

Additivity approximations for molecules and radicals

K N Joshipura, Minaxi Vinodkumar¹, Yogesh Thakar² and Chetan Limbachiya³

Department of Physics, Sardar Patel University, Vallabh Vidyanagar-388 120, India

¹ V P & R P T P Science College, Vallabh Vidyanagar-388 120, India

² M N College, Visnagar-384 315, North Gujarat, India

³ P S Science College, Kadi-384 715, North Gujarat, India

Abstract Various additivity approximations used in literature to calculate electron impact total cross sections for molecules and radicals are highlighted. The simple additivity rule for the e^- - *molecule* TCS is modified and theoretical comparison is made with other such attempts. The present modified additivity rule alongwith single centre expansion of charge density appears to be the best by far for several molecules examined. Specific results on the TCS of CH_4 , SiH_4 , F₂, H₂S and C_2H_6 have been presented vis-a-vis other experimental and theoretical data at energies above 50 eV.

Keywords Additivity rules, optical potential, electron scattering

PACS No. 34.80 -1

1. Introduction

In this paper we highlight various additivity approximations frequently used for molecules and radicals, and use them to present our specific results on electron scattering cross sections, with selected molecules. When free atoms combine to form a molecule or a neutral radical, the number of atomic electrons adds up exactly, while the other static and dynamic properties do not add up simply. One can however make an effective rule of addition of atomic properties to obtain the corresponding molecular properties. Miller [1] has discussed simple prescription to obtain molecular polarisability as a sum of the polarisabilities of constituent atoms or group of atoms. Bader [2] prescribed a simple addition of atomic charge-densities to obtain the molecular charge-density. Approximate additivity rules are also used to represent various cross sections of electrons scattered by diatomic and polyatomic molecules. Deutch *et al* [3] have followed this approach for total cross sections of electron impact ionisation. We [4,5,6] started with coherent superposition of atomic scattering amplitudes to derive for the total (complete) cross sections for e^- - *molecule* collisions. This so called additivity rule (AR) has also been used by Jiang *et al* [7] and by others, with a limited success. The AR is a simple high energy approximation and has been modified by us [5,6] and by Jiang *et al* [8] under different considerations.

The additivity rules are simple and attractive but they should be made more realistic otherwise they tend to overestimate the cross sections. In view of the basic approximations we have considered here the impact energies $E_i \geq 50$ eV, where a large number of inelastic channels are open. It is therefore reasonable to define total elastic cross section Q_{el} and total inelastic cross section Q_{inel} so that the sum of the two is the total (complete) cross section Q_T at a given energy. Further at high energies, the rotational and vibrational excitation channels are weaker and have not been considered here. (see also refs. [5,6]). Thus in this paper we have presented our total (complete) cross sections Q_T at 50-2000 eV for the targets CH_4 , SiH_4 , F_2 , H_2S and C_2H_6 . These are specifically chosen to test our improved additivity methods outlined in Section 2 below. For methane molecule a vast amount of comparative data is available [9a, 9b], while for other targets like C_2H_6 the data available [10] is limited. We could not find comparable results for $e^- - \text{F}_2$ scattering, but the 18-electron targets have been mutually compared here against the background of the isoelectronic Ar atom. The modifications over AR result into better accords with measured data.

2. Theory and calculations

As discussed in [4-6], we consider high-energy short wave-length collisions of an electron with a molecule or a neutral radical, for which the scattering amplitude approximates as the sum of that of its constituent atoms. Use of optical theorem then yields the following simple expression for the total (complete) $e^- - \text{molecule}$ cross section $Q_T(M)$.

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

In this additivity rule (AR), n is the number of atoms in the molecule and $Q_T^{(i)}(A)$ is the total (complete) cross section for i -th atom. Eq. (1) is too simple to be real. We modified this AR by separating the long-range polarisation potential considered at the direct molecular level. The resulting modified additivity rule (MAR), vide [4-6] reads as follows.

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

where the first term on RHS is a sum of the atomic TCS Q_{SR} calculated in short range complex potential and the second term Q_{pol} is obtained through the molecular polarisation potential, viz.

$$V_p(r, k) = - \frac{\alpha_0 \cdot r^{-6}}{2(r^2 + r_c^2)^4} \quad (3)$$

with $r_c = \frac{3k}{8\Delta}$

Here, k is the incident momentum in a.u., and α_0 and Δ are the molecular average spherical polarisability and the effective excitation energy respectively. The MAR, eq. (2) is better than the AR, as it employs molecular properties α_0 and Δ (or I, the ionisation energy). To calculate Q_{SR} for each atom in the target molecule we construct a short range complex potential

which includes static, exchange and absorption model potentials. Well known and reliable models, vide [4-6,7,8], derived from an accurate atomic charge-density $\rho(r)$ are employed in the optical potential calculations [11] to obtain the total elastic cross section $Q_{el}(E_i)$ and the total inelastic cross section $Q_{inel}(E_i)$. Thus, we have for each constituent atom

$$Q_{SR}(E_i) = Q_{el}(E_i) + Q_{inel}(E_i). \quad (4)$$

The cross section Q_{inel} includes electron impact total atomic Ionization cross section $Q_{ion}(E_i)$ along with all other electronic excitation cross sections. The Q_{inel} approaches Q_{ion} at high enough energies, so that from eqs. (2) and (4) one can write an additivity rule for electron impact ionisation, vide [3,6] as

$$Q_{ion}(M) = \sum_{\alpha=1}^n Q_{ion}(\alpha_i), \quad (5)$$

where α labels the constituent atoms.

Thus the molecular total ionisation cross section $Q_{ion}(M)$ is approximated as a sum of atomic total Ionisation cross sections $Q_{ion}(\alpha)$. This approximation is reasonably good only at high enough energies. Deutch *et al* [3] have introduced weighing factors $f(\alpha)$ in the following manner in order to make the above additivity rule (eq. 5) realistic :

$$Q_{ion}(M) = \sum_{\alpha=1}^n f(\alpha) \cdot Q_{ion}(\alpha). \quad (6)$$

This modification succeeds in bringing a closer agreement of calculated $Q_{ion}(M)$ to experimental data in many cases [3]. However, the factors $f(\alpha)$ are static, *i.e.* they depend on structural properties while the cross section $Q_{ion}(\alpha)$ are dynamic or energy dependent quantities. Hence a modification like eq. (6) is difficult to justify theoretically. Jiang *et al* [8] have made a similar attempt to express the molecular TCS in the following additivity approximation :

$$Q_{MT} = Q_{MG}(E_i) + A(k), \quad (7)$$

where on the RHS the first term Q_{MG} is the molecular TCS obtained by weighing over the TCS of atoms or group of atoms in the molecule by geometrical or structural arguments. Further $A(k)$ is an energy dependent empirical factor, introduced to contain the overestimation of calculated molecular cross-sections. The $A(k)$ is so chosen as to reduce eq (7) to the AR (eq. 1) at high energies [8].

Rather than trying to correct the additivity rules for the cross-sections as above, one can try to work at the basic level of electronic charge-density, which is an important input in these calculations. The charge-density of a molecule AB may be approximately written [2] as a sum of the atomic charge-densities ρ_A and ρ_B , *i.e.*

$$\rho_{AB} = \rho_A + \rho_B. \quad (8)$$

where ρ_A and ρ_B are free-atom charge-densities and eq. (8) ignores the overlap or the bonding in the molecule. Now at this stage we consider a hydride molecule AH and expand the H – atom charge-density ρ_H at the heavier atom (nucleus) A, following Watson [12]. The expansion

involves the A-H bond length R as the parameter, so that we can approximate single-centre spherical charge-density of the molecule AH as

$$\rho_{AH}(r; R) = \rho_A(r) + \rho_H(r; R). \quad (9)$$

We propose to improve here the simple addition of atomic charge-densities, by considering the bond charge introduced on the atoms A and H, in the process of molecular bonding. The formation of the bond re-adjusts the electronic charge on the partner atoms and the same can be calculated by molecular HF charge-densities. We have adopted the bond-charges as tabulated by Bader [2]. Thus if $q(A)$ in a.u. is the bond-charge acquired by atom A, then the corresponding amount $1 - q(A)$ is shifted from the H-atom so that to obtain the molecular charge-density a realistic addition of atomic charge-densities must be done in the following manner.

$$\rho_{AH}(r; R) = \left[\frac{N(A) + q(A)}{N(A)} \right] \cdot \rho_A(r) + \left[\frac{N(H) - q(A)}{N(H)} \right] \cdot \rho_H(r; R), \quad (10)$$

where $N(A)$ is the number of electrons in the free atom A and $N(H) = 1$ for the free H-atom. The bond-charge $q(A)$ e.g. -0.535 au on O-atom in OH radical has been adopted from [2]. Let us note that as one might expect, eq. (10) when integrated, yields exactly the total number of electrons in the molecule $N(AH)$, viz.,

$$N(AH) = N(A) + N(H). \quad (11)$$

Eq. (10) offers a better approximation compared to eq. (9).

Now, the single-centre spherical charge-density $\rho_{AH}(r; R)$ can be used to construct the complex optical potential for the $e - AH$ system, to determine the various total cross sections. This approach is more reliable than even the MAR, eq. (2), because the former unlike the latter includes the valence-bonding effects through eq. (10). The single-centre (SC) approach has been adopted in studying the electron collisions with CH, NH, OH and HF in [5]. This method can be coupled with MAR to derive an effective additivity rule for larger polyatomic molecules like C_2H_6 . In this target, two CH_3 groups are bonded with each other *via* C-C bond which is somewhat larger than its C-H bond. Hence, it is reasonable to assume high energy electron scattering to occur through two scattering centres considered at the two carbon atoms in C_2H_6 .

For this purpose a single centred charge-density $\rho_G(r, R_{C-H})$ for each CH_3 group is constructed as follows

$$\rho_G(r, R_{C-H}) = f_C \cdot \rho_C(r) + n \cdot f_H \cdot \rho_H(r; R_{C-H}). \quad (12)$$

In eq. (12) f_C and f_H are bond-charge factors for C and H atoms in each of the C-H bonds, as defined in eq. (10) and $n=3$ shows the number of H atoms in the CH_3 group. Now, we can use $\rho_G(r, r_{C-H})$ as the input to construct the complex optical potential for the electron scattering from each of the two scattering centres in the C_2H_6 molecule. The total molecular scattering amplitude is the sum of the amplitudes from the two groups of atoms, in this approximation. If Q_{SR} is the total cross section for short-range potentials and $\alpha = 1, 2$ denotes the two scattering

centres then proceeding as in eq. (2), we can express the total electron-molecule cross section as

$$Q_T(M) = \sum_{\alpha=1}^L Q_{SR}(\alpha) + Q_{pol}(M). \quad (13)$$

In this additivity rule, called the MAR-SC, the second term is calculated again from a direct molecular polarisation potential, as in eqs. (2) and (3), while Q_{SR} is calculated by starting with $\rho_G(r, R_{C-H})$.

Finally for a polar molecule with dipole moment D , one can define a high-energy grand total cross section

$$Q_{TOT}(M) = Q_T(M) + Q_{rot}(D, E_i), \quad (14)$$

where, the second term shows the first-Born rotational excitation cross section due to the long-range dipole potential of the target. We have found [5, 6] that gradually above 100 eV impact energy, where the above approximations are reliable, the dipole and other anisotropic contributions become unimportant.

3. Results, discussions and conclusions

Various additivity rules for e^- - molecule collisions as discussed above have been employed by several workers in the recent years to provide theoretical comparisons to experimental data. In general, the simple rule of adding atomic cross sections to obtain a molecular cross section as in eqs. (1) and (5), overestimates at low and intermediate energies and it tends to be closer to the experiments only at sufficiently large impact energies. The simple AR is a useful first approximation not only for the measured data but also for assessing improved approximations like those in eqs. (2), (6), (7) and (13). We have shown earlier [4-6] that the MAR eq. (2) fares marginally better than the AR for molecules like CO, NO, CO₂, NO₂, N₂O, NH₃, H₂S, OCS, SO₂ etc., above 50 eV. Our TCS obtained in the SC approach for e^- - HF scattering [5] lie below the molecular orbital calculations [13] at intermediate energies. All the additivity rules discussed here are more or less consistent with the measured TCS at energies progressively above 100 eV, but the MAR-SC, eq. (13), seems to be physically more realistic as it incorporates the actual molecular properties like the bond-lengths, ionisation energy and polarisability.

Table 1. Total (complete) cross sections in 10^{-16} cm², for electron collisions with CH₄ molecules

Energy (eV)	Present Results MAR-SC eq. (13)	Theoretical data Jiang <i>et al</i> *	Experimental Data Zecca <i>et al</i> [9a]
50	12.71	17.80	12.30
80	10.59	13.22	10.30
100	9.38	11.40	9.00
300	4.89	5.02	4.76
500	3.46	3.22	3.18 (3.13)**
700	2.72	2.33	2.49

* Using AR [7]

** Garcia and Manero [9b]

Now in the present paper our calculated total (Elastic + Inelastic) cross sections Q_T on molecular targets CH_4 , SiH_4 , F_2 , H_2S and C_2H_6 have been examined against various experimental results, at impact energies $Ei \geq 50$, eV. In table 1 we have chosen sample energies to exhibit the present Q_T *vis-a-vis* theoretical values of Jiang *et al.* [7] in the AR and the measurements of Zecca *et al.* [9a] as well as Garcia and Manero [9b].

The present Q_T values shown here are calculated through the MAR-Sc, eq. (13). Below 300 eV the AR results [7] are higher than the measurements [9a, 9b]. Our theory shows a better accord with the experiment from about 100 eV onwards. It is physically reasonable to apply the single-centre expansion method, vide eq. (10) to nearly spherical molecules like CH_4 and SiH_4 . The drawbacks of the AR due to valence-bond effect and multiple scattering in the molecule are overcome in the MAR-SC. Our results on the collisions of electrons with Silane molecules are given in table 2. As expected here too, our Q_T values obtained through eq. (13) are in better accord with the experimental data of Zecca *et al* [14], while the AR results [7] are on the higher side, especially below 100 eV. However, it is not clear (Table 2) why the quoted results of [7] are lower than the measured data above 100 eV.

Table 2. Total (complete) cross sections in 10^{16} cm², for electron collisions with SiH_4 molecules

Energy (eV)	Present results MAR-SC eq (13)	Theoretical data Jiang <i>et al</i> *	Experiment data Zecca <i>et al</i> [14]
50	21.39	24.63	–
80	18.74	18.96	16.70
100	16.75	16.51	14.70
300	8.45	7.62	7.92
500	5.89	5.11	5.52
700	4.60	3.76	4.14

* Using AR [7]

The improvement given by Jiang *et al* [8] through eq. (7) does not apply to molecules like CH_4 and SiH_4 . Our modifications *i.e.* MAR and MAR-SC are rather more general and realistic.

Now, we have also selected typical 18-electron targets F_2 , H_2S and C_2H_6 for applying our improved methods. Figure 1 shows the total (elastic + inelastic) cross sections for these molecules, at incident energies 50-2000 eV. Also shown here for reference are the experimental TCS [15,16] of the isoelectronic Argon atom. The 18-electron molecules considered here differ from each other in no. of atoms within, and also in terms of bondlengths, polarisabilities etc. H_2S is of course a weakly polar target, but at the energies of the present interest, the rotational excitation contribution is not important [6]. The TCS of $e^- - \text{F}_2$ collisions calculated in AR, are the lowest of all the other targets, in Figure 1. The TCS of C_2H_6 , on the other hand are relatively the highest. We have inserted in Figure 2, the experimental data points of Sueoka and Mori [17] as well as Szmytkowski and Krzysztofowicz [10] on $e^- - \text{C}_2\text{H}_6$ system. Our MAR-SC calculations on this system tend to agree with the measured data from about 200 eV onwards. In the case of H_2S molecule we have not shown any other data, for the sake of clarity of the diagram, but our theoretical results show a similar accord [6] with the relevant experiments. One notices from the

figure that the H_2S cross sections tend to merge with those of isoelectronic Ar, above 300 eV. Even at 2000 eV there are significant differences among the TCS of all the 18-electron targets studied here. It may be noted that the calculated cross sections of SiH_4 , an 18-electron molecule not covered in Figure 1, are close to that of the Ar atom, beyond 200 eV or so.

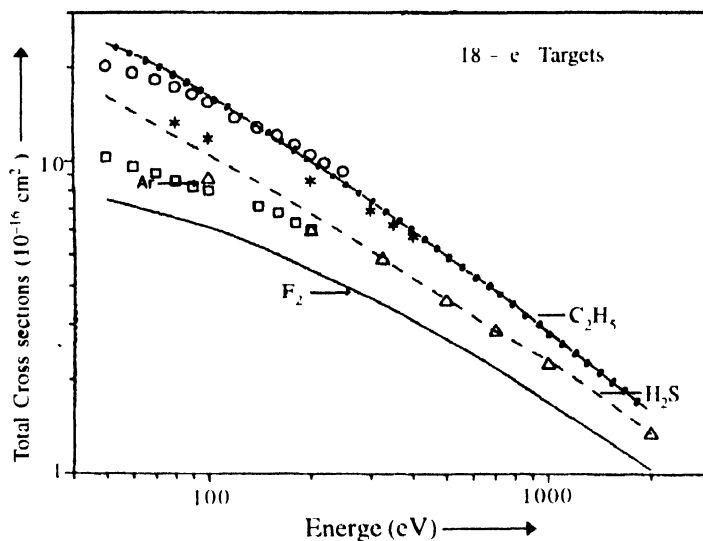


Figure 1. Present results ----- F_2 , - - - - H_2S , - · - · - C_2H_5 , Experimental data \square Ar Atom \square \square \square Ref [15] Δ Δ Δ Ref [16], C_2H_6 molecule \circ \circ \circ \circ \circ Ref [10] ***** Ref [17]

This paper thus examines various additivity rules for e^- - molecule cross sections currently used in literature. We have introduced modifications in the simple AR to obtain reliable cross sections at intermediate and high energies. The MAR-SC, vide eq. (13), is based on a reasonably good representation of molecular charge-distribution. It gives reliable results above 100 eV, for a variety of molecules examined here and elsewhere by the present authors. We now intend to apply it to still larger polyatomic molecules in general and hydrocarbons in particular.

References

- [1] K J Miller *J Am Chem Soc.* **112** 8533 (1990)
- [2] R F W Bader *Atoms in Molecules* (U K Clarendon) (1990)
- [3] H Deutsch, T D Mark, V Tarabovský, K Becker, C Cornhisen, L Cespiva and V Bonacic - Koutecky *Int J. Mass. Spectrom.* **137** 77 (1994)
- [4] K N Joshipura and P M Patel *J Phys* **B29** 3925 (1996)
- [5] K N Joshipura and Minaxi Vinodkumar *Phys Letts.* **A224** 361 (1997)
- [6a] K N Joshipura and Minaxi Vinodkumar *Z. Phys* **D41** 133 (1997)
- [6b] K N Joshipura and Minaxi Vinodkumar *ICPEAC XX Conference*, (Vienna, Austria), Book of abstracts p. WEO71 (1997)
- [7] Y Jiang, J Sun and L Wan *Phys. Rev.* **A52** 398 (1995)
- [8] Y Jiang, J Sun and L Wan *J. Phys* **B30** 5025 (1997)

- [9a] A Zecca, G Karwasz, R S Brusa and C Szymkowski *J Phys* **B24** 2747 (1991)
- [9b] G Garcia and F Manero *Phys Rev* **A57** 1069 (1998)
- [10] C Szymkowski and A M Krzysztofowicz, *J Phys* **B28** 4291 (1995)
- [11] C J Joachain *Quantum Collision theory* (Amsterdam North Holland) (1983)
- [12] G N Watson *Theory of Bessel Functions* (London Cambridge University Press) p 368 (1958)
- [13] A Jain and K L Baluja *Phys Rev* **A45** 202 (1992)
- [14] A Zecca, G Karwasz and R S Brusa *Phys Rev* **A45** 2777 (1992)
- [15] C Szymkowski and K Maciag *Phys Sci* **54** 271 (1996)
- [16] A Zecca, S Oss, G Karwasz, R Grisenti and R S Brusa *J Phys*, **B20** 5157 (1987)
- [17] O Sueoka and S Mori *J Phys* **B19** 4035 (1986)