

## Total cross sections for electron scattering from well-known and exotic molecules

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**Abstract.** In this review paper, scattering of intermediate to high energy electrons on well-known as well as exotic molecular targets is considered. The ‘additivity rule’ and its modifications for calculating various total cross sections are discussed against the background of an extensive experimental data. The theory succeeds at high impact energies ( $E_i > 100$  eV). Tentative upper and lower limits of e-molecule ionization cross sections are identified. Fitting formulas to represent total cross sections as functions of energy are also given.

**Keywords.** Electron scattering; total cross-sections; additivity rule.

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### 1. Introduction

Study of the collisions of electrons with molecules has been a traditional but active area of research. There have been many more experimental investigations in this regard as compared with theoretical ones. The sustained interest in this field is due to its relevance in various pure and applied sciences [1]. The present paper discusses various approximations, called the ‘additivity rules’ employed to calculate the different total cross-sections (TCS) of e-molecule scattering at intermediate to high impact energies  $E_i$ . These approximations have been found to be useful in interpreting the corresponding measurements, if they exist. They can provide reliable high energy data in the absence of measurements in many cases.

At low energies, typically up to about 10 eV, the e-molecule scattering is dominated by anisotropic and long-range dipole and/or quadrupole interactions. With an increase in energy the ionization and excitation channels also open up and the rotational-vibrational channels gradually become weaker. Many experiments performed in this energy domain measure total (complete) cross sections which include elastic as well as non-elastic contributions. It is meaningful to calculate total elastic cross sections  $Q_{el}(E_i)$  and total inelastic cross sections  $Q_{inel}(E_i)$  separately, with the latter quantity being comparable to total ionization cross sections  $Q_{ion}(E_i)$ . We calculate these quantities by starting with the relevant atomic scattering amplitudes.

Although the above theory has so far been applied to a large number of molecules, our focus here is on (a) 10-electron targets viz., HF, H<sub>2</sub>O, NH<sub>3</sub> and CH<sub>4</sub> along with Ne and, (b) 18-electron targets like F<sub>2</sub>, H<sub>2</sub>S, C<sub>2</sub>H<sub>6</sub> etc., along with Ar. Many of these molecules have been experimentally studied by Zecca *et al* [2–4], Szmykowski *et al* [5], Garcia *et al*

[6], Rao and Srivastava [7] and by other groups. Szmytkowski *et al* [5] have recently given a detailed summary of a large number of TCS measurements done over a wide energy range on diatomic and polyatomic molecules. Detailed comparisons of our theoretical results with some of these experimental data can be found elsewhere [8–10]. Comparison of our results with the theoretical work of Jain and Baluja [11] has also been made in our previous papers. These authors [11] have calculated e-molecule TCS in a number of cases by starting with direct molecular wave functions and charge densities.

Further, the TCS obtained theoretically or experimentally are often analysed in terms of correlations with the properties of the target molecules. This is done here by expressing the TCS as functions of energy  $E_i$  and by interpreting the parameters of these fitting formulas in terms of molecular properties (see also ref. [12]).

## 2. Theoretical aspects

In the simplest approximation, the total (elastic + inelastic) cross section  $Q_T(M)$  of e-molecule collision is expressed as a sum of the relevant e-atom cross sections. Thus in the additivity rule (AR) we have [8]

$$Q_T(M) = \sum_{i=1}^n Q_T^{(i)}(A), \quad (1)$$

where  $n$  is the number of atoms in the target molecule and  $Q_T^{(i)}(A)$  is the total (elastic + inelastic) cross section of the  $i$ th atom. Equation (1), though rather too simple, serves as a preliminary result. An improvement over this can be introduced by separating the long-range (spherical) polarization potential of the target from the remaining short range interactions. Thus we introduce [8–10] the ‘modified additivity rule’ (MAR) as follows:

$$Q_T(M) = \sum_{i=1}^n Q_{SR}(i) + Q_{pol}(M), \quad (2)$$

where, on the RHS the first term is the sum of the e-atom TCS calculated in the short-range complex optical potential. This complex potential consists of static, exchange and absorption effects, and the polarization effect is considered at the molecular level through the second term  $Q_{pol}(M)$ . The standard formalism of partial wave analysis is employed to calculate the cross sections. The MAR, eq. (2) is more realistic, as it makes use of molecular properties like the polarizability and ionization energy. Further, a small non-spherical (mainly dipole) contribution can be added to  $Q_T(M)$  to define the grand total cross sections in polar molecules.

Now, one can write the additivity rule for molecular total inelastic cross sections in a similar manner, i.e.,

$$Q_{inel}(M) = \sum_{i=1}^n Q_{inel}^{(i)}(A), \quad (3)$$

in which  $Q_{inel}^{(i)}$  is the total inelastic cross section for the  $i$ th atom. At high enough energies, where the ionization dominates the non-elastic processes, the e-molecule total ionization

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cross section  $Q_{\text{Ion}}(M)$  can be expressed similarly, viz.,

$$Q_{\text{Ion}}(M) = \sum_{\alpha=1}^n Q_{\text{Ion}}(\alpha), \quad (4)$$

where  $Q_{\text{Ion}}(\alpha)$  is the corresponding quantity for atom  $\alpha$  of the molecule. The simple additivity rules, like eq. (1) and (4) are in general known to overestimate. Deutsch *et al* [13] modified eq. (4) as follows:

$$Q_{\text{Ion}}(M) = \sum_{\alpha=1}^n f(\alpha) \cdot Q_{\text{Ion}}(\alpha), \quad (5)$$

where  $f(\alpha)$  is a weighing factor for atom  $\alpha$ . It depends on structure properties like the number of valence electrons and the 'radius' of outermost orbitals in the constituent atoms. It is difficult to understand how the static factor  $f(\alpha)$  in eq. (5) provides a weightage over the atomic TCS  $Q_{\text{Ion}}(\alpha)$ , which is a dynamic quantity.

Let us note that the additivity method itself has also been employed in predicting the average spherical polarizability ( $\alpha_0$ ) of many molecules. Miller [14] has discussed empirical methods to develop molecular  $\alpha_0$  as a sum over the atomic polarizabilities.

Now, the MAR for e-molecule scattering can be extended to polyatomic targets like  $\text{C}_2\text{H}_6$  molecule in an another form. In this molecule the two  $\text{CH}_3$  groups are bonded to each other at a relatively larger C-C bond length. The two C atoms can be identified here as approximately independent scattering centres. The charge-density of H atoms in the  $\text{CH}_3$  group is expanded and brought to a single-centre at C, which becomes the scattering centre for further calculations. The single-centre total charge-density is employed to construct complex short-range potential and to calculate the corresponding cross sections. Thus in our MAR-SC approach [12],

$$Q_{\text{T}}(M) = \sum_{j=1}^n Q_{\text{SR}}(j) + Q_{\text{pol}}(M). \quad (6)$$

In eq. (6),  $j$  stands for one of the two scattering centres and  $Q_{\text{SR}}(j)$  is the TCS obtained in the short-range complex potential. Further, an equation similar to (3) can as well be written down for  $Q_{\text{inel}}$  in the present case. These calculations, though approximate, do employ the actual properties of the target molecules.

Finally, we turn briefly to the fitting formulas to represent the energy dependence of the molecular cross sections  $Q_{\text{T}}$ . In [15] we proposed the following general form, in the energy range 100–1000 eV,

$$Q_{\text{TOT}}(E_i) = a \cdot (E_i)^{-b}, \quad (7)$$

where the LHS is in  $\text{cm}^2$  and  $E_i$  is in eV. The parameters  $a$  and  $b$  have been correlated to the target properties. Alternatively we also employ

$$\frac{Q_{\text{T}}}{a_0^2} = A \left( \frac{\alpha_0}{E_i} \right)^B \quad (8)$$

which shows an explicit dependence on  $\alpha_0$ .

### 3. Results, discussion and conclusion

The present theoretical approach has so far yielded satisfactory results in a large number of e-molecule systems. These include diatomic and triatomic molecules made up of C, N and O atoms [8, 9], together with heavier triatomic polar molecules like H<sub>2</sub>S, SO<sub>2</sub> and OCS [10]. Several other authors [16, 17] have employed the additivity rules for high energy electron scattering with other well-known and exotic polyatomic targets. The total (complete) cross sections in diatomic molecules compare favourably with experiments above 100 eV roughly. The results for polyatomic molecules are in a similar accord above 300 eV or so. Towards lower energies the present approximations yield overestimating results, but are qualitatively correct. The polarization effect, vide eq. (2) offers a small contribution at intermediate energies, and it decreases rapidly with  $E_i$ . For polar molecules the dipole rotational excitation cross sections also offer a small contribution which slowly decreases with  $E_i$ . The simple additivity rule eq. (1), becomes effective at large  $E_i$  when the scattering is mainly through static and absorption potentials.

The present method also gives a high energy estimate of the ionization cross section in the form of  $Q_{\text{inel}}$ , eq. (3). Up to about 1000 eV, we have  $Q_{\text{inel}} > Q_{\text{ion}}$  as expected. Khare and Meath [18] calculated  $Q_{\text{ion}}$  for a large variety of molecules under different approximations. These results are found to be lower than the measured data on ionization. The quantity  $Q_{\text{inel}}$  on the other hand, sets an upper limit to  $Q_{\text{ion}}$  for a molecule.

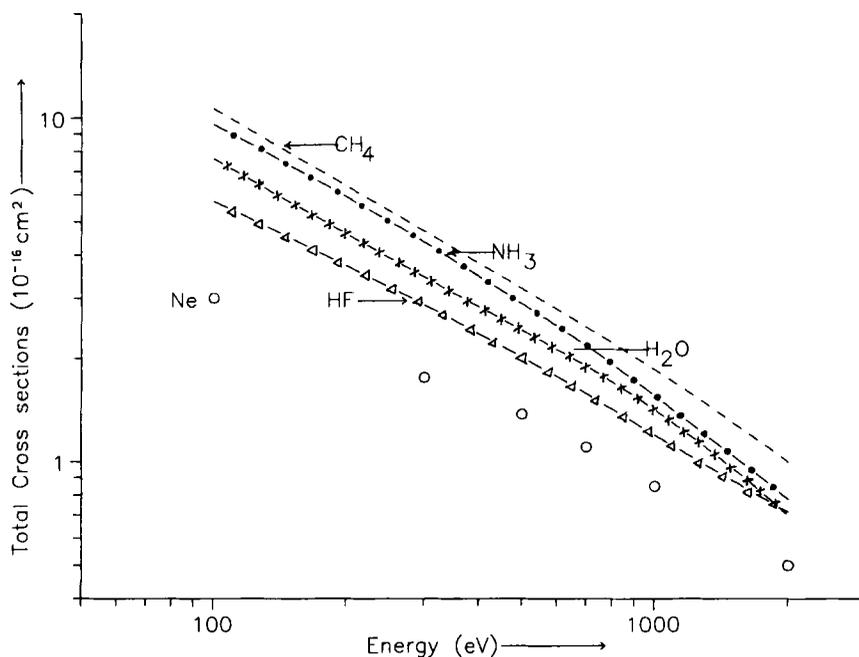
The AR in the form of eq. (1) or (4) shows that the cross sections simply increase with the number of atoms of the same kind, contained in the molecule. Deutch *et al* [13] have pointed out a failure of such a rule i.e. eq. (4) for ionization.

Now, the present theoretical methods are examined here to see the relative behaviour of the TCS  $Q_T(M)$ , of the sequence HF–H<sub>2</sub>O–NH<sub>3</sub>–CH<sub>4</sub>, containing 10 electrons each. Our results vide MAR, eq. (2) (see [9, 10]) for these target molecules are plotted in figure 1. The experimental data on e-Ne scattering, given by Zecca *et al* [3] serve as a reference. At a given energy, the TCS becomes larger as we pass on from HF to CH<sub>4</sub>. The differences in the TCS decrease with  $E_i$  and are quite small above 1000 eV, but still all the molecular values are larger than the Ne cross sections. We have fitted the TCS of the 10 electron targets HF through CH<sub>4</sub> to analytical formula of eq. (8). The fitting parameters  $A$  and  $B$  are given in table 1.

Now, the H<sub>2</sub>O molecule has long since been the target of scattering studies. We have separately investigated [19] the electron scattering cross section of H<sub>2</sub>O in the usual vapour phase, together with that in the ice and liquid phases.

Let us next discuss the relative behaviour of the TCS of F<sub>2</sub>, H<sub>2</sub>S and C<sub>2</sub>H<sub>6</sub> molecules typically representing 18-electron targets. We have exhibited the MAR cross sections of these molecules in figure 2, along with the experimental data [3] on Ar atoms. In the case of e-F<sub>2</sub> scattering probably there are no other data on intermediate and high energy TCS. Again here, the cross section at a given energy becomes larger along the sequence F<sub>2</sub>–H<sub>2</sub>S–C<sub>2</sub>H<sub>6</sub>. The cross sections of C<sub>2</sub>H<sub>6</sub> are calculated in the MAR-SC approach. The nonpolar diatomic molecule F<sub>2</sub> offers the smallest values among these three targets. The half bond length of F<sub>2</sub> is somewhat larger than the orbital radius (1.25  $a_0$ ) of the Ar atom, but the polarizability of Ar is more than that of F<sub>2</sub>. It is, therefore, noticeable that, in figure 2 the cross sections of F<sub>2</sub> are at the lowest. There are differences in the bonding in the three molecules, and these are reflected in the results in figure 2. The molecular cross

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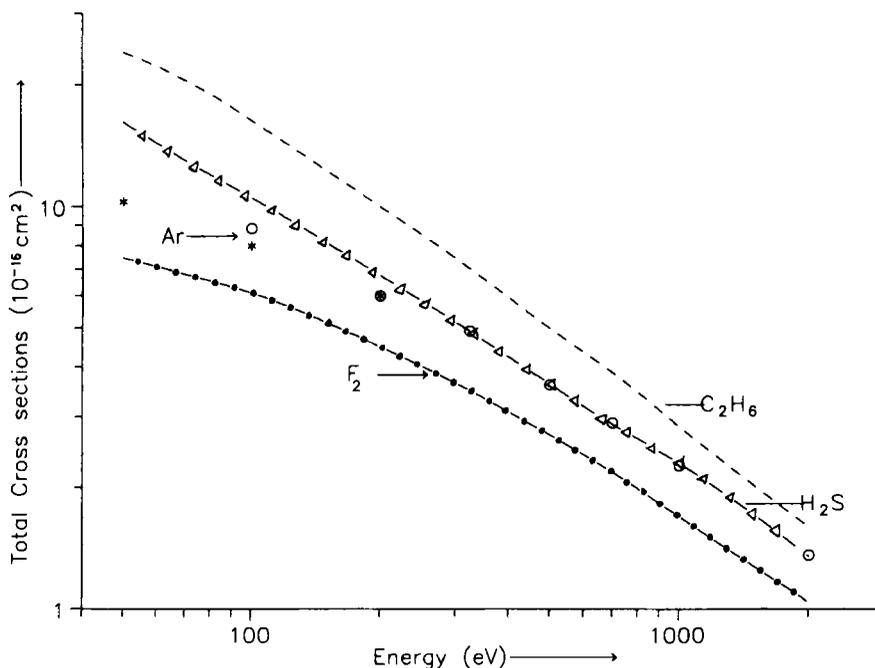
**Figure 1.** Total cross sections for 10 electron systems. Experimental data for Ne:  $\circ \circ \circ \circ \circ$  [3]; present results:  $-\triangle-\triangle-\triangle-\triangle$  HF;  $-x-x-x-x-x-x-x-x-x-x$  H<sub>2</sub>O;  $-●-●-●-●-●-●-●-●-●-●$  NH<sub>3</sub>;  $- - - - -$  CH<sub>4</sub>.

**Table 1.** The fitting parameters of eq. (8) for 10-electron systems.

Target	A	B
Ne atom	70.89	0.51
HF	179.9	0.71
H <sub>2</sub> O	157.3	0.74
NH <sub>3</sub>	141.1	0.75
CH <sub>4</sub>	144.0	0.76

sections tend to merge slowly at high energies above 2000 eV. The TCS of the 18-electron targets were fitted to eq. (8) and the parameters *A* and *B* are shown in table 2.

Thus the present paper has considered the scattering of intermediate and high energy electrons by a large variety of molecules. Simple but effective theoretical approximations allow us to study the total electron collision cross sections for different groups of molecular targets. We have presented here the TCS of the 10-electron as well as the 18-electron molecules, together with those of the corresponding inert gas atom (Ne and Ar) serving as reference. The fitting parameter *A* of eq. (8) is found to depend on the molecular geometry. The parameter *B* varies over a narrow range between 0.5 and 0.7. The value 0.5 is in accordance with Vogt and Wannier [20] but for molecules  $Q_T \simeq (\alpha_0)^{0.7}$  has been observed [12].



**Figure 2.** Total cross sections for 18-electron systems. Experimental data for Ar:  $\circ \circ \circ \circ$  [3];  $****$  [5]. Present results:  $-\bullet-\bullet-\bullet-\bullet-$   $F_2$ ;  $-\triangle-\triangle-\triangle-\triangle-$   $H_2S$ ;  $----$   $C_2H_6$ .

**Table 2.** The fitting parameters of eq. (8) for 18-electron systems.

Target	A	B
Ar atom	108.4	0.56
$F_2$	78.7	0.54
$H_2S$	82.4	0.61
$C_2H_6$	140.8	0.71

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