

A note on the use of the additivity rule for electron–molecule elastic scattering

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For a sample of four molecules (O_2 , CO , CO_2 and CF_4) investigated here it is found that the additivity rule gives almost the same values of the momentum transfer cross section (MTCS) as obtained within the framework of the independent atom model (IAM) for elastic scattering of electrons at intermediate and high incident energies. However, large differences are noted between the two values in the case of the integral elastic cross section.

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 hetero-nuclear molecules) and its nuclear motion. Hence, for electron–molecule scattering different approaches have been proposed and developed. The independent-atom model (IAM) [1] is one of the approaches which has been employed to study electron–molecule elastic scattering at intermediate and high incident energies. Similarly for the electron impact ionisation empirical, semi-empirical and semi-classical approaches [2] along with the additivity rule [3] have been employed to obtain the total ionisation cross section for the molecules.

The differential cross section in IAM [1] for a molecule containing N atoms averaged over all the orientations of the rotating molecule is given by

$$I_{\text{IAM}}(\theta) = \sum_{i=1}^N |f_i(\theta)|^2 + \sum_{i \neq j=1}^N f_i(\theta) f_j^*(\theta) \frac{\sin Kr_{ij}}{Kr_{ij}}, \quad (1)$$

where $f_i(\theta)$ is the scattering amplitude proper to the i th atom, constituting the molecule. K is the magnitude of the momentum transfer by the incident electron during the collision and r_{ij} is the distance

between the nuclei of the i th and j th atom. On the other hand according to the additivity rule [3] the differential cross section (DCS) of the molecule is given by

$$I_{\text{Ad}}(\theta) = \sum_{i=1}^N |f_i(\theta)|^2. \quad (2)$$

Thus it is evident that IAM (eq. (1)) includes the contributions from the interference occurring between the scattering amplitudes originating from the different constituent atoms of the molecule. Such interference terms are not included when the additivity rule (eq. (2)) is applied. In other words we can say that in IAM [1] the atomic scattering amplitudes referred to a single centre are added coherently while in the additivity rule [3] the incoherent sum is taken. It may further be pointed out that in IAM the geometry of the molecule is involved but the additivity rule ignores it. However, in both the above-mentioned approaches the molecular scattering problem is reduced to the atomic scattering problem which is easier to handle. In a recent investigation Margreiter et al. [4] have remarked that the additivity rule is a successful concept and used it to obtain the electron impact total ionisation cross sections for a large number of molecules. However, it may be added here that the same authors [4] also reported a case of failure for the additivity rule for ionisation cross sections of radicals. Hence, it is of

interest to test its applicability to the evaluation of integral and momentum transfer cross sections for electron-molecule elastic scattering. For this purpose we have chosen homo- as well as hetero-nuclear molecules, namely O_2 , CO, CO_2 and CF_4 and calculated the values of the elastic integral $Q_I(E)$ and the momentum transfer $Q_M(E)$ cross sections for these molecules over the incident energies 100–800 eV. The integral and momentum transfer cross sections are obtained, respectively, from the following relations,

$$Q_I(E) = 2\pi \int_0^\pi I_{A/M}(\theta) \sin \theta d\theta \quad (3)$$

and

$$Q_M(E) = 2\pi \int_0^\pi I_{A/M}(\theta) (1 - \cos \theta) \sin \theta d\theta, \quad (4)$$

where $I_{A/M}(\theta)$ is the differential cross section for the relevant atom/molecule.

To obtain the values of $Q_I(E)$ and $Q_M(E)$ we have used the values of the differential cross sections of our previous calculations [5–7] for the relevant constituent atoms, obtained by the method of partial waves. The interaction potential was taken as the sum of the static and dynamic polarisation potentials. The differential cross sections for electron-molecule scattering obtained within the framework of IAM are found to be in fairly good agreement with the experimental data in the case of O_2 , CO and CO_2 [5,8] for incident energies $E \geq 200$ eV. In the present in-

vestigation eq. (2) is utilised to obtain $I_{Ad}(\theta)$. Finally $Q_I(E)$ and $Q_M(E)$ are obtained following both the approaches. The two sets of results obtained by the use of the additivity rule (column a) and the other obtained in IAM (column b) are shown in tables 1 and 2 for the momentum transfer and the integral cross sections, respectively. The experimental data [9] for one of the molecules (namely O_2) is also included for comparison (column c).

It is evident from table 1 that the values of $Q_M(E)$ obtained by the additivity rule (column a) are almost the same as those obtained in IAM (column b) for all the four molecules and at all the incident energies considered. The maximum difference between the two sets of values is less than 5% for the homo- as well as the hetero-nuclear molecules at the lowest energy considered (100 eV). It indicates that the contribution of the interference terms present in $I_{IAM}(\theta)$ to $Q_M(E)$ is almost negligible at all the incident energies. However, for the elastic integral cross sections $Q_I(E)$ we find large differences between the two sets of values (table 2). The values of $Q_I(E)$ obtained by the use of the additivity rule for CF_4 and CO_2 are about 35% and 32% smaller, respectively, than those obtained in IAM at 100 eV. For CO and O_2 this difference is about 24% and 20%, respectively, again at 100 eV. Thus the differences are larger for the polyatomic molecules than for diatomic molecules. It may be noted that as the incident energy increases, the difference between the two sets of values decreases (table 2). At the highest energy (i.e. 700 eV for CF_4 and 800 eV for the remaining molecules) the values of $Q_I(E)$ obtained by the use of

Table 1

Atomic and molecular momentum transfer cross sections for elastic scattering of electrons (in units of a_0^2). Column a: values obtained by the use of the additivity rule. Column b: values obtained in IAM. Column c: experimental data from ref. [9].

E (eV)	C	O	F	O_2			CO		CO_2		CF_4	
				a	b	c	a	b	a	b	a	b
100	4.25	5.73	7.16	11.46	10.86	–	9.98	9.80	15.71	15.23	32.89	33.97
150	2.47	–	3.72	–	–	–	–	–	–	–	17.35	17.38
200	1.66	2.26	2.52	4.52	4.50	–	3.92	3.96	6.18	6.24	11.74	11.65
300	0.92	1.30	1.47	2.60	2.61	2.4 ± 0.32	2.22	2.22	3.52	3.52	6.80	6.78
400	0.59	0.86	–	1.72	1.72	1.71 ± 0.26	1.45	1.45	2.31	2.31	–	–
500	0.42	0.62	0.71	1.24	1.24	1.141 ± 0.184	1.04	1.03	1.66	1.65	3.26	3.25
700	0.24	–	0.43	–	–	–	–	–	–	–	1.96	1.97
800	0.19	0.30	–	0.60	0.60	–	0.49	0.49	0.79	0.80	–	–

Table 2

Atomic and molecular integral cross sections for elastic scattering of electrons (in units of a_0^2). Column a: values obtained by the use of the additivity rule, column b: values obtained in IAM, Column c: experimental data from ref. [9].

E (eV)	C	O	F	O ₂			CO		CO ₂		CF ₄	
				a	b	c	a	b	a	b	a	b
100	11.37	12.70	13.95	25.40	31.76	—	24.07	31.54	36.77	53.74	67.17	102.99
150	8.30	—	8.99	—	—	—	—	—	—	—	44.26	69.92
200	6.56	6.27	6.50	12.54	15.15	—	12.83	16.02	19.10	26.25	32.56	47.51
300	4.88	4.55	4.50	9.10	10.68	10.8 ± 2.1	9.43	11.43	13.98	18.45	22.88	31.80
400	3.93	3.70	—	7.40	8.51	9.28 ± 1.82	7.63	9.12	11.33	14.64	—	—
500	3.31	3.15	3.11	6.30	7.18	7.25 ± 1.41	6.46	7.67	9.61	12.28	15.75	21.40
700	2.59	—	2.44	—	—	—	—	—	—	—	12.35	16.29
800	2.26	2.24	—	4.48	5.03	—	4.50	5.31	6.74	8.43	—	—

the additivity rule (column a) are still smaller by about 24%, 20%, 15% and 11% for CF₄, CO₂, CO and O₂, respectively, than those obtained in IAM (column b). We also note that the values of $Q_M(E)$ and $Q_I(E)$ obtained in IAM are in fairly good agreement with the experimental data of Iga et al. [9] for e-O₂ elastic scattering (columns b and c of tables 1 and 2). Since the experimental data of Iga et al. [9] is available only up to 120°, to make the comparison between the theory and the experiment more meaningful the results in column c of tables 1 and 2 include the experimental results [9] for scattering angles θ from 0° to 120° and the theoretical results [8] for scattering angles $\theta > 120^\circ$ since in a recent investigation [8] we have shown that the contributions from the large scattering angles particularly to $Q_M(E)$ are quite significant.

To explain the above observations we have plotted in figs. 1 and 2, $I_M(\theta)(1 - \cos \theta) \sin \theta$ and $I_M(\theta) \sin \theta$ which are integrands of $Q_M(E)$ and $Q_I(E)$, respectively, versus scattering angle for e-O₂ elastic scattering at 100 and 800 eV. It is clear from fig. 1 that the solid curve which includes interference ($I_M(\theta) = I_{IAM}(\theta)$) lies higher than the curve without interference (dashed curve, $I_M(\theta) = I_{Ad}(\theta)$) in some angular range (0°–30° and 62°–105°) but lies lower in the other ranges at 100 eV. However, for scattering angles $\theta > 165^\circ$ both curves merge into each other. Furthermore, at 800 eV both curves overlap almost throughout the whole angular range. Thus on the average the contribution of the interference terms from the whole angular range turns out to be negligible and hence the additivity rule is successful for $Q_M(E)$. On

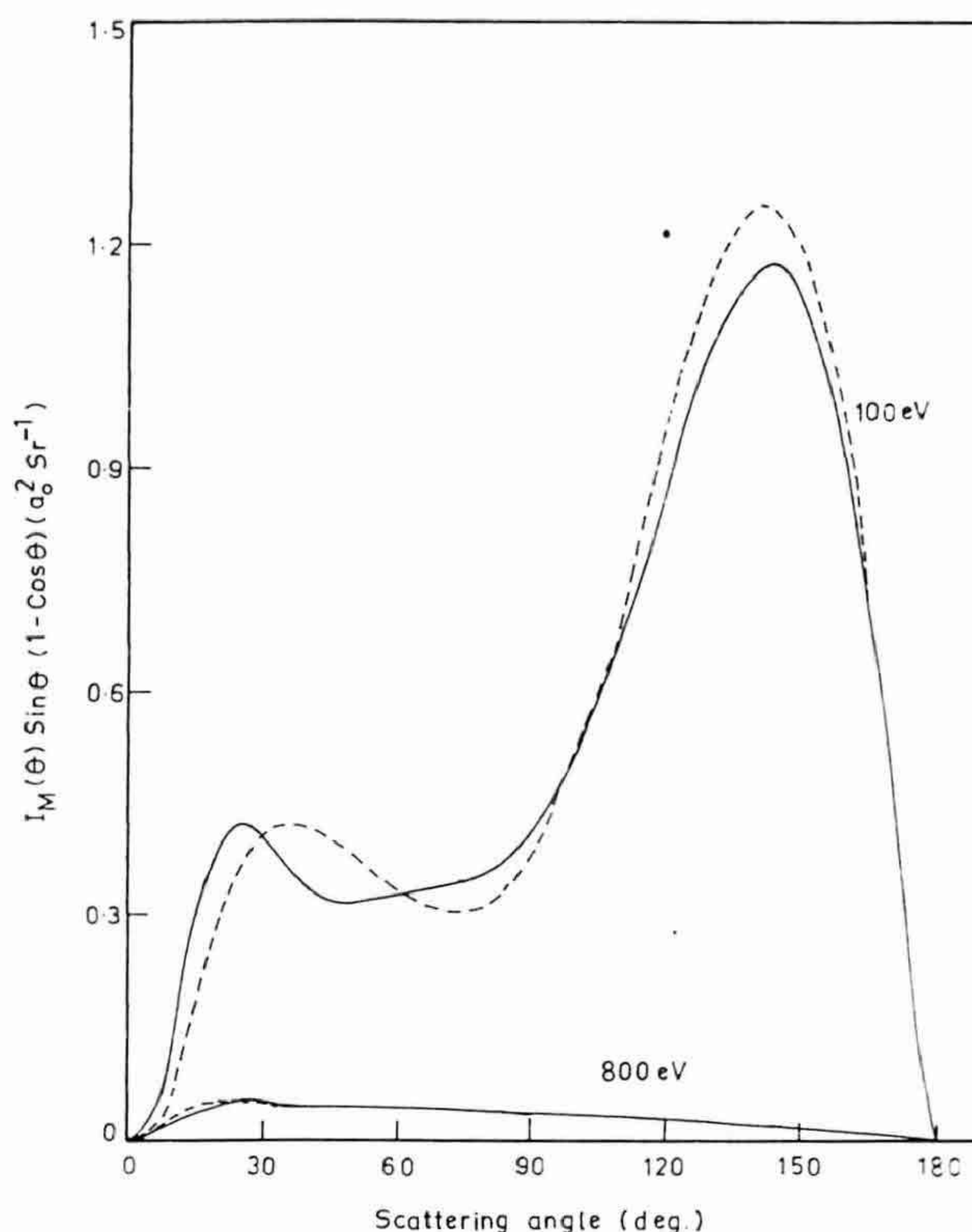


Fig. 1. Integrand of momentum transfer cross section, $I_M(\theta) \sin \theta (1 - \cos \theta)$ versus scattering angle for e-O₂ elastic scattering at 100 and 800 eV incident energies. For the solid curve $I_M(\theta) = I_{IAM}(\theta)$ and for the dashed curve $I_M(\theta) = I_{Ad}(\theta)$.

the other hand for the integral cross sections we find that the curve without interference terms (dashed curve) lies much lower than that with interference terms (solid curve) at low scattering angles (fig. 2) from where the maximum contribution to it is at 100

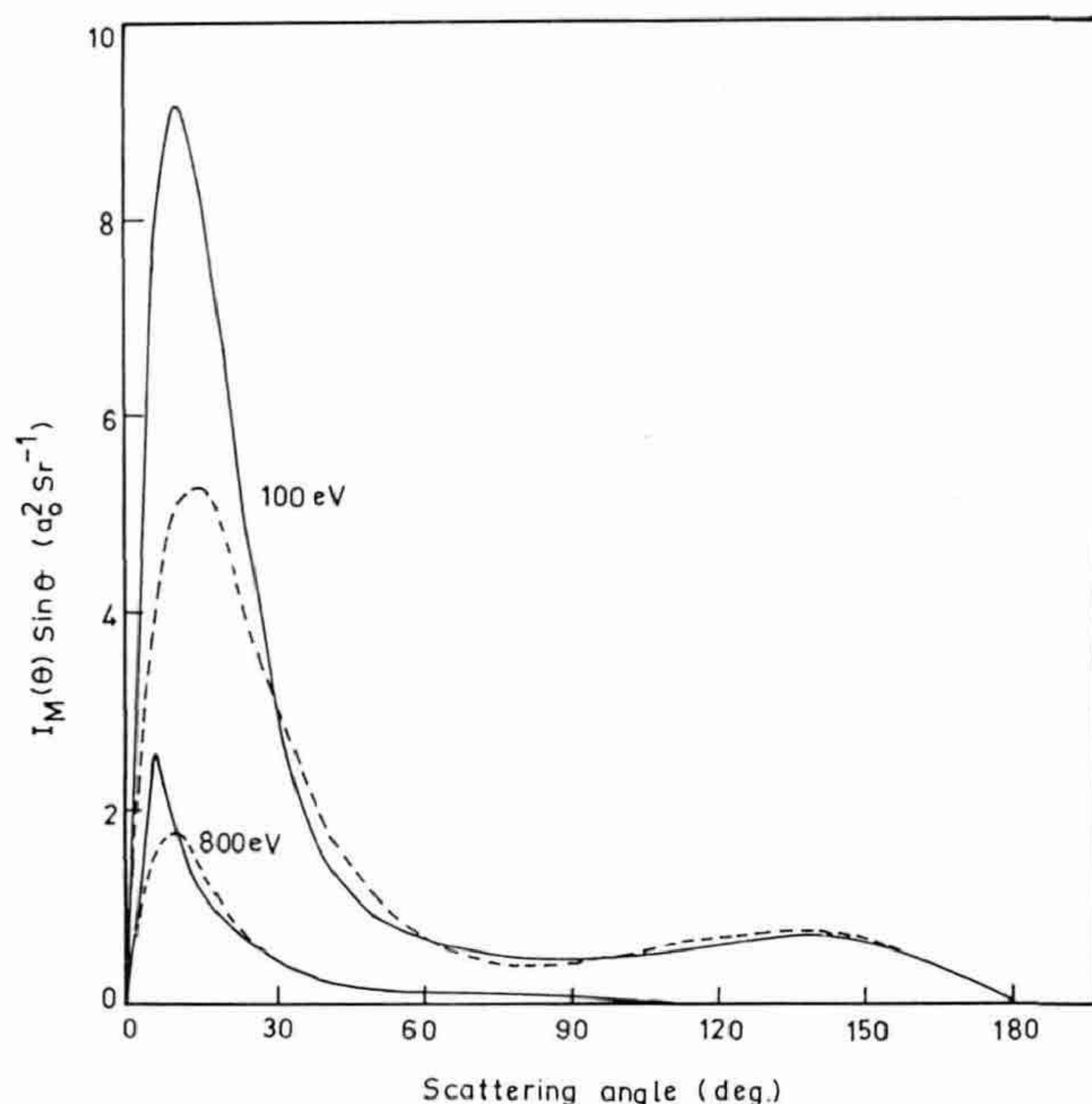


Fig. 2. Integrand of integral cross section, $I_M(\theta) \sin \theta$ versus scattering angle for e- O_2 elastic scattering at 100 and 800 eV incident energies. Other details are the same as in fig. 1.

eV. Thus the values of the integral cross sections obtained by the use of the additivity rule are much smaller than those obtained in IAM. As the incident energy increases, the amplitude of oscillations of the interference terms die out at low scattering angles also and consequently the difference between the two sets of values of the integral cross section decreases.

Finally, it is concluded that the values of the momentum transfer cross sections obtained by the use of the additivity rule are almost the same as those obtained in the independent-atom model for the elastic scattering of electrons by a sample of four molecules (O_2 , CO, CO_2 and CF_4) at intermediate

and high incident energies and these values are in fairly good agreement with the available experimental data [5,7,8]. Hence, it is expected that the fairly simple approach based on the additivity rule where no molecular geometry is involved may give satisfactory values of the momentum transfer cross sections for other molecules also. However, to arrive at a definite conclusion, the applicability of the additivity rule to other molecules for the elastic scattering should be explored.

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