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Additivity rule for electron scattering on hydrocarbon molecules —considering two different shielding effects*

Sun Jin-Feng(孙金锋)[a)b)], Du Chao-Ling(杜朝玲)[a)†],
Shi De-Heng(施德恒)[a)], and Liu Yu-Fang(刘玉芳)[a)b)]

[a)] *Department of Physics, Henan Normal University, Xinxiang* 453002, *China*

[b)] *China Center of Advanced Science and Technology (World Laboratory), PO Box* 8730, *Beijing* 100080, *China*

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Considering the overlapping among atoms in the molecule and the not full transparency of the molecule by electron, we propose a new formulation of the additivity rule (AR). Here the new AR is employed to calculate the total cross sections (TCS) for electron scattering on hydrocarbon molecules C_2H_2, C_2H_4, C_2H_6, and C_3H_8 over an incident energy range of 10–2000eV. The results are compared with the experimental data and other available theoretical calculations. This gives good agreement.

Keywords: additivity rule, total cross sections, effective cross section coefficient
PACC: 3410, 3480

1. Introduction

In recent years, there has been increased interest in the study of the total cross section (TCS) for electron scattering from atoms and molecules at intermediate energies.[1] The absolute TCSs are needed for understanding the interaction process. They also have important applications in space, plasma, laser, atmospheric and chemistry physics.[2] At the present energy range concerned by us almost all inelastic channels (rotational, vibrational and electronic excitation, ionization process, etc.) are open which makes the conventional close-coupling method[3−5] almost impossible to carry out.

To deal with this problem, many approaches have been proposed and developed. One such approach is the additivity model which ignores anisotropic e–molecule interactions and the molecule problem is reduced to the atomic problem which is easier to handle. At a hundred to a few thousand eV it gave encouraging results,[6−8] but it failed completely at lower energy. Furthermore, on complex molecules (C_2H_4, C_2H_6, C_3H_8) it gave larger discrepancy.[7] This is obviously because of the shielding effect in molecules which exhibits larger contributions for cross sections on complex molecules at the low and intermediate energy region.[9] However, some progress has been made in extending AR validity to lower energy and to more complex molecules. Joshipura and Patel[10] separated e–molecule interaction into short range and long range parts. They modified the AR by including the molecular polarization potential. Jiang *et al*[11,12] considered the molecular geometrical properties and presented an energy-dependent geometry AR (EGAR). In EGAR, the geometrical shielding effect in the molecules was semi-empirically included, but at lower energies its results are still higher than experiments, because the overlapping effect between atoms in $Q_{//}$ and in $Q_{\perp}$ was still not considered[11,12] where $Q_{//}$ and $Q_{\perp}$ refer to the TCSs for an electron approaching the molecule parallel and perpendicular to its axis respectively, which will also result in shielding effect. Zecca *et al*[13] took account of the geometrical screening of the component atoms and presented a geometrical approach to the AR. However, its accuracy depends on the experimental errors.

In this paper, considering the overlapping among atoms in molecule and the not full transparency of

*Project supported by the National Natural Science Foundation of China (Grant No 10174019).
†E-mail address: duchaoling@yahoo.com.cn

the molecule by electron, both of which will result in shielding effect, we propose a new formulation of the AR. The new modified AR along with complex optical potential is employed to calculate the TCS for electron scattering on C_2H_2, C_2H_4, C_2H_6, and C_3H_8 at 10–2000eV. The present results are compared with other available theoretical calculations[7,11] and the experimental data.[1,14–18] This gives encouraging agreement.

2. Theoretical approach

The original AR[6,9,19,20] is based on the assumption in that anisotropic interaction between electron and molecule can be ignored. So the TCS of e–molecule scattering is written as the sum of the TCSs of atoms which is given by

$$\begin{aligned} Q_{\mathrm{MA}} =& \frac{4\pi}{k}\mathrm{Im} f_M(\theta=0) \\ =& \frac{4\pi}{k}\mathrm{Im}\sum_{j=1}^{N} f_j(\theta=0) = \sum_{j=1}^{N} q_T^j(E) \end{aligned} \qquad (1)$$

where $q_T^j(E)$ and f_j are the TCS and the complex scattering amplitude due to the jth atom of the molecule, respectively. But the original AR (we denote it as 100% AR) has not considered two important shielding effects. One is that there always exists overlapping among atoms in a molecule; the other is that the molecule is not fully transparent for the low and intermediate energy electron. So the inner atoms are shielded by the external atoms and do not contribute to the cross sections of the molecule.

Firstly, we consider the overlapping effect among atoms in the molecule. As we know, the distance between two nuclei is always less than the sum of the two atomic radii in molecules. Thus there always exists overlapping or mutual shielding between two atoms. Here we choose the symmetrical axis of the molecule as the Z axis, the centre of one atom as the origin, and then the centre-to-centre distance of the two atoms equals the bond length d, the angle between Z axis and the bond is θ, and r_1, r_2 are the radii of the two atoms, respectively, as labelled in Fig.1. The projection of the two atoms on the XOY plane is given in Fig.2 which has two different cases. In case (1), the second atomic centre is out of the first atom, while in case (2), the second atomic centre is in the first atom. In this paper the bond length and the radii of the atoms are obtained from Ref.[21] and Ref.[22], respectively.

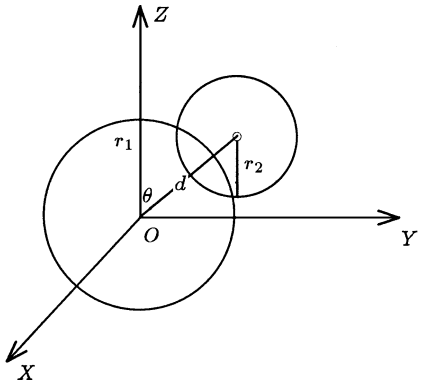


Fig.1. Schematic of electron scattering on diatomic molecule.

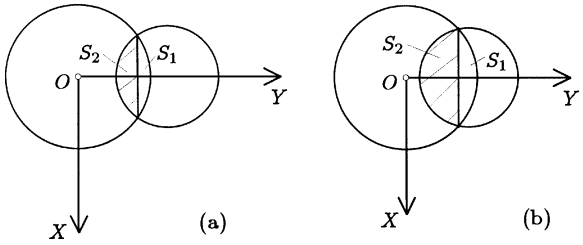


Fig.2. The two cases of the projection on XOY plane of Fig.1. (a) The second atomic centre is out of the first atom. (b) The second atomic centre is in the first atom.

We denote the total projecting area of the two atoms as S_1' and S_2', and the projecting area of the shielding parts of them as S_1 and S_2, respectively. The expressions of S_1 and S_2 are the same for the two cases of Figs.2(a) and 2(b) as follows:

$$S_i = \frac{\arccos(F_i(\chi))}{\pi}\pi r_i^2 - r_i^2\cos(F_i(\chi))\sin(F_i(\chi)), \quad i=1,2, \qquad (2)$$

where $\chi = \cos\theta$ and

$$F_i(\chi) = \frac{r_i^2 - r_j^2}{2dr_i\sqrt{1-\chi^2}} + \frac{d}{2r_i}\sqrt{1-\chi^2}, \quad i,j=1,2, \quad i\neq j. \qquad (3)$$

However, in real experiments, the molecules are randomly oriented and the observed cross sections are averaged over different relative beam-to-molecule orientations. Considering this, we define the effective area coefficient as $C_i = \left(1 - \frac{S_i}{S_i'}\right)$ $(i=1,2)$ and average it over the solid angle. Then we get the average effective cross section coefficients of the two atoms:

$$\begin{aligned} \overline{C}_i(\chi) =& k - (1-k)h(r_i - r_j) - \frac{1}{\pi}\int_0^k (\arccos F_i(\chi) \\ & - F_i(\chi)\sqrt{1-F_i^2(\chi)})\mathrm{d}\chi, \end{aligned}$$

$$i, j = 1, 2, \quad i \neq j, \tag{4}$$

where h is the Heaviside function, and

$$k = \sqrt{1 - \left(\frac{r_1 - r_2}{d}\right)^2}. \tag{5}$$

We find that the form of $\overline{C}_i (i = 1, 2)$ in Eq.(4) is the same as Eq.(16) in Ref.[13], but there r_1, r_2 are unknown and they are obtained from the experimental data which depend on the experimental errors. It is also necessary to point out that when the bond length d is larger than or equal to the sum of the two atomic radii we choose $\overline{C}_i (i = 1, 2)$ as 1.

As far as polyatomic molecules are concerned, we define the final effective cross section coefficients $\overline{C}_j$ for every atom. Here $\overline{C}_j$ equals the average value of the ratio (the unshielded parts to the total projecting area of the atom) over the solid angle. So for the TCS of the e–molecule scattering, Eq.(1) can be rewritten as

$$Q_{\mathrm{MA}} = \sum_{j=1}^{N} \overline{C}_j q_T^j. \tag{6}$$

Secondly, we consider the not full transparency effect. For this we adopt the method proposed by Jiang *et al*[11,12] who have discussed this effect in detail, and accordingly we can modify Eq.(1) into

$$Q_{\mathrm{MG}} = \frac{1}{3} Q_{//} + \frac{2}{3} Q_{\perp}, \tag{7}$$

where $Q_{//}$ and $Q_{\perp}$ are the TCS for the electron approaching the molecule parallel and perpendicular to the Z axis, respectively. But there $Q_{//}$ and $Q_{\perp}$ have still not incorporated the overlapping effect between two atoms in the molecule which means that $Q_{//}$ and $Q_{\perp}$ have the form of Eq.(4). So we have the final TCS as follows:

$$Q_{\mathrm{MT}} = \frac{1}{3} \sum_{j=1}^{m} \overline{C}_j q_T^j + \frac{2}{3} \sum_{j=1}^{n} \overline{C}_j q_T^j, \tag{8}$$

where m, n are the total number of atoms in the unit of $Q_{//}$ and $Q_{\perp}$, respectively.

For the present investigation the $q_T^j(E)$ in Eq.(8) is obtained by solving the radial equation with the method of partial waves, which is presented in detail in Ref.[20]. The choice of $Q_{//}$ and $Q_{\perp}$ for C_2H_2, C_2H_4 and C_2H_6 is the same as in Ref.[11]; for C_3H_8, we choose $Q_{//}$ as $Q_{C_2H_5}$, and $Q_{\perp}$ as $Q_{C_3H_8}$, respectively, which is different from Refs.[11,12].

3. Results and comparison

In this paper, employing the new formulation of Eq.(8) along with the optical potential model we have obtained the TCS for e–molecule (C_2H_2, C_2H_4, C_2H_6 and C_3H_8) scattering at 10–2000eV. The present results are compared with other available theoretical calculations[7,11] and experimental data,[1,14–18] shown in Figs.3–6.

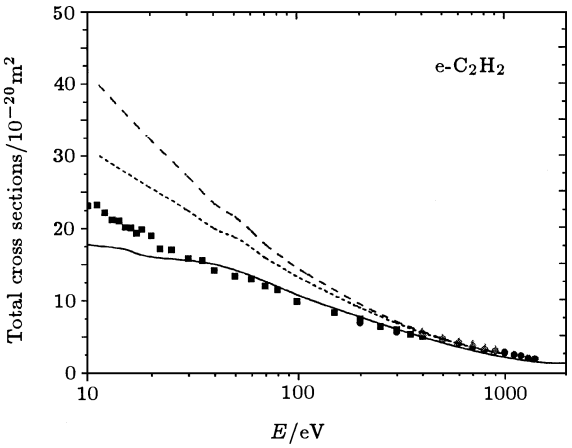


Fig.3. Total cross sections for e–C_2H_2 scattering. Solid curve, present results; dashed curve, the 100% AR results;[7] short dashed curve, the EGAR results.[12] The experimental data: ■, Ref.[17]; ●, Ref.[1]; ▲, Ref.[18].

For the e–C_2H_2 scattering, the three groups of measurements of Sueoka and Mori,[17] Xing *et al*,[18] and Ariyasinghe and Powers [1] are shown in Fig.3. We find that the present results are lower but much closer to the experimental data[1,17] than the 100% AR and EGAR results at $E \leq$300eV. They are in good agreement with Xing's measurements at whole overlapping energy ($E \geq$400eV). Yet the present results are lower than the experimental data at $E \leq$20eV. The discrepancy may lie in the C≡C bonding in the C_2H_2 molecule which presents a large contribution for the TCS. We also note that at higher energies the present results are lower than the experimental data, which may come from the fact that the overlapping shielding effect proposed here is only an averaging effect, which will underestimate the TCS with the increasing of the energies, especially at high energy.

In Figs.4 and 5 we present the comparison between the present calculation and experimental data and other calculations for e–C_2H_4 and e–C_2H_6 scattering. This shows that the present results merge well with the various experimental data at the whole energies concerned here. The 100% AR and EGAR results exceed the present results and experimental data at $E \leq$60 eV and give poorer results compared with

the present method. We also notice that the present results are a little lower than the experimental data at high energies (at around 1900eV). This may also come from the fact that the effective cross section coefficients $\overline{C}_j$ proposed by us here is only an average effect which overestimates the shielding effect at higher energies.

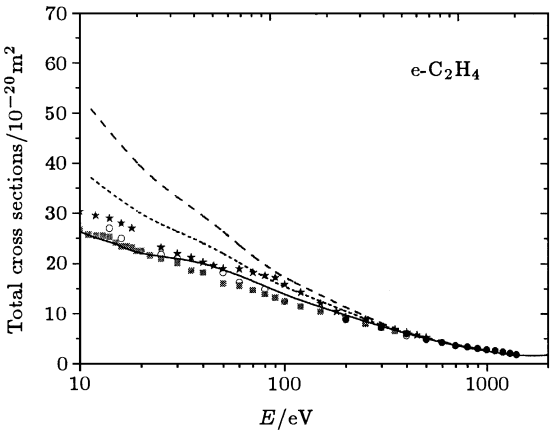


Fig.4. As in Fig.3 but for the C_2H_4 case. The experimental data: ■, Ref.[16]; ●, Ref.[1]; ○, Ref.[14]; ⋆, Ref.[15].

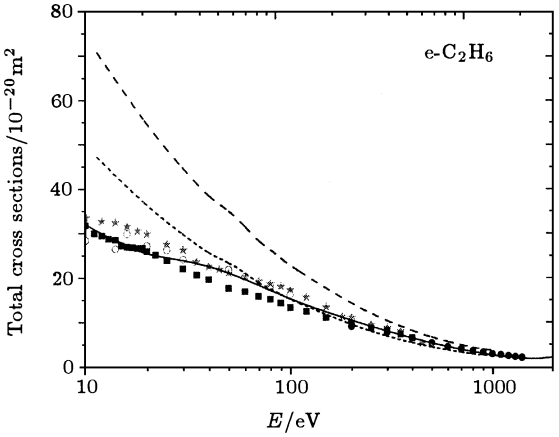


Fig.5. As in Fig.3 but for the C_2H_6case. The experimental data: ■, Ref.[16]; ●, Ref.[1]; ○, Ref.[14]; ⋆, Ref.[15].

In Fig.6 we report the total cross section of e–C_3H_8 scattering. It is found that at $E \geq$100eV the present calculation is in good agreement with the experimental data and the EGAR results, while for $E \leq$60eV the present results are closer to the experimental data than EGAR results. But they are in good agreement with experiments with the energy increasing. Comparing the three theoretical calculations we come to the conclusion that the contribution of the shielding effect to the TCS is larger for the low and intermediate energy range, particularly for more complex polyatomic molecules (C_3H_8).

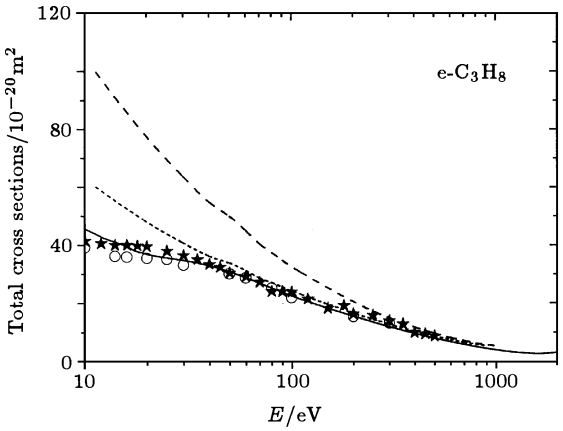


Fig.6. As in Fig.3 but for the C_3H_8 case. The experimental data: ⋆, Ref.[15]; ○, Ref.[14].

4. Conclusions

A new formulation of the modified AR has been proposed here with the purpose of predicting the TCS of electron scattering from polyatomic molecules at intermediate energy regions. Considering the overlapping among atoms in the molecule and the not full transparency of the molecule by electron, the present approach gives better results for the TCS on hydrocarbon molecules C_2H_2, C_2H_4, C_2H_6, and C_3H_8 than the 100% AR and EGAR theories. It also gives an attempt on the TCS of electron scattering from complex molecules which is valuable for further research. But there still exists some discrepancy between our results and experimental measurements, since the $\overline{C}_j$ in Eq.(8) proposed by us here is only an average effect which will overestimate the shielding effect at high energies. How to include the multiple scattering in the theoretical calculation is also another problem which still requires research. More experiments are also expected to be performed at high energies, especially on complex molecules.

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