Additivity Rule for Electron–Molecule Total Cross Section Calculations at 50–5000 eV: A Geometrical Approach *

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To quantify the changes of the geometric shielding effect in a molecule as the incident electron energy varies, we present an empirical fraction, which represents the total cross section (TCS) contributions of shielded atoms in a molecule at different energies. Using this empirical fraction, a new formulation of the additivity rule is proposed. Using this new additivity rule, the TCSs for electron scattering by CO_2, C_2H_2, C_6H_{12} (cyclo-hexane) and C_8H_{16} (cyclo-octane) are calculated in the range 50–5000 eV. Here the atomic cross sections are derived from the experimental TCS results of simple molecules (H_2, O_2, CO). The quantitative TCSs are compared with those obtained by experiments and other theories, and good agreement is attained over a wide energy range.

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There is a lack of accurate theoretical calculations over the intermediate- and high-energy ranges. To calculate the accurate total cross sections (TCSs) for electron scattering by molecules at higher energies, many new approximation methods have been developed so far. Of these methods, the additivity rule (AR) model[1] is a fairly simple and practical one, particularly for simpler and smaller molecules at high enough energies. However, for complex molecules,[2,3] great discrepancies still exist even at energies of several hundreds of eV.

In order to extend the AR model validity to lower energies, a number of investigations have been made in recent years. Bobeldijk *et al.*[4] presented two geometric AR (GAR) methods, and obtained encouraging electron impact ionization cross section (ICS) of several molecules at energies of several tens of eV, however they did not calculate the TCS of electron scattering by molecules. Deutsch *et al.*[5] applied a modified AR (with an atomic weighted factor) to the molecular ICS, whereas they did not calculate the molecular TCS, too. Joshipura and Patel[6] separated the polarization interaction from the optical potential, and obtained atomic cross sections from the remainder. Then, they summed atomic cross sections with the cross sections for scattering on the molecular polarization potential. Employing this approach, they calculated the TCSs for a number of molecules and improved their results in this way. Zecca *et al.*[7] presented a new AR formula, which takes into account the geometrical screening of the component atoms in a molecule. Using this formula, they calculated the TCSs of electron scattering by several molecules. Favourable agreement with measurements is obtained at intermediate and high energies. However, their results are smaller than the measurements at lower energies. Recently, to find the TCS of electron scattering by molecules, Antony *et al.*[8] have also proposed a modified AR named the group additivity method, in which the cross section arising from each constituent group of a molecule was added together to obtain the molecular TCS. Using this method, they calculated the TCSs of electron scattering by several molecules. Good agreement with experiment is attained over a wide energy range. Jiang *et al.*[9] proposed a modification method named the energy-dependent geometric AR (EGAR) approach, and calculated the TCS for electron scattering by a number of molecules. Since the target molecular dimension is not considered, obvious deviations still exist at lower energies for complex molecules. To improve the agreement between theory and experiment, in this Letter we take into consideration of the shielding effect of atoms in a molecule and discuss further modifications to the AR model, which depends on the target molecular dimension and the energy of the incident electrons.

In the original AR model, the molecular TCS is given by[1]

$$Q_{AR}(E) = \frac{4\pi}{k}\mathrm{Im}F_m(\theta=0) \approx \frac{4\pi}{k}\mathrm{Im}\sum_{j=1}^{N} f_j(\theta=0) = \sum_{j=1}^{N} q_T^j(E), \quad (1)$$

where $F_m(\theta = 0)$ is the electron–molecule scattering amplitude for the forward direction; $q_T^j(E)$ and $f_j(\theta = 0)$ denote the TCS and the complex scattering amplitude for the jth constituent atom, respectively.

In Eq. (1), one main effect is not considered: a close-packed molecule is not fully transparent for low-energy electrons, and the 'inner' atoms are partially shielded by the 'outer' atoms and contribute less to

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the molecular TCS at lower energies than those at higher energies. The shielding effect, which leads to negative contributions to the TCS in the AR model, is dependent on the molecular geometry. Accounting for the shielding effect, Bobeldijk *et al.*[4] introduced the GAR method to calculate the molecular ICS. We find that the GAR model is also a good approach to obtain the TCS for electron scattering by molecules, particularly for complex molecules at low energies.[9] When the GAR model is applied to the calculation of TCSs, it can be expressed as

$$Q_{GAR}(E) = \frac{1}{3}Q_{\parallel}(E) + \frac{2}{3}Q_{\perp}(E), \qquad (2)$$

where $Q_{\parallel}(E)$ and $Q_{\perp}(E)$ are the TCS for electrons approaching the molecule parallel to the Z axis ($\theta = 0^{\circ}$) and the TCS for an approach perpendicular to the Z axis ($\theta = 90^{\circ}$), respectively. Here the coordinate system is fixed at the centre of the molecule and the Z-axis is attached to the longest axis of the symmetry. For instance, in the case of C_6H_{12}, $Q_{\parallel}(E)$ and $Q_{\perp}(E)$ are equal to $3Q_{CH_2}$ and $6Q_{CH}$, respectively. In the case of molecule C_8H_{16}, $Q_{\parallel}(E)$ and $Q_{\perp}(E)$ are equal to $4Q_{CH_2}$ and $8Q_{CH}$, respectively. More precisely, Q_{CH_2} and Q_{CH} are the TCSs of electron scattering by CH_2 and CH, and are obtained still by the AR model [Eq. (1)].

Calculations have shown that the GAR model is valid at lower energies[9] and overestimates the shielding effect in molecules over the high-energy region, resulting in lower TCS results. In comparison, the AR model is accurate at higher energies[2,3] and disregards the shielding effect at lower energies, resulting in higher TCS results compared with experiments, especially for complex polyatomic molecules. We know that a close-packed molecule is not fully transparent for low-energy electrons, while the transparency will increase with the electron energy. That is to say, when the energy is very low, the inner atoms are shielded partially by the outer atoms, thus the GAR model can give encouraging results, but the AR model not. When the energy is high enough, the molecule is fully transparent and each atom in the molecule can scatter independently. Thus the interaction effect between atoms can be neglected at sufficiently high energies. Hence, the AR model is valid, but the GAR model not. Taking into account these factors, we incorporate the advantages of GAR and AR, and present a new AR formula,

$$Q_{TCS}(E) = Q_{GAR}(E) + A[Q_{AR}(E) - Q_{GAR}(E)], \qquad (3)$$

where A is an empirical fraction, which signifies the contribution of shielded atoms for different molecules at different energies. There are two methods to determine the parameter A: through the theoretical calculation or using an empirical approach. The formal calculation of the contribution of a shielded unit to the molecular TCS is highly complicated by the geometry and composition of the molecule as the energy is varied.[4] Thus, we choose the empirical approach. The suitable expression of the parameter A should correctly reflect that the geometric shielding effect varies with the energy and the target molecular specifications, such as target molecular geometric dimension, total electron number and atom number in a molecule. For determining the parameter A, three factors should be considered. Firstly, when the energy is low enough, since the GAR model is valid, the value of A must satisfy $Q_{TCS}(E) \approx Q_{GAR}(E)$. When the energy is high enough, because the AR model is accurate, the A must satisfy $Q_{TCS}(E) \approx Q_{AR}(E)$. This means that the empirical fraction $A \longrightarrow 0$ if $E \longrightarrow 0$, and $A \longrightarrow 1$ if $E \longrightarrow \infty$. That is to say, the higher the energy is, the less effect geometrical shielding will have on the TCS of the molecule. Secondly, at a given energy, the larger the size of a molecule, the greater the discrepancy between the TCSs calculated according to Eq. (1) and the experimental values. This implies that the larger the volume of a molecule is, the smaller the empirical fraction A should be. The calculations also show that when molecules have the same total number of electrons, the greater the total atomic number in the molecule, the smaller the empirical fraction A. When molecules have the same total atomic number, the more the total number of electrons in the molecule, the smaller the empirical fraction A, too. Thirdly, the calculations show that Eq. (1) can not give the correct shape of the TCS curve. This can be clearly seen in the log-log curves plotted using the TCS results given in Refs. [2,3]. The main problem is that these log-log curves are steeper than those obtained by the corresponding measurements. Figures 1–4 in this study are good examples. Thus, the empirical fraction A relating to E and some molecular parameters should ensure the reasonable shape for TCSs against the experimental data in the whole energy range. Taking into account these factors, we assume that the A over the whole energy range behaves as

$$A = \frac{E}{mndC + E}, \qquad (4)$$

where m and n are the electronic and atomic numbers in the molecule, respectively; d is the target molecular dimension in atomic units, which can be roughly determined by the bond length and bond angle given in Ref. [10]; E is in units of eV and C is a constant considering the reasonable dimension relation, which is equal to $1\,\mathrm{eV}/a_0$.

Is the problem, of which the log-log curves are steeper than those obtained by the experimental findings, brought by the AR model itself, or by the theoretical calculation accuracy for electron-atom scattering? In order to avoid the theoretical calculation suspicion of electron-atom cross sections, here we use the inversion algorithm to determine the atomic cross sections of electron scattering by H, O and C from the

measured TCSs of H_2, O_2 and CO, which come from the Trento laboratory.[11–13] The derived atomic cross sections are tabulated in Table 1.

Table 1. TCSs in units of a_0^2 for electron scattering by atoms H, O and C.

E (eV)	C	H	O
50	23.607	22.429	7.857
100	19.179	18.179	5.250
200	13.714	13.000	3.071
500	7.107	6.893	1.393
1000	3.964	3.929	0.750
2000	2.143	2.107	0.393
5000	0.893	0.893	0.254

Employing the modified AR model, we have calculated the TCSs of electron scattering by two simple molecules (CO_2 and C_2H_2) and two complex ones (C_6H_{12} and C_8H_{16}). The present results are depicted in Figs. 1–4. It should be noted that there have not been any other theoretical investigations about electron scattering by C_6H_{12} and C_8H_{16} due to their complexity.

CO_2 offers a large amount of experimental and theoretical data for comparison. Figure 1 shows the present modified and unmodified AR results together with measurements obtained by Szmytkowski *et al.*[14] at 50–3000 eV, Kwan *et al.*[15] at 100–500 eV, Xing *et al.*[16] at 500–4250 eV, García *et al.*[17] at 400–5000 eV, as well as theoretical results obtained by Zecca *et al.*[7] at 50–5000 eV and Jain *et al.*[18] at 50–5000 eV. For clarity, numbers of results, such as the ones obtained by Joshipura *et al.*[6] at 50–2000 eV, Blanco and García[19] at 50–1000 eV, García and Manero[20] at 500–5000 eV, Jiang *et al.*[21] at 50–1000 eV and Joshipura and Patel[22] at 100–2000 eV, are omitted in Fig. 1. Comparing the present modified AR results with the measurements,[14–17] we find that there is excellent agreement between them at all the overlapping energies, and the problem, of which the TCS log–log curve is steeper than those obtained by the experimental findings, almost disappears. In comparison, the present unmodified AR results are in poor agreement with all the measurements below 200 eV. 1

Figure 2 depicts the present modified and unmodified AR results of electron scattering by C_2H_2 along with the measurements obtained by Ariyasinghe and Powers[23] at 200–1400 eV, Xing *et al.*[24] at 400–2600 eV, Sueoka and Mori[25] at 50–400 eV, as well as the theoretical results obtained by Jain *et al.*[18] at 50–5000 eV and Vinodkumar *et al.*[26] at 50–2000 eV. Similarly to Fig. 1, to avoid congestion in Fig. 2, some results, such as the ones obtained by Jiang *et al.*[27] at 50–1000 eV and Joshipura and Vinodkumar[28] at 50–500 eV, are not included. From Fig. 2, we can see that the present modified AR results are in good agreement with almost all the measurements at all the overlapping energies. However, there are large discrepancies between the present unmodified AR results and all the measurements at lower energies, especially below 300 eV. In addition, the problem, of which the TCS log–log curve is steeper than those obtained by experiments, almost disappears for the present modified AR model.

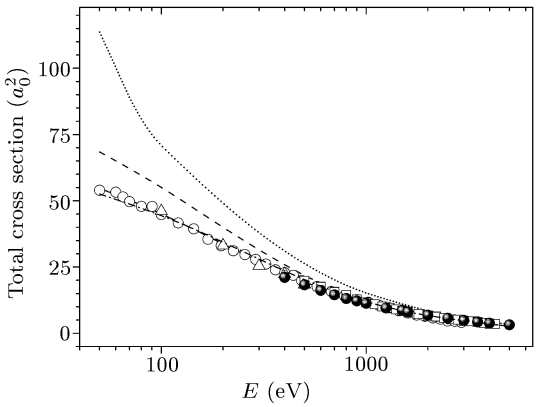

Fig. 1. TCSs for electron–CO_2 scattering. Theoretical results: solid line for the present modified AR calculations; dashed line for the present unmodified AR calculations; dotted line from Jain *et al.*;[18] dash-dotted line from Zecca *et al.*[7] Experimental findings: open circle from Szmytkowski *et al.*;[14] triangle from Kwan *et al.*;[15] square from Xing *et al.*;[16] closed circle from García and Manero[17]

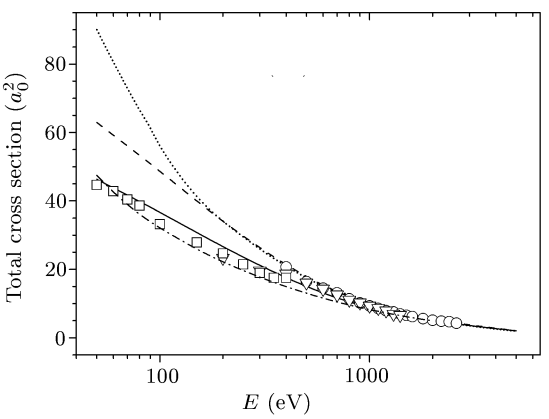

Fig. 2. TCSs for electron–C_2H_2 scattering. Theoretical results: solid line for the present modified AR calculations; dashed line for the present unmodified AR calculations; dotted line from Jain and Baluja;[18] dash-dotted line form Vinodkumar *et al.*[26]) Experimental findings: triangle from Ariyasinghe and Powers;[23] open circle from Xing *et al.*;[24] square from Sueoka and Mori[25]

As far as the TCS of electron scattering by C_6H_{12} is concerned, only group of measurements[29] at 0.4–1000 eV can be found in the literature. The present modified and unmodified AR results as well as the measurements are shown in Fig. 3. We can clearly seen that the present modified AR results are in good accord with the measurements[29] almost at all the overlapping energies. For example, the differences between them are 12.8%, 11.7%, 10.5% and 0.2% at 50, 100, 200 and 1000 eV for C_6H_{12}, respectively. Above 1000 eV, no experiments have been found to date. However, according to the good agreement between

the present calculations and the experimental results at 50–1000 eV, we conclude that the present modified AR results above 1000 eV must be reliable.

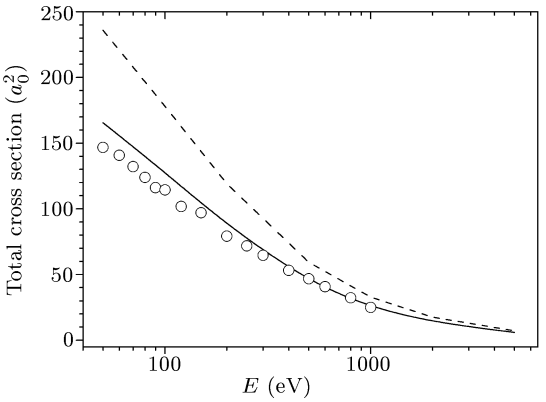

Fig. 3. TCSs for electron–C_6H_{12} scattering. Theoretical results: solid line for the present modified AR calculations; dashed line for the present unmodified AR calculations. Experimental findings: circle from Sueoka *et al.*[29]

In Fig. 4, we report the comparison between the present modified and unmodified AR results and only the group of measurements obtained by Sueoka *et al.*[30] at 50–1000 eV. Good agreement is found between the modified AR results and the measurements above 200 eV. The discrepancy is quickly decreased when the energy increases. As can be seen from Figs. 3 and 4, there is poor agreement between the present unmodified AR results and the measurements almost at all overlapping energies.

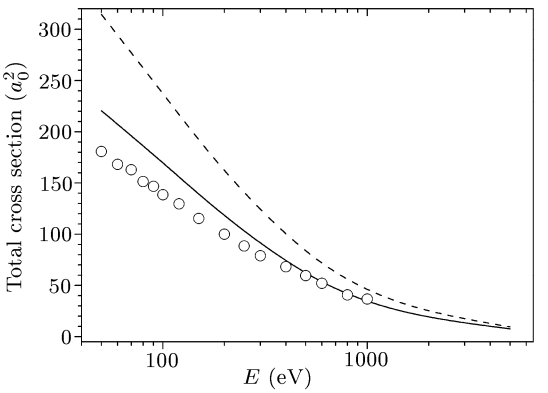

Fig. 4. TCSs for electron-C_8H_{16} scattering. Theoretical results: solid line for the present modified AR calculations; dashed line for the present unmodified AR calculations. Experimental findings: circle from Sueoka *et al.*[30]

Now we briefly summarize the present TCS results of electron scattering by the four molecules. (1) For the present modified AR model, the problem, of which the TCS log–log curve is steeper than those obtained by experiments, almost disappears. However, for the original AR model, the more complex the molecule, the steeper the TCS curve when compared with the corresponding experiments. (2) The present modified AR results agree well with the measurements over a wide energy range. In comparison, the present unmodified AR results show great discrepancies, especially at lower energies.

In the final remarks, we must stress that the accuracy of the present result depends on the experimental errors presenting in the starting data of measured molecular cross section. As the experimental accuracy improves, or as the result of electron scattering from atom is accurately calculated, the present modified AR model should give more reliable TCSs of electron scattering from complex molecules.

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