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A modification potential method of calculating total cross sections of electrons scattering from complex molecules C_2H_6, C_2F_6, C_6H_6 and C_6F_6 at 100 eV–5000 eV*

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A complex optical model potential modified by incorporating the concept of bonded atom, which takes into consideration the overlapping effect of electron clouds between two atoms in a molecule, is first employed to calculate the total cross sections for electrons scattering from such complex molecules as C_2H_6, C_2F_6, C_6H_6 and C_6F_6 using the additivity rule model at Hartree–Fock level over the energy range from 100 eV to 5000 eV. The total cross sections are quantitatively compared with those obtained by experiments wherever available, and they are in good agreement with each other over a wide energy range. It is shown that the modified potential together with the additivity rule model is completely suitable for the calculation of total cross sections of electrons scattering from such complex molecules as C_2H_6, C_2F_6, C_6H_6 and C_6F_6 above 200 eV–300 eV.

Keywords: total cross section, electrons scattering, additivity rule, atomic and molecular collision
PACC: 3410

1. Introduction

In recent years, much attention has been paid experimentally to the total cross sections (TCSs) for electrons scattering from molecules over the intermediate- and high-energy ranges because the TCSs for electron–molecule scatterings have important applications in several fields of physics, such as gaseous lasers, astrophysics, plasma physics, atmospheric physics and chemical physics. However, electron–molecule scattering presents a more complex problem than electron–atom scattering due to its multicentred nature, the lack of a symmetric centre, and its nuclear motion, especially for such complex molecules as C_2H_6, C_2F_6, C_6H_6 and C_6F_6. Though many new approaches, such as the complex Kohn variational method,[1] the spherical complex optical potential (SCOP) method,[2] the Born-closure Schwinger variational method,[3] the distorted-wave approximation,[4] the Schwinger variational iterative method[5] and the R-matrix method,[6] have been proposed and developed recently, few of them can be used to calculate accurately the TCSs of electrons scattering from such complex molecules as C_2H_6, C_2F_6, C_6H_6 and C_6F_6 over the intermediate- and high-energy ranges. This is because, on the one hand, acquiring the accurate single-centre molecular wavefunction is very difficult due to their multicentred nature and nuclear motion; on the other hand, over this energy range, the conventional close-coupling theory for electrons scattering from those complex molecules is almost impossible to be established due to almost all inelastic channels (rotational, vibrational, and electronic excitation and ionization processes, etc) being opened. So, it is not surprising that many previous TCS calculations for electron–molecule scattering were restricted to simple molecules and low energies.

In order to avoid using the single-centre molecular wavefunction in the TCS calculation process of electron–molecule scattering, recently, a fairly sim-

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ple approach, namely the additivity rule (AR) model, wherein a molecular cross section is an incoherent sum of the cross sections of the constituent atoms, was put forward. The model was first employed by Raj[7] to obtain the TCSs for electrons scattering from several small molecules at 100 eV–500 eV. Lately, the model has been widely used to calculate the TCSs, the momentum transfer cross sections and the elastic integral cross sections.[8−10] The model can reproduce quantitatively the TCS experimental findings of electrons scattering from simple molecules at higher energies, but large differences[7−10] can be seen between the calculated results and the experimental ones for complex molecules or at lower energies.

Two methods can improve the agreement between theories and experiments. One is to establish more accurate theoretical models which can be used to calculate the TCSs over the intermediate- and high-energy ranges, but we must obtain an accurate single-centre molecular wavefunction. It is very difficult for such complex molecules as C_2H_6, C_2F_6, C_6H_6 and C_6F_6. The other is to continue using the simple AR model, but we must modify the complex optical model potential so as to obtain the accurate TCS values at lower energies. It is obvious that the latter is much easier than the former.

To date, researchers have proposed various modification methods[11−15] in the complex optical model potential. Taking into consideration that the present widely-used absorption potential[16] overestimates TCS values, Raj and Kumar[11] have presented a modification factor $m = 1/k$, but they calculated only the differential cross sections of electrons scattering from O_2. Baluja and Jain[12] have presented a modification factor $m = 1/k^{1/2}r$ and replaced the energy gap (Δ)[16] between the target ground state and the lowest excited electronic state with the positronium formation energy, but great TCS differences between theories and experiments are still seen at lower energies for relatively large molecules. Taking into account the polarization of target molecule, Jain[13] has employed the polarized electron density in the absorption potential. Meanwhile, Jain,[13] Raizada and Baluja[14] and Baluja *et al*[15] have replaced the Δ value with the ionization potential of the atom. However, TCS calculations on only several molecules[11−15] have difficulty in expressing general behaviours.

This paper presents the complex optical model potential modified by the concept of bonded atom (modified potential), which takes into consideration the overlapping effect of electron clouds between two atoms. The modified potential is first employed to calculate the TCSs of electrons scattering from such relatively complex molecules as C_2H_6, C_2F_6, C_6H_6 and C_6F_6 using the AR model at Hartree–Fock level over the energy range from 100 eV to 5000 eV. In the next section, we describe in detail the modified potential and the AR model. In Section 3, we present the TCS calculations and discussion for the target molecules and compare them with measurements wherever available. Final remarks are made in Section 4. Atomic units are employed throughout this paper unless otherwise specified.

2. Theory and method

In the AR model, the TCS $Q_{\rm T}(E)$ of electrons scattering from a molecule containing M atoms is given by

$$\begin{aligned} Q_{\rm T}(E) =& \frac{4\pi}{k}{\rm Im}F_{\rm m}(\theta=0) \\ \approx& \frac{4\pi}{k}{\rm Im}\sum_{j=1}^{M} f_j(\theta=0) = \sum_{j=1}^{M} q_{\rm T}^j(E), \end{aligned} \quad (1)$$

where $F_{\rm m}\,(\theta = 0)$ is the electron–molecule scattering amplitude for the forward direction; $q_{\rm T}^j(E)$ and $f_j(\theta = 0)$ are the TCS and the complex scattering amplitude for the jth constituent atom, respectively.

In the present method, the potential of a constituent atom in a molecule can be expressed as follows:

$$V_{\rm opt}(r) = V_{\rm s}(r) + V_{\rm p}(r) + V_{\rm e}(r) + {\rm i}V_{\rm a}(r), \quad (2)$$

where $V_{\rm opt}$ incorporates all the important physical effects. The details of the repulsive static potential $V_{\rm s}(r)$,[17] the exchange potential $V_{\rm e}(r)$,[18] the polarization potential $V_{\rm p}(r)$[19] and the absorption potential $V_{\alpha}(r)$[16] could be found in the publications.[16−19] Here, it is noted that we let Δ in the absorption potential $V_{\alpha}(r)$ equal the ionization potential of the atom, but not equal the energy gap between the target ground state and the lowest excited electronic state.[16]

In Eq.(1), the TCS of electron–molecule scattering simply equals the sum of the TCSs of electrons scattering from each constituent atom. Obviously, no molecular geometry is taken into consideration. Thus large differences are seen between theories and experiments over a wide energy range (see dashed lines in Figs.1–4) if we directly employ Eq.(2) to calculate the

TCSs for electron–molecule scattering. The reason is that many complicated interactions, such as the valence bond-distortion effect, the shielding effect and the atomic overlapping effect, exist in the scattering process, especially for such complex molecules as C_2H_6, C_2F_6, C_6H_6 and C_6F_6.

Here, we take into consideration only the atomic overlapping effect in molecules. Atomic overlapping is substantially the overlapping of electron clouds between atoms. Atoms in a molecule are all bonded atoms, which greatly differ from the free ones. The reason is that the electron clouds overlapped between atoms exhibit a weaker impact than the corresponding ones of free atoms in the electron–molecule scattering process due to various reasons. That is to say, virtual charge density from a bonded atom should be smaller than that from a free atom. According to this, we may introduce the concept of bonded atom and modify the virtual charge density of bonded one as follows:

$$\rho'(r) = f \cdot \rho(r), \tag{3}$$

where f is a modification factor, which reflects the overlapping degree of electron clouds between bonded atoms. $\rho(r)$ and $\rho'(r)$ are the real charge density and the virtual charge density of a bonded atom, respectively. In order to obtain the factor f, the following three points are considered.

1. The potential described by Eq.(2) overestimates the TCSs of electron–molecule scattering at 100 eV–5000 eV using the AR model (See dashed lines in Figs.1–4), especially at lower energies. Thus, to obtain accurate TCSs, the effect of the potential described by Eq.(2) should be weakened.

2. Numerous calculations using Eq.(2) show that the more the electron number of the outmost shell in the constituent atom is, the more the TCS difference between theory and experiment is. When we investigate the target molecules resembling each other in structure, calculations also show the results similar to the total electron number of the constituent atom. It indicates that the modification should have relations with the electron number of the outmost shell and the total electron number of the constituent atom.

3. The atoms in molecules are bonded whereas the free ones not. Thus there exists the overlapping effect of electron clouds between two atoms in a molecule, but it does not exist between the free ones. The overlapping degree of electron clouds may have relations with the internuclear distance between the two bonded atoms (i.e. the bond length), and the radius of the constituent atom. Thus the modification should have relations with the bond length and the radius of the constituent atom, too.

Keeping these in mind, a number of f factors are tried and the best agreement between theories and experiments is obtained for

$$f = 1 - \frac{r}{r_1 + r_2} \times \frac{Z}{N}, \tag{4}$$

where r is the bond length, r_1 and r_2 are the radii of the two bonded atoms, respectively. r, r_1 and r_2 values in the target molecules are taken from Ref.[20]. Z and N are the number of electrons in the outmost shell and the total number of electrons in the atom, respectively. So, Eq.(2) can be modified as

$$V_{\rm opt}(r) = f \cdot V_{\rm s}(r) + V_{\rm p}(r) + V_{\rm e}(r) + {\rm i} f \cdot V_{\rm a}(r), \tag{5}$$

with

$$V_{\rm e} = -\frac{1}{4}\{\sqrt{[k^2 - 2(f \cdot V_{\rm s} + V_{\rm p})]^2 + 16\pi f \cdot \rho(r)} - [k^2 - 2(f \cdot V_{\rm s} + V_{\rm p})]\}. \tag{6}$$

The $q_{\rm T}^j$ in Eq.(1) is obtained by using the method of partial waves,

$$\begin{aligned} q_{\rm T}^j(E) =& q_{\rm e}^j(E) + q_{\rm a}^j(E) \\ =& \frac{\pi}{k^2} \cdot \sum_{l=0}^{l_{\max}} (2l+1)[|1 - S_l^j|^2 + (1 - |S_l^j|^2)], \end{aligned} \tag{7}$$

where $q_{\rm e}^j(E)$ and $q_{\rm a}^j(E)$ are elastic and absorption cross sections of the jth constituent atom, respectively. S_l^j is the lth complex scattering matrix element of the jth constituent atom. To obtain S_l^j, we solve the following radial equation:

$$\left(\frac{{\rm d}^2}{{\rm d}r^2} + k^2 - V_{\rm opt} - \frac{l(l+1)}{r^2}\right) u_l(r) = 0, \tag{8}$$

under the boundary condition $r \to \infty$,

$$u_l(r) \sim kr[j_l(kr) - {\rm i} n_l(kr)] + S_l kr[j_l(kr) + {\rm i} n_l(kr)], \tag{9}$$

where j_l and n_l are spherical Bessel and Neumann functions, respectively. The limit $l_{\max}$ is taken to be large enough to generate the higher partial-wave contributions until a convergence of less than 0.5% is again achieved in the TCSs.

3. Calculations and discussion

Using the AR model combined with the modified and unmodified potentials, we calculate the TCSs of electrons scattering from several simple molecules.

And the results show that the modified calculations are in much better agreement with those measurements than the unmodified ones over a wide energy range. It is proved that the expression f is reasonable for the TCS calculations of electrons scattering from simple molecules. In this paper, we first calculate the TCSs for electrons scattering from such complex molecules as C_2H_6, C_2F_6, C_6H_6 and C_6F_6 at 100 eV–5000 eV. The modified and unmodified calculations together with the measurements in Refs.[21–31] are given in Figs.1–4, respectively.

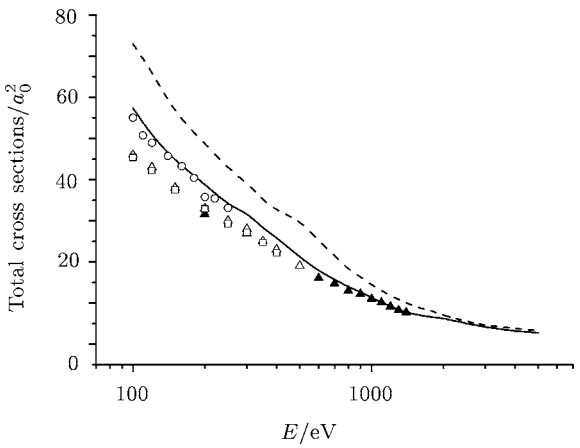


Fig.1. Total cross sections for e-C_2H_6 scattering. Theories: solid line for present modified calculations; dashed line for present unmodified calculations. Experiments: circle for Szmytkowski and Krzysztofowicz;[21] open triangle for Nishimura and Tawara;[22] square for Sueoka;[29] solid triangle for Ariyasinghe and Powers.[24]

Now we start by discussing the TCSs for e-C_2H_6 scattering. Figure 1 shows present modified and unmodified calculations together with the measurements obtained by Szmytkowski and Krzysztofowicz[21] at 100 eV–250 eV, Nishimura and Tawara[22] at 100 eV–500 eV, Sueoka and Mori[23] at 100 eV–400 eV and Ariyasinghe and Powers[24] at 200 eV–1400 eV. Obviously, the modified calculations are in excellent agreement with the measurements obtained by Szmytkowski and Krzysztofowicz[21] over the whole overlapping energy range, and also in good agreement with the measurements obtained by Nishimura and Tawara,[22] Sueoka and Mori[23] and Ariyasinghe *et al*[24] above 200 eV–250 eV. For example, The differences between the modified calculations and the measurements obtained by Sueoka *et al*[23] are about 18.3% at 200 eV and 15.3% at 250 eV, respectively. And the deviations between the modified calculations and the measurements obtained by Ariyasinghe and Powers[24] are about 23.3% at 200 eV and 18.9% at 300 eV, respectively, too. And the differences between present modified calculations and the measurements[22–24] decrease quickly as the energy increases.

Figure 2 shows TCSs for electrons scattering from C_2F_6 together with the measurements obtained by Szmytkowski *et al*[25] at 100 eV–250 eV, Sueoka *et al*[26] at 100 eV–600 eV and Ariyasinghe[27] at 100 eV–1500 eV. At intermediate and high energies, no other theoretical calculations about e-C_2F_6 scattering can be found in the publications to our knowledge. From Fig.2, we can easily see that the modified calculations are in good agreement with the measurements obtained by Sueoka *et al*,[26] Ariyasinghe[27] at above 200 eV–300 eV and Szmytkowski *et al*[25] over the whole overlapping energy range, but are in slightly poor agreement with the measurements obtained by Sueoka *et al*[26] and Ariyasinghe[27] below 200 eV.

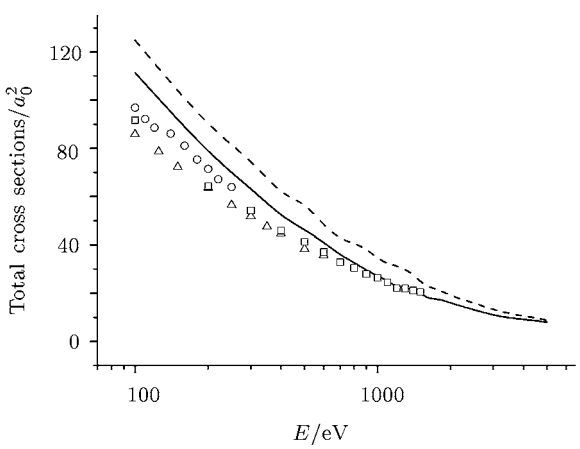


Fig.2. Total cross sections for e-C_2F_6 scattering. Theories: solid line for present modified calculations; dashed line for present unmodified calculations. Experiments: circle for Szmytkowski *et al*;[25] open triangle for Sueoka *et al*;[26] open square for Ariyasinghe.[27]

As shown in Figs.1 and 2, the modified calculations are obviously closer to the measurements than the unmodified ones over a wide energy range, especially below about 800 eV–1000 eV. The reason is that the bonded atom substantially contributes less molecular TCS than the free one. The modified potential takes into consideration the overlapping effect of electron clouds between two atoms in a molecule, which reflects the overlapping degree of electron clouds of one atom with the others, whereas the unmodified potential does not. That is to say, for the AR model with the unmodified potential, the overlapped clouds

in polyatomic molecules, especially in complex polyatomic molecules, are still used to calculate the TCS of the constituent atom, but in fact they have less contributions to molecular TCS. So, the unmodified potential gives poorest calculations. Similar analyses are suitable for the following e-C_6H_6 and e-C_6F_6 scatterings.

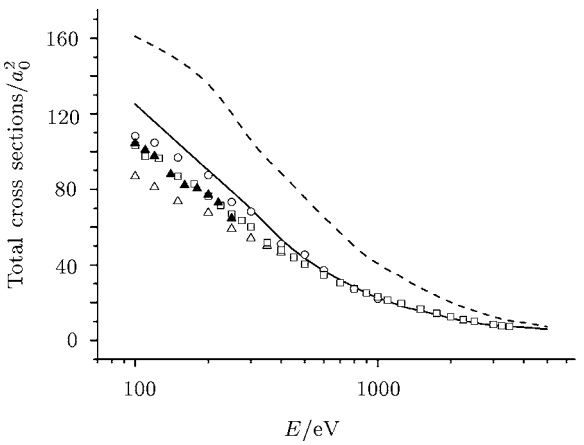


Fig.3. Total cross sections for e-C_6H_6 scattering. Theories: solid line for present modified calculations; dashed line for present unmodified calculations. Experiments: circle for Makochekanwa *et al*;[28] open triangle for Sueoka;[29] open square for Trento group;[30] solid triangle for Gdansk group.[30]

Figures 3 and 4 show the TCSs for electrons scattering from C_6H_6 and C_6F_6. From Fig.3, we can easily see that the modified calculations are in good agreement with the measurements obtained by Makochekanwa *et al*[28] above 200 eV and Trento group[29] above 250 eV, but are in slightly poor agreement with the measurements obtained by Gdansk group[30] and Sueoka[29] at lower energies. Very obviously, there still exist large differences between the unmodified calculations and the above-mentioned results over a wide energy range. From Fig.4, we can also see that the modified calculations are in good accord only with the two groups of measurements[28,31] at higher energies, but in poor agreement with them at lower energies. It should be noted that there are great differences between the measurements obtained by Makochekanwa *et al*[28] and the ones obtained by Kasperski *et al.*[31] Due to C_6F_6 being a very complex molecule, no other theoretical calculations about it can be found in the literature at intermediate and high energies to our knowledge. So, its further comparison cannot be made. However, as our modified calculations about e-C_2H_6, e-C_2F_6 and e-C_6H_6 scatterings are in good agreement with the measurements[20−30] above 200 eV–300 eV, we can conclude that our TCS calculations about e-C_6F_6 scatterings at intermediate and high energies are surely reasonable.

At lower energies, as seen from Figs.1 and 4, the modified calculations are still higher than all the measurements because we have ignored the multicentre scattering, the shielding effect and the valence-bond distortion effect[4] in the present investigation. At lower energies, the de Broglie wavelength associated with the incident particle will become comparable with or larger than the bond length of the molecule, which will increase the possibility of multiple scattering effects. It is expected that the inclusion of multiple scattering effects at lower energies will reduce the TCSs by a significant amount.[32] In addition, a close-packed molecule is not fully transparent for low energy electrons. So, though we have taken into consideration the overlapping effect of electron clouds between two atoms, TCS differences still exist at lower energies between present calculations and the experimental findings.

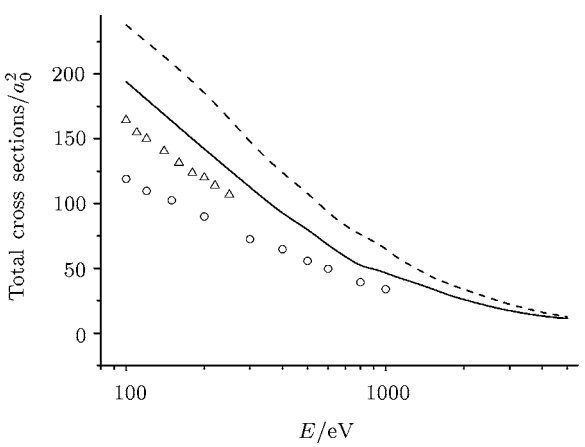


Fig.4. Total cross sections for e-C_6F_6 scattering. Theories: solid line for present modified calculations; dashed line for present unmodified calculations. Experiments: circle for Makochekanwa *et al*;[28] open triangle for Kasperski *et al.*[31]

With the energy increasing, the wavelength of the incident electrons gradually becomes small compared with the bond length of the molecule. Then the valence-bond distortion effect and the shielding effect contribute to the TCS less and less. Therefore, the higher the energy is, the better the modified calculation is. And above 200 eV–300 eV, the contribution of molecular structure and shielding effect to the TCSs may be neglected. So, the AR model combined with the modified potential can attain good calculations, as verified in Figs.1 and 4.

4. Conclusion

The AR model neglects the molecular geometry and its nuclear motion, so the electron–molecule scattering reduces to the electron-atom scattering problem. The modified calculations are encouraging, even though we ignore the molecular geometry and its nuclear motion. It is shown that the AR model together with the complex optical model potential modified by taking into consideration the overlapping effect of electron clouds between two atoms in a molecule can be successfully used to calculate the TCSs of electrons scattering from such complex molecules as C_2H_6, C_2F_6, C_6H_6 and C_6F_6 over a wide energy range.

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