. 2, we highlight the relevant aspects of the theoretical methods and computational aspects used in the calculations. The results are presented and discussed in Sect. 3, and some conclusions are summarized in Sect. 4.

2 Theory and computational aspects

The ionization cross section in the BEB model is given by

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

where $t = T/B$, T being the incident energy, B the binding energy, $u = U/B$, U the orbital kinetic energy, $S = 4\pi a_0^2 N(R/B)^2$, N is the electron occupation number, the Rydberg constant is $R = 13.6057$ eV and Q the dipole constant. As usual, we make $Q = 1$ and $n = 1$.

We consider the following problem. An electron with momentum \mathbf{k}_i hits an atom (or molecule), and as a result from the collision, we obtain an electron with momentum \mathbf{k}_f , an ionized electron with momentum \mathbf{k}_g . The atom has acquired a momentum \mathbf{k}_A . The momentum conservation writes as $\mathbf{k}_i = \mathbf{k}_f + \mathbf{k}_g + \mathbf{k}_A$, while the energy conservation becomes $k_i^2 = k_f^2 + k_g^2 + B$ and the kinetic energy acquired by the atom is negligible. We are using the atomic units of Rydberg, where the electron mass is 1/2. The extreme situation which we study is $k_g^2 \ll 1$, that is, the ionized electron has a kinetic energy close to zero.

The transition probability due to a potential $V_{\text{ionization}}$ is proportional to

$$W_{i,f} = \frac{k_i^2 - B}{R + (k_i^2 - B)} \left| \int d^3r e^{i(\mathbf{k}_i - \mathbf{k}_f) \cdot \mathbf{r}} V_{\text{ionization}} \right|^2 \quad (2)$$

where we use the Fermi golden rule for one electron from \mathbf{k}_i to \mathbf{k}_f , completed by a factor translating the density of final states for the collision. $W_{i,f}$ is the probability of the transition $(\mathbf{k}_i, \phi) \longleftrightarrow (\mathbf{k}_f, \mathbf{k}_g)$, where \mathbf{k}_g is the ionized electron momentum and ϕ is a target orbital which lost the electron on ionization. The probability is written as a Fermi rule due to a Gaussian potential. But we must include a density of states for the ionized electron, according to Eq. (2),

$$W_{i,f} = \frac{k_i^2/B - 1}{R/B + k_i^2/B - 1} C^2 \exp[2D(\mathbf{k}_i - \mathbf{k}_f)^2] \quad (3)$$

Integrating the last equation over the solid angles, we obtain

$$W = 4\pi \frac{k_i^2/B - 1}{R/B + k_i^2/B - 1} C^2 \times \exp[-2DB \frac{k_i^2 + k_f^2}{B}] \frac{\sinh[\frac{4k_i k_f}{B} DB]}{\frac{4k_i k_f}{B} DB}. \quad (4)$$

From the energy conservation, one has

$$k_f^2/B = k_i^2/B - 1 \quad (5)$$

$$k_i k_f/B = \sqrt{k_i^2/B(k_i^2/B - 1)} \quad (6)$$

So, with Eq. (4), we have

$$W = 4\pi S \frac{k_i^2/B - 1}{R/B + k_i^2/B - 1} C^2 \times \exp[-2DB(\frac{2k_i^2}{B} - 1)] \times \frac{\sinh[4\sqrt{k_i^2/B(k_i^2/B - 1)}DB]}{4\sqrt{k_i^2/B(k_i^2/B - 1)}DB}. \quad (7)$$

Equation (7) is our fitting equation to σ_{BEB} [Eq. 1] and C and D the adjusting parameters obtained by each target.

To verify the viability of this model potential, we want to obtain integral cross sections from the scattering amplitude given by the first Born approximation (FBA) and compare to the fitted curve. The FBA cross section is

$$\sigma = \frac{k_f}{k_i} \frac{1}{4\pi} \int d\hat{k}_i \int d\hat{k}_f |\langle \mathbf{k}_f | V | \mathbf{k}_i \rangle|^2. \quad (8)$$

To obtain the same result of the equation obtained with the Fermi's golden rule [Eq. 7], we employed the follow-

Table 1 Atoms and their potential parameters

Atom	N	B (eV)	β	ϵ
H	1	13.598	17.28361	1.95664
C	2	11.260	27.15160	3.67466
N	3	14.534	44.20264	3.38459
O	4	13.618	68.35319	8.96317

ing model of potential:

$$V(|\mathbf{r} - \mathbf{r}_A|) = \sqrt{\frac{k_i}{k_f}} \sqrt{\frac{k_i^2/B - 1}{R/B + k_i^2/B - 1}} \times S^{1/2} \epsilon \exp[-\beta|\mathbf{r} - \mathbf{r}_A|^2], \tag{9}$$

where \mathbf{r}_A is the position of the nuclei A . The equivalence between these parameters and the fitting parameters is given by $\beta = 1/4D$ and $\epsilon = C(\beta/\pi)^{3/2}$.

As the first attempt to take into account ionization cross sections for molecules, we have summed up the potentials obtained by each atom that constitutes the molecule

$$V_{\text{molecule}} = \frac{S_{\text{molecule}}^{1/2}}{N} \sum_A V(|\mathbf{r} - \mathbf{r}_A|) \frac{N_{\text{atom},A}}{S_A^{1/2}}. \tag{10}$$

In this case, B is equal to the first ionization potential of the molecule, the constant R now is the Rydberg constant and the factor is $S_{\text{molecule}} = 4\pi a_0^2 N(R/B)^2$, with the occupation number N of molecular orbital of interest. As we will show below, the results are not in good agreement with the BEB results. So, to obtain TICS for molecules, we decided to fit the molecular cross sections and obtain parameters for a Gaussian potential which reproduce the BEB results. In addition, the molecular geometries were obtained from the *Computational Chemistry Comparison and Benchmark DataBase* [31]. The constants B and N for molecules have been used as in the NIST database [26].

3 Results and discussion

We can now show the results obtained with the model we developed. The parameters of the potentials obtained for different atoms are shown in Table 1. With these parameters, it is possible to obtain TICSs similar to those obtained with the BEB model.

Figures 1, 2, 3 and 4 show the results obtained with our procedure for the hydrogen, carbon, nitrogen and oxygen atoms. The fitting procedure using a modified Gaussian potential reproduces well the BEB TICS, with small deviations (an exception is the O atom, which has larger deviations), and is in perfect agreement with the results from the FBA calculation. In general, the agreement with the most recent experimental data (only

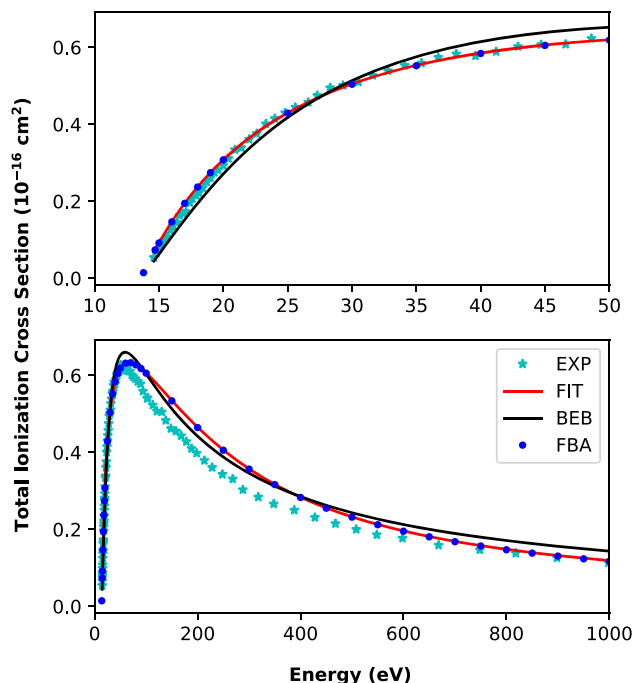


Fig. 1 Total ionization cross sections for the hydrogen atom. The blue dots are the FBA results for a potential centered at origin, black line the σ_{BEB} of Ref. [26] and the red line the fitting equation W . The cyan stars are the experimental results from Ref. [32]

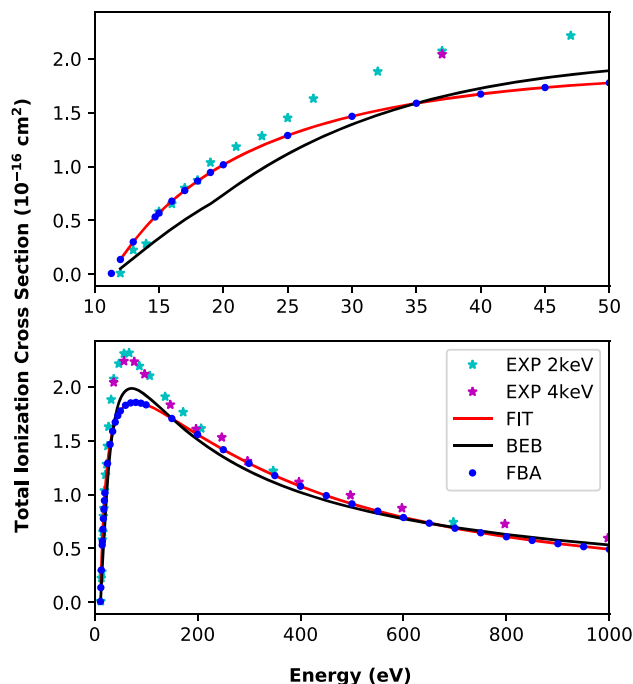


Fig. 2 As in Fig. 1, but for carbon atom. The stars are the experimental results from Ref. [33], which are measurements at atom beams of 2 keV (cyan) and 4 keV (magenta)

these ones are showed) is reasonable in the ionization threshold and in greater energies.

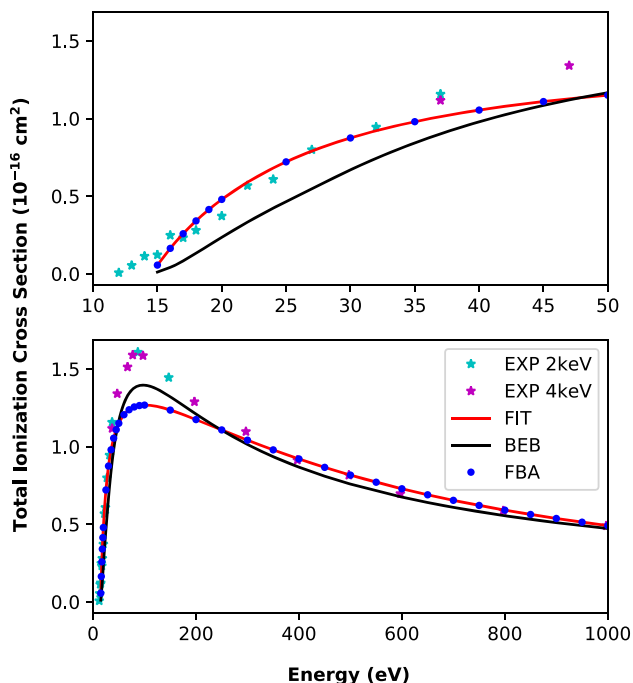


Fig. 3 As in Fig. 1, but for nitrogen atom

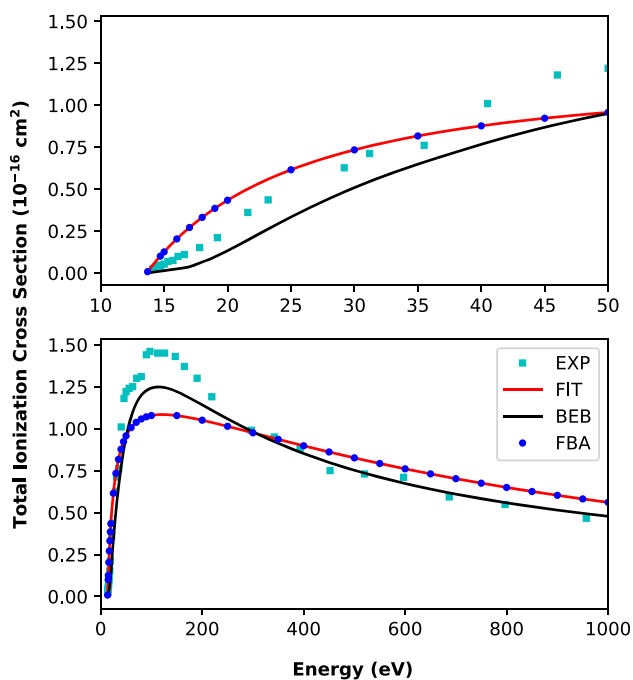


Fig. 4 As in Fig. 1, but for oxygen atom. The cyan squares are the experimental results from Ref. [34], which are measurements for single ionization

Let us discuss the results for molecules. The first attempt was to add up the atom’s potential, as we discussed in Sect. 2 (see Eq. 10). To illustrate what happened with this model, we calculated the FBA TICS for the hydrogen, nitrogen and water molecules and compared the results with the BEB TICS. Table 2 shows the

Table 2 Molecules and their potential parameters

Atom	N	B (eV)	β	ϵ
H ₂	2	15.426	21.65930	2.64936
N ₂	2	15.581	46.53473	12.36292
H ₂ O	2	12.619	50.03768	10.39948
CH ₄	2	14.25	27.30659	6.24210
C ₂ H ₄	2	10.51	35.57611	7.80568
C ₆ H ₆	2	9.37	36.78272	12.48772

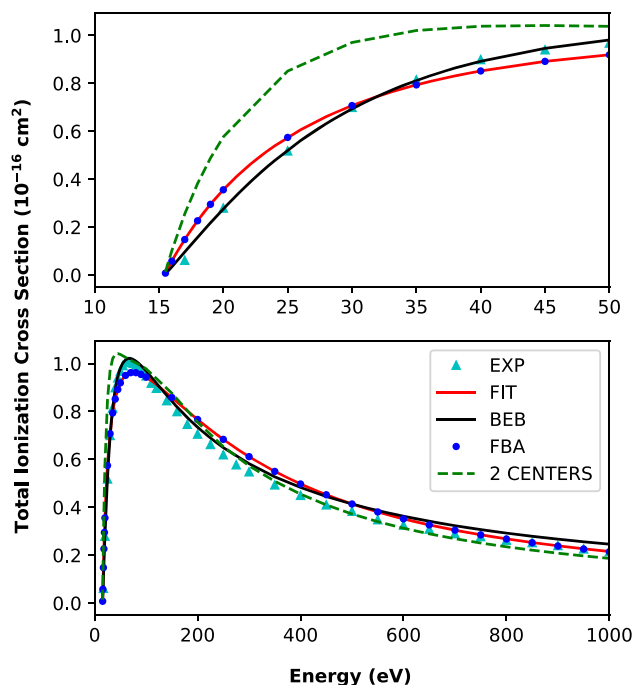


Fig. 5 Total ionization cross sections for the hydrogen molecule. The blue dots are the FBA results for a potential centered at origin, black line the σ_{BEB} of Ref. [26], the red line is the fitting equation W and the green line is the results of two center FBA calculation using hydrogen atom potential parameters. The cyan triangles are the experimental results from Ref. [35]

molecular potential parameters, and the corresponding cross sections are shown in Figs. 5, 6 and 7. For H₂ and N₂, the shape of the cross section is quite different from the BEB method and displays the characteristic of the independent atom model: two different peaks in TICS, which we can be assigned to each atom in this approximation. Furthermore, the peak in the curve displays a feature as an *interference effect*. For H₂O, the resultant TICS overestimates the magnitude of all other cross sections by a factor of ≈ 3 . In general, it is important to emphasize that the approximation of independent atoms should not work well, mainly at low energies, since the molecular occupied orbitals are important to describe the ionization effects instead of just the sum of the potentials generated by the curves of TICS from atomic orbitals.

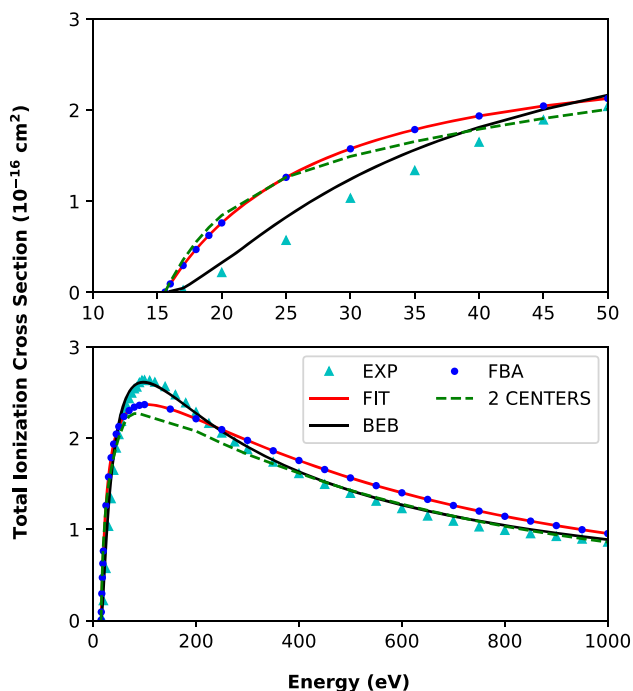


Fig. 6 As in Fig. 5, but for the nitrogen molecule. The cyan triangles are the experimental results from Ref. [35]

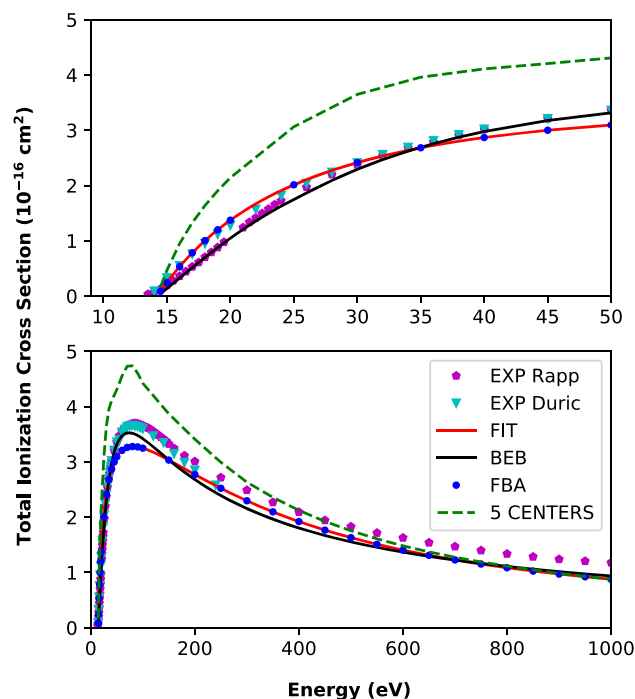


Fig. 8 As in Fig. 7, but for the methane molecule. The green line is the results of six center FBA calculation using the atoms potential parameters, normalized at 1000 eV to W (multiplied by 0.75). The magenta pentagons and cyan triangles are the experimental results from Refs. [37,38]

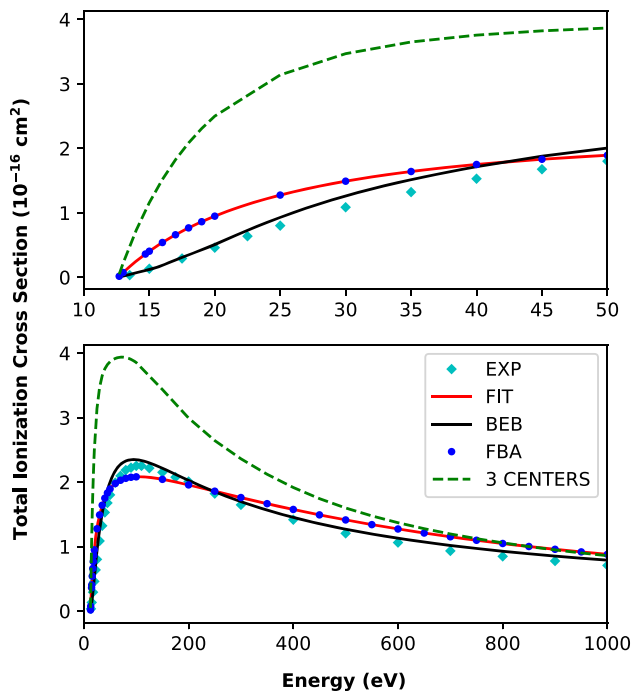


Fig. 7 As in Fig. 5, but for the water molecule. The green line is the results of two center FBA calculation using the atoms potential parameters, normalized at 1000 eV to W (multiplied by 0.3). The cyan diamonds are the experimental results from Ref. [36]

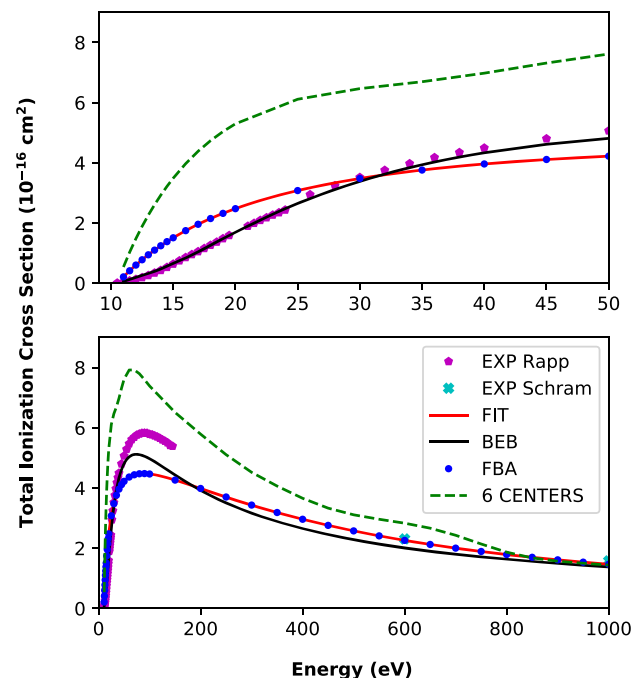


Fig. 9 As in Fig. 7, but for the ethylene molecule. The green line is the results of six center FBA calculation using the atoms potential parameters, normalized at 1000 eV to W (multiplied by 0.57). The magenta pentagons and cyan crosses are the experimental results from Refs. [37] and [39]

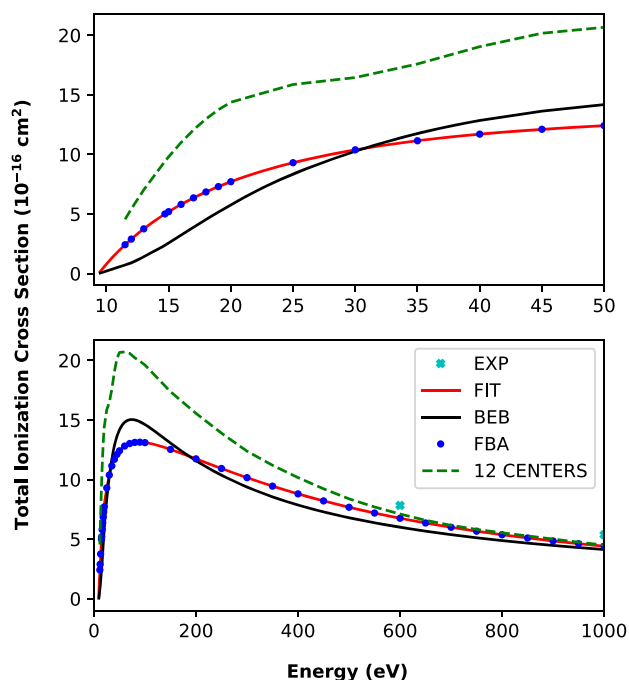


Fig. 10 As in Fig. 7, but for the benzene molecule. The green line is the results of six center FBA calculation using the atoms potential parameters, normalized at 1000 eV to W (multiplied by 0.59). The cyan crosses are the experimental results from Ref. [39]

This problem can be more critical for larger systems, as showed for the water molecule, and therefore, we decided to construct a potential from the molecular TICS of the BEB model. To simplify the problem, we considered the molecular modified Gaussian potential centered at the molecular center of mass. The shape of the fitting is better than the obtained by the sum of atom potentials. The drawback in this approach is to do a parametrization for each molecule of interest, but with the facility to obtain the input parameters (TICS from BEB and molecular information as B and N), the problem is somewhat minimized. Furthermore, we applied the strategy to more larger molecules, as methane (CH_4), ethylene (C_2H_4) and benzene (C_6H_6), and the results are shown in the Figs. 8, 9 and 10. The TICS fitted and calculated has reasonable agreement with BEB model, showing the same quality find in the small molecules. We found a reasonable agreement in comparison with the available experimental data since the fitting to the BEB model is qualitatively good considering the approximations used.

These results show the efficiency of this model potential, which can be used to mimic the ionization effects. Some hypothesis can explain the discrepancies: (i) considering just the first ionization potential (or B) to calculate the cross sections (except for H and H_2) changes the shape of the curve, and (ii) the lack of a better parametrization, which can be improved in future works. In addition, it is important to note that we chose the simplest version of the BEB model to parametrize

the potentials. For more accurate results in relation to the experimental data, one can change the input data for a more sophisticated model.

4 Conclusions

We proposed a model potential to compute TICS, which is parametrized in order to reproduce the results of the BEB model. The present results are quite satisfactory, considering the approximations used in the fitting procedure. This methodology can be improved using more terms in the expansion of the potentials for a specific target and/or calculating the TICS using all ionization potentials of the molecule, to obtain more reliable ionization cross sections. Our next step is to implement this model potential in the Schwinger multichannel method code to compete with the flux with the elastic and electronically inelastic channels.

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Author contributions

All authors contributed to the theory development, potential implementation, coding, cross section calculations, analysis and discussion of the results and also in paper writing and proof reading.

Data Availability Statement This manuscript has no associated data or the data will not be deposited. [Authors’ comment: All data published in this manuscript are available under request to the authors].

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