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Total cross sections for scattering of electrons from O_2, H_2O, H_2, O_3, CO and CO_2 at 100–2000eV*

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A complex optical model potential rewritten by the concept of bonded atom, which considers the overlap of electron clouds, is employed to calculate the total cross sections for electron scattering from several simple molecules (O_2, H_2O, H_2, O_3, CO and CO_2) consisting of C, H and O atoms in an incident energy range of 100–2000eV by the use of the additivity rule at Hartree–Fock level. In the study, the complex optical potential composed of static, exchange, correlation polarization plus absorption contributions firstly uses the bonded-atom concept. The quantitative molecular total cross section results are compared with experimental data and with the other calculations wherever available and good agreement is obtained. It is shown that the additivity rule along with the complex optical model potential rewritten by the concept of bonded atom can be used successfully to calculate the total cross section of electron–molecule scattering above 100eV, whereas the rule together with the complex optical model potential not rewritten by the concept of bonded atom is only successfully used above 300–500eV. So, the introduction of the bonded-atom concept in the complex optical potential can improve the accuracy of the total cross section calculations.

Keywords: atomic and molecular collision, additivity rule, bonded atom, total cross section
PACC: 3480, 3440

1. Introduction

In recent years there has been a renewed interest in the calculation of total cross sections (TCS) for scattering of electrons from several simple molecules (O_2, H_2O, H_2, O_3, CO and CO_2) consisting of C, H and O atoms. The reason is threefold. Firstly, the availability of new experimental results of TCSs (especially at higher incident energies) allows a fairly detailed comparison of theories and experiments; secondly, the need for TCSs has become apparent, since the applicability of these theories should be tested against experimental measurements over a wide range of incident energy; and thirdly, calculations can be used for a variety of plasma-assisted material processing, industrial production, military and aeronautical fields, and the like.

However, it is well known that electron–molecule scattering presents a more complex problem than the corresponding electron–atom scattering due to the multicentre nature, the lack of a centre of symmetry (in the case of polyatomic and heteronuclear molecules) and its nuclear motion. Hence, for electron–molecule scattering, many different approaches have been proposed.[1,2] In the intermediate and high energy regions, acquiring a molecular wavefunction is very difficult, as almost all inelastic channels (rotational, vibrational, electronic excitation and ionization process, etc.) are open, and a conventional close-coupling theory for electron–molecule scattering is an arduous task and almost impossible to carry out. It is, therefore, not surprising that many previous calculations on the TCSs for electron–molecule scattering have been restricted to the low-energy region.

A fairly simple approach, namely the additivity rule, wherein a molecular TCS is an incoherent sum of TCSs of the constituent atoms, was employed successfully by Raj[3] to obtain the elastic cross sec-

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tions (the momentum transfer cross section, the integral elastic cross section) for electron scattering by a sample of four molecules (O_2, CO, CO_2 and CF_4) at 100–500eV. Lately, Joshipura and Patel [4] also employed the additivity rule and complex optical potential to obtain the TCS for electron scattering with four molecules (O_2, N_2, CO and CO_2) at 100–1000eV. Subsequently, many authors [5,6] made calculations on the TCSs for a variety of molecules. We [7−11] also gave the TCSs for electron scattering by a few molecules through the use of the additivity rule and complex optical potential below 1000eV. However, large differences are noted between theory and experiments at the lower energy range (100–500eV). Calculations have seldom been performed for incident energy above 1000eV due to solution divergence of the differential equation. So, in order to acquire more accurate calculations, many authors gave various correlation methods. Using the spherical complex optical potential (SCOP) and molecular wavefunction, Jain and Baluja [12] performed TCS calculations on many e–molecule scattering systems. Because acquiring the molecular wavefunction is very difficult, this method is limited to a considerable degree. Considering the molecular geometrical properties, Jiang *et al* [13] presented an energy-independent geometry AR (EGAR), but compared with the experimental data, the results are still not very good at lower energies.

In this paper, the complex optical model potential rewritten by the concept of bonded atom, which considers the overlap of electron clouds, is employed to calculate the TCSs for electron scattering from several simple molecules (O_2, H_2O, H_2, O_3, CO and CO_2) consisting of C, H and O atoms in an incident energy range of 100–2000eV by the use of the additivity rule at Roothaan–Hartree–Fock level. In the next section we describe in detail the complex optical model potential rewritten by the concept of bonded atom, which considers the overlap of electron clouds, and the additivity rule. In Sec.3 we present the calculations and discussions for the TCSs on these molecules at 100–2000eV based on the additivity rule, and compare them with the available experimental data and other theoretical results. Concluding remarks are made in Sec.4. We employ atomic units throughout this paper.

2. Theory and method

The TCS of the additivity rule [1] for a molecule containing N atoms is given by

$$\begin{aligned} Q_T(E) =& \frac{4\pi}{k}\mathrm{Im}F_m(\theta) \\ \approx& \frac{4\pi}{k}\mathrm{Im}\sum_{j=1}^{N} f_j(\theta=0) = \sum_{j=1}^{N} q_T^j(E), \end{aligned} \quad (1)$$

where $F_m(\theta)$ represents the sum of complex scattering amplitude for constituents, E is the energy of the incident electron and θ is the incident angle of electron, $q_T^j(E)$ and f_j are the TCS due to the jth atom of the molecule and complex scattering amplitude for the constituent atoms of the molecule, respectively. Here it is obvious that no molecular geometry is involved in the additivity rule of the TCS. Thus, the molecular scattering problem is reduced to the atomic problem which is easier to handle.

$q_T^j(E)$ in Eq.(1) is obtained by the method of partial waves

$$\begin{aligned} q_T^j(E) =& q_{\mathrm{e}}^j(E) + q_{\mathrm{a}}^j(E) \\ =& \frac{\pi}{k^2}\sum_{l=0}^{l_{\mathrm{MAX}}}(2l+1) \\ & \times [|1 - S_l^j|^2 + (1 - |S_l^j|^2)], \end{aligned} \quad (2)$$

where $q_{\mathrm{e}}^j(E)$ and $q_{\mathrm{a}}^j(E)$ are elastic and absorption cross sections respectively. S_l^j is the lth complex scattering matrix element of jth atom, which is related to the partial wave phase shift as $S_l^j = \exp(2\mathrm{i}\delta_{ij})$. To obtain S_l^j, we solve the following radial equation:

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} + k^2 - V_{\mathrm{opt}} - \frac{l(l+1)}{r^2}\right) u_l(r) = 0 \quad (3)$$

under the boundary condition ($r \sim \infty$)

$$\begin{aligned} u_l(kr) \sim & kr[j_l(kr) - \mathrm{i}n_l(kr)] \\ & + S_l kr[j_l(kr) + \mathrm{i}n_l(kr)], \end{aligned} \quad (4)$$

where r is the distance between incident electron and the scattering centre. $j_l(kr)$ and n_l (kr) are spherical Bessel and Neumann functions respectively. The limit l is taken large enough to generate the higher partial-wave contributions until again a convergence of less than 0.5% is achieved in the TCSs. V_{opt} is the appropriate complex optical model potential which incorporates all the important physical effects.

In the present investigation the V_{opt} of the atoms of a molecule in Eq.(3) is given by

$$V_{\mathrm{opt}}(r) = V_{\mathrm{s}}(r) + V_{\mathrm{p}}(r) + V_{\mathrm{e}}(r) + \mathrm{i}V_{\mathrm{a}}(r). \quad (5)$$

In detail, the static potential $V_{\mathrm{s}}(r)$ for an e–atom system is calculated by using the atomic charge density,

determined from the well-known Roothaan–Hartree–Fock atomic wavefunctions.[14] Exchange potential $V_e(r)$ provides the semiclassical energy-dependent form of Riley and Truhlar.[15] Polarization potential $V_p(r)$ was given by our group,[16] which has a correct asymptotic form $-\alpha/2r^4$ for large r and approaches the free-electron-gas correlation energy $V_{CO}(r)$ proposed by Perdew in the near-target region,

$$V_p(r) = -\frac{\alpha}{2(r^2 + r_{CO}^2)^2}, \tag{6}$$

where the constant r_{CO} can be determined by letting $V_P(0) = -\alpha/2r_{CO}^4 = V_{CO}(r = 0)$ and α is the atomic polarizability. The absorption potential $V_\alpha(r)$[17] represents the combined effect of all the inelastic channels. It is written as

$$V_\alpha(r) = -\rho(r)(T_L/2)^{1/2}(8\pi/5k^2k_f^3) \times H(k^2 - k_f^2 - 2\Delta)(A + B + C). \tag{7}$$

Here

$$T_L = k^2 - V_s - V_e - V_p,$$

$$A = 5k_f^3/2\Delta,$$

$$B = -k_f^3(5k^2 - 3k_f^3)/(k^2 - k_f^2)^2,$$

$$C = 2H(2k_f^3 + 2\Delta - k^2)\frac{(2k_f^2 + 2\Delta - k^2)}{(k^2 - k_f^2)^2},$$

where Δ is the mean excitation energy, $\rho(r)$ the atomic charge density. k and k_f are the energies of incident electron and Fermi momentum, respectively. $H(x)$ is a Heaviside function defined by $H(x) = 1$ for $x \geq 0$, and $H(x) = 0$ for $x < 0$.

In the previous investigations, the additivity rule of the TCS did not consider the formation of the chemical bond and overlap of electron clouds in molecules. So, calculation errors are great at lower energies. In addition, calculations were seldom performed for incident energy above 1000eV due to the solution divergence of the differential equations in our former works.

Here, we introduce the concept of bonded atom and consider the overlap of electron clouds in molecules. That is to say, the atom in molecules is different from the free one in state, and the atoms in different molecules are also different. Thus, electron charge density $\rho(r)$ must be rewritten as follows:

$$\rho'(r) = f\rho(r), \tag{8}$$

$$f = 1 - \frac{r}{R} \times \frac{Z}{N}. \tag{9}$$

Here, f is an adjustable factor. r and R are the bond length and the sum of the radii of the two atoms respectively. Z and N are the electron number of the outmost shell and the total number of the atoms. So, Eq.(5) can be rewritten as

$$V_{opt}(r) = fV_s(r) + V_p(r) + V_e(r) + ifV_a(r). \tag{10}$$

According to the concept of bonded atom mentioned above, the TCS is different for the same atom in different molecules because of the different overlap of the electron clouds of the same atom in different molecules.

Values of parameters R in molecules (O_2, H_2O, H_2, O_3, CO and CO_2) are achieved by using the atomic charge density, determined from the well-known Roothaan–Hartree–Fock atomic wavefunction.[14]

3. Results and discussion

Employing the additivity rule along with the complex optical potential model rewritten by the concept of bonded atom, we have calculated the TCSs for e–molecules (O_2, H_2O, H_2, O_3, CO and CO_2) consisting of C, H and O atoms scattering over an incident energy range of 100–2000eV. The reason for selecting these molecules (O_2, H_2O, H_2, O_3, CO and CO_2) as targets is twofold. Firstly, all of the molecules have experimental data in a wide energy range and secondly, the structure of the targets is not too complicated, thus calculation is easily made. The present TCS results at 100–2000eV along with available experimental and theoretical data are given in Figs.1–6.

Now we start by discussing the TCSs for the e–O_2 scattering system. Figure 1 shows the present TCS results with the complex optical model potential rewritten (solid line) and not rewritten (dashed line) by the concept of bonded atom along with the available experimental data of Dalba's group [18] (triangles), Dababneh's group [19] (squares) and theoretical data of Jain group [12] (dotted line). From Fig.1 we notice that a very good agreement between the present values of TCSs resulting from the use of the additivity rule along with the complex optical model potential rewritten by the concept of bonded atom and experimental data of Dalba's group [18] and Dababneh's group [19] at 100–1600eV and discrepancies are only 7.7% at most. It is also noted that there is excellent agreement between the present values of TCSs resulting from the use of the additivity rule along with the complex optical model potential not rewritten by

the concept of bonded atom and the SCOP results of Jain's group;[12] but they are much higher than the TCS results correlated by the concept of bonded atom. That is to say, the rule together with the complex optical model potential rewritten by the concept of bonded atom is successful for e–O_2 scattering at above 100eV. We should notice that the present TCSs (solid line) are also reliable even at those energies ($E \geq$1600eV) where no other experimental data could be found in the literature to the best of our knowledge.

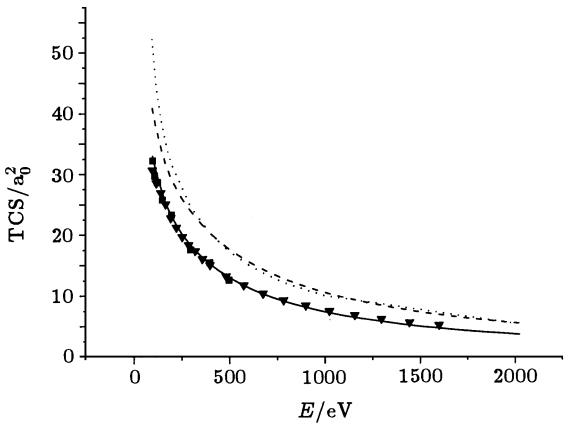


Fig.1. Total cross section for e–O_2 scattering.

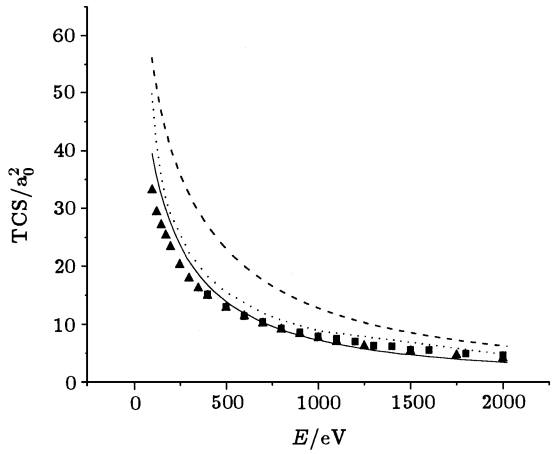


Fig.2. Total cross section for e–CO scattering.

Figure 2 shows the TCSs of electron scattering from CO determined by the use of additivity rule and the complex optical model potential rewritten (solid line) and not rewritten by the concept of bonded atom (dashed line) together with the experimental data of Karwasz's group [20] (triangles), Xing's group [21] (squares) at 100–2000eV and the theoretical results of Jain and Baluja [12] (dotted line) at 100–2000eV. The present values correlated by the concept of bonded atom (solid line) are higher than the experimental data of Karwasz's group [20] by about 19.5% at 100eV. It is noted that the discrepancies rapidly decrease as the incident energy increases. Unfortunately, we should notice that, at higher incident energies, our calculations are slightly lower than the experimental data of Karwasz's group [20] and Xing's group,[21] but they are lower than the calculations of Jain and Baluja.[12] In a word, the present results are in good agreement with the experimental data at 100–2000eV.

Figure 2 also shows the values not correlated by the concept of bonded atom (dashed line). Obviously, these values are much higher than the results (solid line) and the experimental data of Karwasz's group [20] and Xing's group [21] by at least about 40% at 100–2000eV.

Figure 3 shows the TCSs of electron scattering from CO_2 determined by the use of the additivity rule and the complex optical model potential rewritten by the concept of bonded atom (solid line) and not rewritten by the concept of bonded atom (dashed line) together with the experimental data of Szmytkowski's group [22] (triangles) at 100–2000eV and Kwan's group [23] (squares) at 100–500eV and the theoretical results of Jain and Baluja [12] (dotted line) at 100–2000eV. From Fig.3, we see that the agreement with the experimental data [22,23] is good and better than the SCOP results of Jain and Baluja.[12] For such an anisotropic system, our results are very encouraging. But it is noted that our calculations (solid line) are higher at lower energies and lower at higher energies than the experimental results. That is to say, our V_{opt} decreases too rapidly as the incident energy increases, and this is similar to those in Figs.1, 2, and 4–6. This is because we have ignored the multicentre scattering and the valence-bond effect in the additivity rule. At the additivity rule level, calculations will be better if we add the energy correlation.

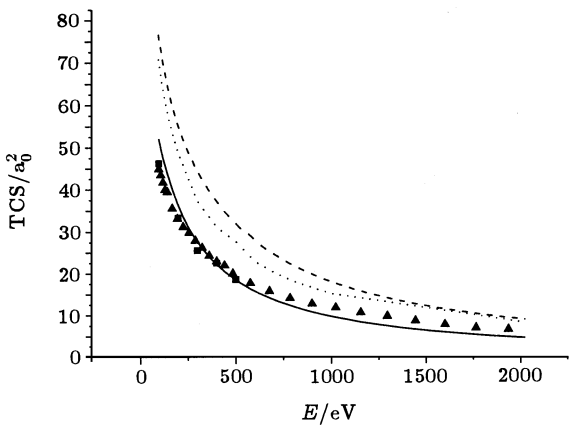


Fig.3. Total cross section for e–CO_2 scattering.

The results not correlated by the concept of bonded atom (dashed line) are much higher than the experimental data and the calculations correlated by it. Thus, we can say that the use of the additivity rule together with the complex optical potential rewritten by the concept of bonded atom can better the accuracy of the TCS calculated results.

Figure 4 shows the TCSs of electron scattering from H_2O determined by the use of the additivity rule and the complex optical model potential rewritten (solid line) and not rewritten (dashed line) by the concept of bonded atom together with the experimental data of Zecca's group [24] (squares) at 100–2000eV and Sueoka's group [25] (triangle) at 100–400eV and the theoretical results of Jain [26] (dotted line) at 100–2000eV. From Fig.4 we notice that the present values (solid line) are in very good agreement with the measurements of Zecca's group [24] and Sueoka's group [25] at 100– 2000eV. Above 1500eV, our calculations are only about 10% lower than the measurements of Zecca's group [24] if we take into account the experimental errors. As shown in Fig.4, our results (dashed line) are basically in agreement with the theoretical results of Jain.[26] But large margins are evident between the measurements or our calculations (solid line) and Jain or our results (dashed line) at 500–1500eV by about 20%–30%. So, the introduction of bonded-atom concept in complex optical model potential might reflect more actual situations.

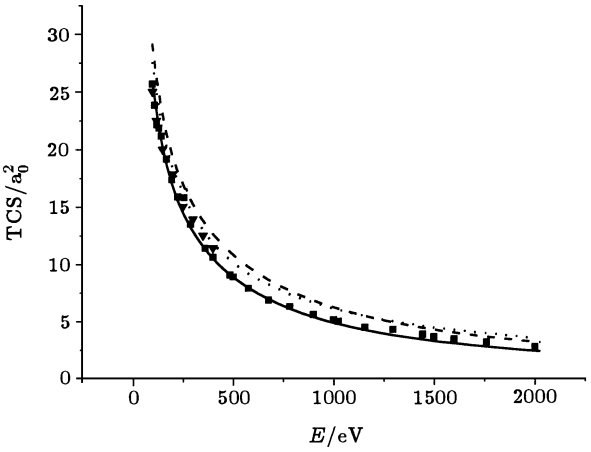


Fig.4. Total cross section for e–H_2O scattering.

Figure 5 shows our TCS calculations for e–O_3 scattering by using the complex optical model potential rewritten (solid line) and not rewritten (dashed line) by the concept of bonded atom against the available experimental data of Pablos's group [27] (squares) and the theoretical results of Joshipura *et al* [28] (dotted line). Below 1200eV, the present TCSs (solid line) are in excellent accord with the measurements of Pablos's group,[27] and are well within the experimental error of about 13% at all energies. But below 350eV, no other experimental data are available to the best of our knowledge. Above 1200eV, the discrepancy goes down as electron incident energy goes up, and at 2000eV, it reaches about 25.5%. As the figure shows, the present TCSs (dashed line) give bad agreement at above 1500eV and the disagreements are about 22%–30%, whereas below 1500eV, the present TCS values (dashed line) agree with the experiments better and better as the incident energy ascends.

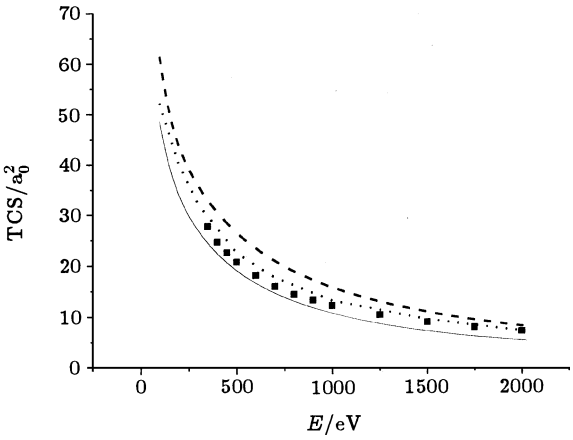


Fig.5. Total cross section for e–O_3 scattering.

As seen in Fig.5, obviously, the theoretical results of Joshipura *et al* [28] are in better agreement with the measurements of Pablos's group [27] than our results (solid line and dashed line) at 100–2000eV. This is because their calculations proceed through a complex energy-dependent potential derived from the atomic/molecular electron charge density. If we consider the changes of the shielding effect in molecules as the energy of the incident electrons and use a complex energy-dependent potential, we can also obtain better results.

The H_2 molecule is the simplest neutral molecular system that has been studied extensively in the laboratory to determine TCS values.[29–32] But it is surprising that most of the studies are of the low-energy experimental data,[30–32] especially below 100eV. To the best of our knowledge, only Ref.[29] have the data at above 500eV. In Fig.6, we show the TCSs of electron scattering from H_2 determined by the use of the additivity rule and the complex optical model potential rewritten by the concept of bonded atom (solid

line) along with the experimental data of Wingerden's group [29] (circles) at 100–800eV. Obviously, our results are in good agreement with the experimental data, especially below 500eV.

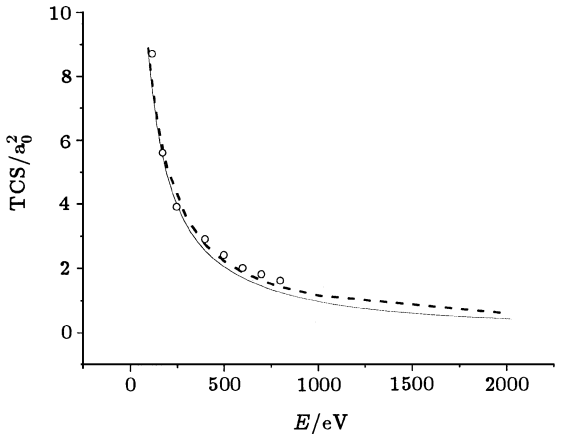


Fig.6. Total cross section for e–H_2 scattering.

TCS calculations have also been carried out by Jain and Baluja [12] (dashed line) employing the SCOP including quadrupole contribution with Δ=10.6eV in the energy range of 100–2000eV. Apparently, Jain's calculations are in very excellent accord with the experiments of Wingerden.[29] Our results are also in good agreement with Jain's data in the incident energy range of 100–2000eV, especially below 1000eV.

4. Conclusions

We have presented the total (elastic+inelastic) cross sections of electron impact with several simple molecules (O_2, H_2O, H_2, O_3, CO and CO_2) consisting of C, H and O atoms in the incident energy range of 100–2000eV, where experimental studies have been carried out recently. A complex optical model potential, which is composed of static, exchange, correlation polarization plus absorption and rewritten by the concept of the bonded atom, is employed to yield TCSs at Roothaan–Hartree–Fock level under the partial wave analysis. At and above 100eV, our results for all the molecules studied here are in good agreement with available experiments except at a few energy points, whereas the former method, which employs the complex optical potential not correlated by the concept of bonded atom, is not suitable for TCS calculations until the energy is above 200–400eV. We never use that method to calculate TCS when the energy is above 1000eV because of solution divergence of the differential equation (3) under the former conditions. It is worthwhile to mention that our present calculations give relatively bad agreement with the experiments as the incident energy goes up, especially above 1500eV.

We need more experimental data for these molecules, particularly in the keV energy region. We plan to investigate several other molecules, especially large molecules, where experimental data exist (for example, SF_6, SO_2, OCS, N_2O, NO, several hydrocarbons, etc.). The method employed here is easy and practical and requires no detailed information of the molecular structure. We have extended this work for positron–molecule total cross sections for several molecular gases where recent experimental data are available at 100–2000eV.

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