Chapter 4

Elastic scattering of fast electrons by molecules

4.1 Introduction

The problems of scattering of electrons from molecules are reasonably more difficult than the electron-atom problems. The internal degrees of freedom of a molecule divide into rotational and vibrational parts, in addition to the electronic part. For none of these, do the exact wave functions exist for any molecule (by ond H_2^+). The most striking difference is the axial symmetry of molecular charge distribution, as against the spherical one of an atom. Also an electron-molecule problem is essentially a multicentre problem. Special theoretical methods are required for electron-molecule collisions. A recent review mainly on low-energy problems in this subject is by Lane (1980). A hydrogen molecule being the simplest two-centre neutral system, offers a convenient means of study. Here we confine ourselves to homonuclear diatomic molecules and in particular, H_2. Other molecules are occasionally mentioned. In the recent past, many theories of electron-atom collisions are extended to electron-molecule collisions also. To take a full advantage of the progress in electron-atom theories, methods are devised to reduce the molecular scattering problem to a suitable atomic scattering problem. In the next section we discuss, the independent atom model for electron scattering from molecules. In the literature of the last ten years for so, one finds many applications of this model. With the experimental results coming up, there is a surge of activities in studying the scattering of fast electrons by molecules. In the present chapter, the e-H_2 cross-sections are also calculated by using a simple wave function of the H_2 molecule~~s~~. We have also mentioned in outline the elastic electron scattering from O_2, N_2, CO etc. molecules. We work in a. u. if not specified.

4.2 The Independent Atom Model

If the different atoms of a molecules are assumed as separate scattering centres, interference would occur between the electron waves scattered from the individual atoms of a molecule. The nature of these interference effects will depend on the structure of the molecule. The diffraction of electrons is a powerful tool of studying the molecular structure (Massey, 1969, see also M. Chandra, 1979).

The independent atom model (IAM) for elastic scattering is based on the following assumptions.

1. Each atom of the molecule scatters the

incident electron as if it were free and independent; this means that we ignore the fact that the atom is bound in the molecule and that an incident electron would simultaneously feel the field of other constituents of the molecule.

2. Multiple scattering effects are neglected. Thus, an electron after hitting an atom, goes to the detector directly without being scattered again by any other atom. The scattering from the molecule is the coherent superposition of scattered waves from each atom. The first assumption is better understood in terms of an optical analogy. The familiar two-slit interference phenomenon of light will become the diffraction from a single slit, provided the separation of the two slits is quite large and the slit-width is small enough. For electron scattering by molecules the 'slits' are the atoms, the separation of the slits means the interatomic separation and the 'size' of an individual slit corresponds to the range of the potential of an atom. Thus, the first assumption holds for short wavelength or high energy electrons. The term 'high' will now be defined in terms of interatomic separation or bond length and the range of the potential due to an atom. Since the wavelength is related to the wave number through

$\lambda = 2\pi/k_i$ we write the condition for the IAM to hold, in the following manner,

$$k_i a^2 \gg R \tag{4.1}$$

where 'a' is the range of the atomic potential and 'R' is the interatomic distance. For a polyatomic molecule, this must hold for any pair of atoms. Let an electron of momentum k_i along the direction of unit vector $\underline{n}_o$ (also the z-axis), be incident on a molecule, having a fixed orientation. Taking the nucleus of ith atom as the origin, we write the incident plus scattered wave,

$$e^{ik_i z} + r^{-1} e^{ik_i r} f(\theta) \tag{4.2}$$

see fig. 4.1a. Now change the origin to a point O, relative to which the position vector of the nucleus A_i is $\underline{r}_i$. Then the expression (4.2) changes to take into account the phase change. We follow Massey (1969) to write for the scattered wave from ith atom, as hereunder,

$$r_o^{-1} e^{ik_i r_o} e^{i(\underline{n}_o-\underline{n})k_i\cdot\underline{r}_i} f_i(\theta) \tag{4.3}$$

where, $\underline{n}$ is the unit vector in the direction of observation. Thus, the waves scattered from different atoms

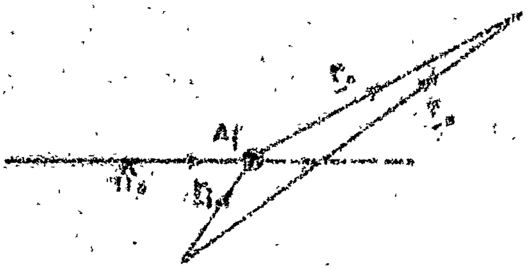

FIG. 4.1(a)
SEE THE TEXT

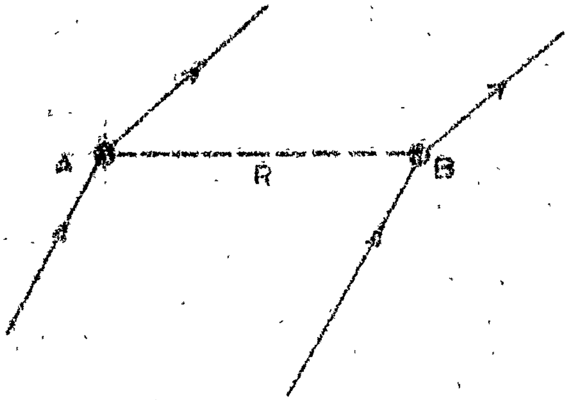

FIG. 4.1(b)
SINGLE SCATTERING ONLY

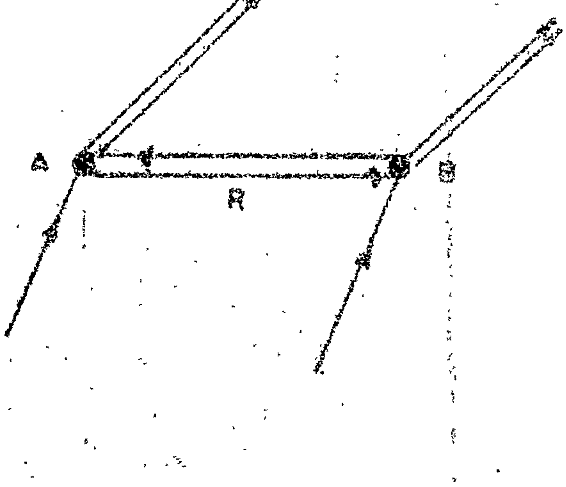

FIG. 4.1(c)
SINGLE AND DOUBLE SCATTERING

in the molecule have different phases and amplitudes, hence the differential cross-section,

$$I(\theta) = \left| \sum_i e^{ik_i (\underline{n}_o - \underline{n}) \cdot \underline{r}_i} f_i(\theta) \right|^2 \qquad (4.4)$$

Defining the internuclear separation,

$$\underline{r}_{ij} = \underline{r}_i - \underline{r}_j \qquad (4.5)$$

we have, from equation (4.4),

$$I(\theta) = \sum_{i,j} f_i f_j^* \, e^{i(\underline{n}_o - \underline{n})k \cdot \underline{r}_{ij}} \qquad (4.6)$$

Now, since the molecules are oriented at random relative to the electron beam, we must average out eqn. (4.6) over all orientations of the molecule for which purpose we must consider each term separately. Choosing $(\underline{n}_o - \underline{n})$ as the polar axis, the average overall orientations of the vector $\underline{r}_{ij}$ will be

$$\frac{1}{4\pi} \int_0^{2\pi} d\phi_{ij} \int_0^{\pi} \sin\theta_{ij} \times \exp(iq\, r_{ij} \cos\theta_{ij})\, d\theta_{ij} \qquad (4.7)$$

Thus, the averaged DCS are

$$\overline{I}(\theta) = \sum_{ij} f_i f_j^* \frac{\sin q r_{ij}}{q r_{ij}} \qquad (4.8)$$

Finally, due to vibrations, the separations $\underline{r}_{ij}$ are not fixed. Let $P_{ij}(r)\,dr$ denote the probability that the separation of the atomic nuclei i and j would be between r and r + dr. Thus,

$$\overline{I}(\theta) = \sum_{ij} f_i f_j^* P_{ij}(r) \frac{\sin qr}{qr}\,dr \qquad (4.9)$$

Consider for simplicity a homonuclear diatomic molecule. A simple, through not rigorous, assumption is to fix the nuclei at the equilibrium separation R, i.e. $P_{ij}(r)$ is replaced by the delta function $\boxed{\delta(r-R)}$ and we arrive at,

$$\overline{I}(\theta) = 2I_a(\theta)\left(1 + \frac{\sin qR}{qR}\right) \qquad (4.10)$$

where, $I_a(\theta)$ is the DCS of electron scattering by an individual atom. The anisotropy of the molecule is inherent in the factor, $\left(1 + \frac{\sin qR}{qR}\right)$. This diffraction factor has a maximum value i.e. 2 at $q = 0$, and it oscillates about 1. For large 'q' it tends to 1. Thus in this basic equation of the IAM, the difficulties like, (i) multicentre nature of the problem and (ii) problems of an accurate molecular wave function are removed. The problem is now essentially reduced to determination of the atomic scattering amplitudes, for which separate assumptions may be required.

The IAM is a high-energy approximation which fails to hold whenever the incident wavelength is larger than the equilibrium internuclear distance R, i.e. the validity criterian for the model is

$$\lambda \leq R \tag{4.11}$$

For the hydrogen molecule, with $R = 1.4$ a.u., the IAM should not hold for incident energy below 270 ev. In the table 4.1 we show this limit for several well-known molecules. For polyatomic molecules (e.g. H_2O) we have considered the smallest band.

One of the most serious drawbacks of the above model is that, it supposes the atoms in the molecules to be 'free', actually they are 'bound'. When the atoms form a molecule there is a distortion in the atomic charge and this can reduce the effective volume and hence can lead to a smaller cross-section than would be expected with the atoms scattering 'freely'. The

Table 4.1

The Limit of Validity of the IAM for a few molecules

Molecule (internuclear distance R)	Limit
H_2 (0.74 A)	270 ev
N_2 (1.1 A)	120 ev
O_2 (1.21 A)	100 ev
LiH (1.6 A)	60 ev
CN (1.17 A)	110 ev
NO (1.15 A)	110 ev
H_2O (R_{min} = 0.958 A)	170 ev
O_3 (R_{min} = 1.28 A)	90 ev
CO_2 (R_{min} = 1.16 A)	110 ev

effect of molecular binding for H_2 molecule is taken into account by modifying variationally the charge Z of the 1S orbital e^{-Zr} of the constituent hydrogen atom. In Wang's (1928) treatment $Z = 1.193$ and in Wienbaum's treatment (1933), $Z = 1.2005$, both these being able to produce a satisfactory value of inter-nuclear equilibrium distance R. Accordingly, the first change in the simple IAM eqn. (4.10) is to determine the atomic scattering amplitude, not for free atoms but for bound atoms, by considering the valance distortion effect. In an earlier work, this type of calculation was done by Khare and Moiseiwitch (1965, 1966).

Consider now, the effect of exchange of electrons. Again this has been analysed for H_2 molecule only. Srivastava et al (1978) have considered in the H_2 molecule, the two electrons with opposite spin to account for the spin-singlet state of the molecule. Hence, the scattering amplitude with exchange, due to one of the atoms must be $f_a = f + g$ and that due to the other must be $f_b = f - g$, where f and g are the atomic direct and exchange amplitudes respectively. So, these authors obtain in the IAM,

$$I(\theta) = 2\left(|f|^2 + |g|^2 + (|f|^2 - |g|^2)\,\frac{\sin qR}{qR} \right) \qquad (4.12)$$

However, in this treatment both singlet and triplet scattering are allowed. Now the ground state of H_2 molecule being the singlet state, the singlet scattering would leave the molecule in a triplet state, and the scattering would not be truely elastic. Hence this way of incorporating the exchange is not correct, and only triplet scattering is possible. Jhanwar et al (1980 b) have argued that both the target electrons belong to both the nuclei. Thus, the probability of an electron of spin say α, being close to any one of the two nuclei must be 1/2, the two atoms in the H_2 molecule are identical and the triplet scattering amplitude due to any one of them, must be,

$$f_A = f_H(Z) - \frac{1}{2} g_H(Z) \qquad (4.13)$$

Here, the argument 'Z' refers to the amplitude with effective nuclear charge $Z > 1$. Thus, the IAM with a properly incorporated exchange effect yields,

$$I(\theta) = 2\left|f_H(Z) - \frac{1}{2} g_H(Z)\right|^2 \left(1 + \frac{\sin qR}{qR}\right) \qquad (4.14)$$

It is thus seen that now the problem boils down to an accurate description of the atomic scattering amplitudes $f_H(Z)$ and $g_H(Z)$. In the last chapter, we have obtained the amplitude of e-H scattering in the HHOB of Yates (1979), we now combine the same with the IAM to obtain the cross-sections of elastic $e-H_2$ scattering.

4.3 Application of HHOB to $e-H_2$ Elastic Scattering

The hydrogen atom is represented by the orbital,

$$v(r) = \left(\frac{Z^3}{\pi} \right)^{1/2} e^{-Zr} \qquad (4.15)$$

The direct scattering amplitude consists of the first Born term the second Born term of the HHOB and the third Glauber term, i.e.

$$f_H(Z) = f_{B1}(Z) + i \, \mathrm{Im}\, f^{(2)}_{HEA}(Z) + \mathrm{Re}\, f^{(2)}_{HEA}(Z) + f_{G3}(Z) \qquad (4.16)$$

The wave function parameter 'λ' of the previous chapter is now, $\lambda = 2Z$. The above amplitude is consistent through $O(k_1^{-2})$, hence the exchange amplitude is taken by using the first order Ochkur approximation. The effects of absorption and the target polarization are considered through the imaginary and real parts of the second Born terms, in eqn. (4.16). We have calculated the e-H_2 elastic DCS by considering three values of the variational parameter Z i.e. Z = 1, Z = 1.193 and Z = 1.2005, and employing eqn. (4.14) (Joshipura and Desai, 1981). It is important to consider the calculations with and without valance-bond correction, i.e. taking Z = 1 and Z > 1, respectively, because the conclusions derived can help us to predict with confidence in cases like O_2, N_2, etc. where the valance-bond effects are hitherto not known. We have shown in table 4.2 the DCS of e-H_2 scattering at 100 ev in the IAM by taking the three values of 'Z'. As noted by Jain et al (1979) the valance-bond correction (Z > 1) reduces the cross-sections and brings a closer agreement with experiments. This effect persists even at high energies such as 700 ev. At 200 ev and 5° scattering angle, the difference between the DCS with and without the said correction is more than 30 %. It is also quite appreciable at large scattering angles. The choice of 'Z' as 1.193 or 1.2005 has a small effect on the DCS which diminishes with energy. As shown in fig. 4.2 the small difference in DCS (at 200 ev) due to these two values of 'Z' appears at very small and at large angles. Also in table 4.2 the DCS of e-H_2 scattering at 100 ev calculated in the IAM with Z = 1.193 and Z = 1.2005, are given.

Table 4.2

100 ev DCS at three values of 'Z' (IAM)

θ	Z = 1	Z = 1.193	Z = 1.2005
5	15.98	8.9	9.3
10	9.26	5.6	5.4
20	3.16	2.1	2.0
30	1.19	0.83	0.82
60	0.14	0.10	0.10
110	0.061	0.042	0.042

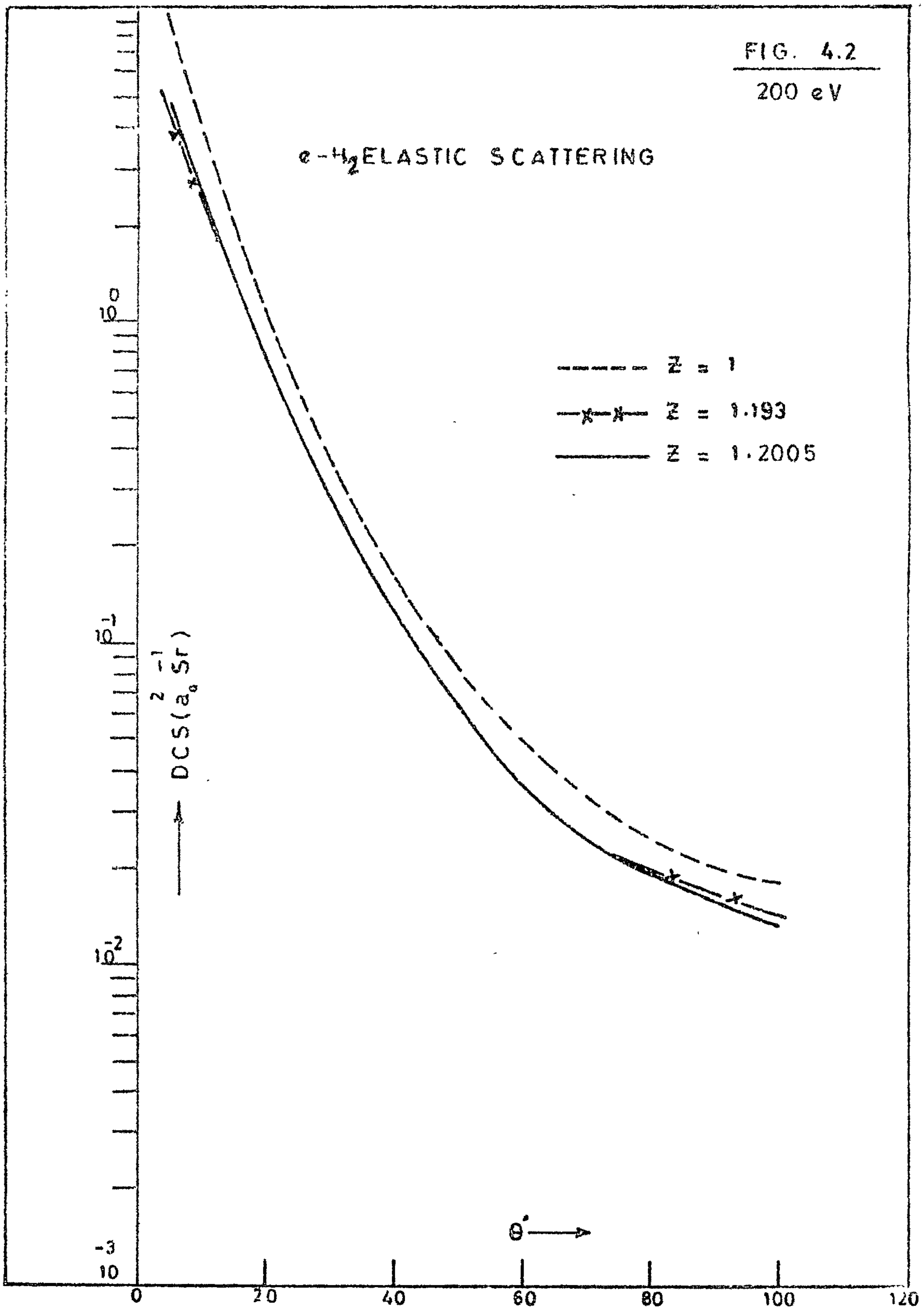
FIG. 4.2
200 eV
e-H$_2$ ELASTIC SCATTERING
Z = 1
Z = 1.193
Z = 1.2005
10^{0}
10^{-1}
10^{-2}
10^{-3}
DCS(a_0^2 Sr^{-1}) →
θ° →
0
20
40
60
80
100
120

In the range of intermediate angles, the difference vanishes, hence, we take into account the valance-correction and keep $Z = 1.2005$. At this stage, let us mention that in the forward direction, $q = 0$, yields,

$$I(0) = 4 \left| f_H (Z, \theta = 0) \right|^2 \qquad (4.17)$$

This equation together with the optical theorem can be employed to calculate the total collisional cross-sections for the e-H_2 scattering, from the knowledge of forward elastic amplitudes $f_H(Z, \theta = 0)$. This is evaluated and compared in section (4.9) of this chapter. Presently we exhibit only the DCS of e-H_2 system.

4.4 Discussion of the Present IAM DCS

We have calculated the HHOB amplitudes of eqn. (4.16) with $Z = 1.2005$ and have obtained the DCS of elastic scattering of electrons by molecular hydrogen employing the IAM via. eqn. (4.14). In the table 4.3 the diffraction factors are shown at 100 and 200 ev. Further in the table 4.4 our DCS are reported at 200 and 400 ev incident energy. This is followed, in figs. 4.3 through 4.6 by the graphical comparison of these results with available theoretical and experimental data. In these figures the number in the bracket at the top

Table 4.3

Independent atom model. Diffraction factors

$(1 + \frac{\sin qR}{qR})$ at 100, 200 and 700 ev.

Scattering angle θ_{deg}	100 ev	200 ev	700 ev
0	2.00	2.00	2.00
5	1.873	1.966	1.88
10	1.915	1.858	-
20	1.641	1.512	0.90
30	1.322	1.124	-
60	0.797	0.857	1.09
90	1.067	-	-
110	1.157	1.10	-
120	1.16	-	-

Table 4.4

The IAM results* $\bar{I}(\theta)/2\ (1 + \frac{\sin qR}{qR})$ at 200 and 400 ev (Z = 1.2005)

θ_{deg}	$\bar{I}(\theta)/2\ (1 + \frac{\sin qR}{qR})$	
	200 ev	400 ev
5	1.2	0.66
10	0.680	0.38
20	0.28	0.13
30	0.12	0.046
40	0.06	0.02
50	0.03	0.01
60	0.02	0.006
80	0.01	0.003
100	0.006	0.0017
120	0.005	0.0012
130	0.004	0.0011

*values of $| f_H(Z) - \frac{1}{2} g_H (Z) |^2$

left indicates the value of our DCS at $\theta = 0$. Before ~~in~~ we discuss our results, we mention briefly some ~~t~~ other theoretical calculations with which comparisons are made.

First of all, we refer to the work of Jain et al (1979) who have used the exchange framework of eqn. (4.12) and have employed the EBS atomic scattering amplitude with Z = 1.193 in the IAM. These results are plotted as curve E in the graphs (figs. 4.3 - 4.6). These are not shown whenever they closely agree with other results. Jhanwar et al (1980 b) have made two modifications, i.e. (i) they have shown the correct method of including the exchange as mentioned here, through eqn. (4.14) and (ii) the modified ~~b~~ Glauber amplitude, which is more accurate than the EBS one has been employed, with Z = 1.2005. (Please see curve C). The work of Jhanwar et al (1980 a) represented by curve D and our calculations leading to curve B, in these figures are both discussed in the section (4.8). Our emphasis at present is on the IAM, hence in this connection, the noteworthy points of discussion are enlisted in the following.

1. Although we have not shown explicitly the results with and without the exchange, it is found as one might expect, that the exchange effect is important at small angles and lower energies.

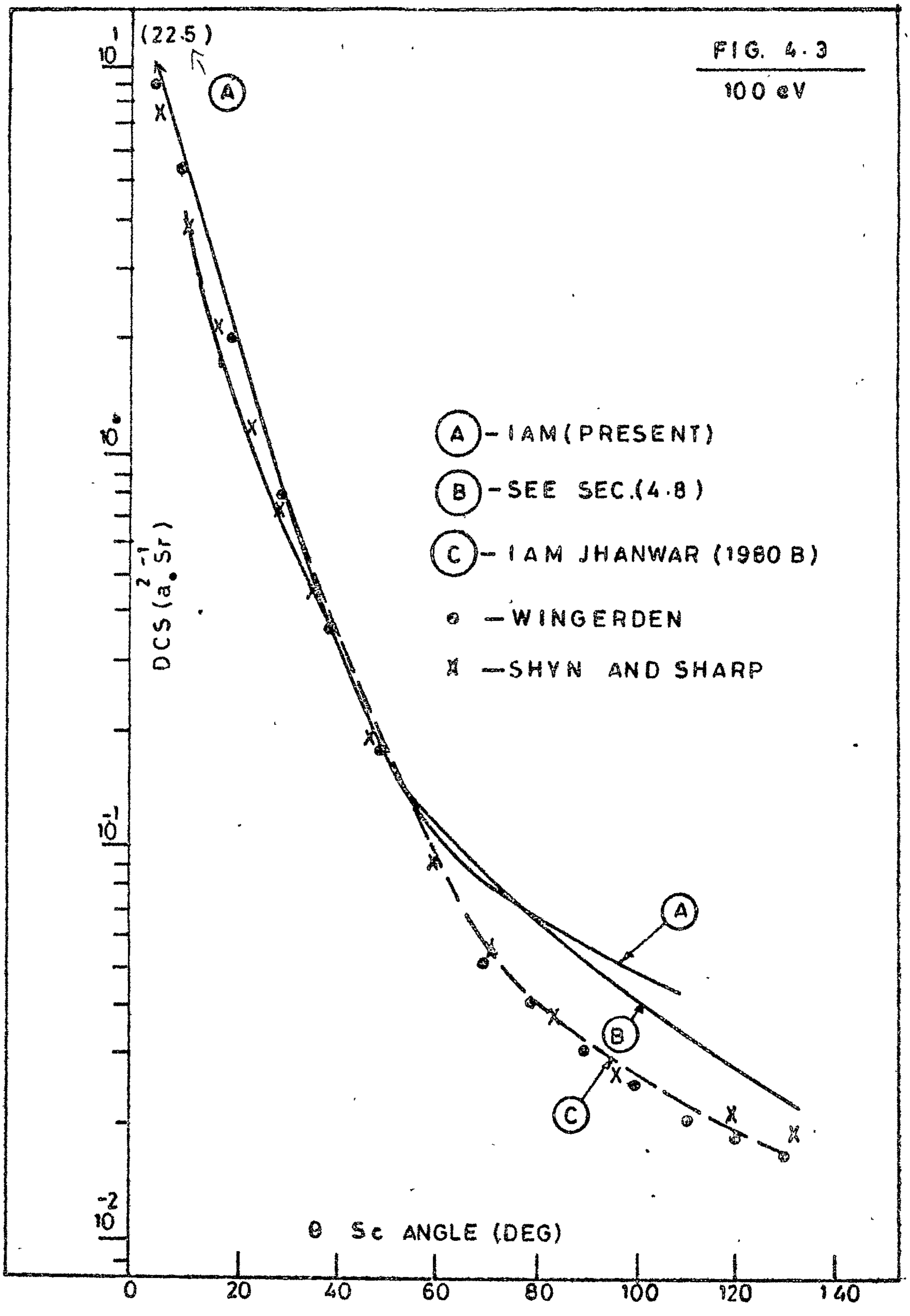

FIG. 4.3

100 eV

(22.5)
A
10^{1}
10^{0}
10^{-1}
10^{-2}
DCS ($a_0^2\,Sr^{-1}$)
Ⓐ – IAM (PRESENT)
Ⓑ – SEE SEC.(4.8)
Ⓒ – IAM JHANWAR (1980 B)
⊙ – WINGERDEN
X – SHYN AND SHARP
A
B
C
θ Sc ANGLE (DEG)
0
20
40
60
80
100
120
140

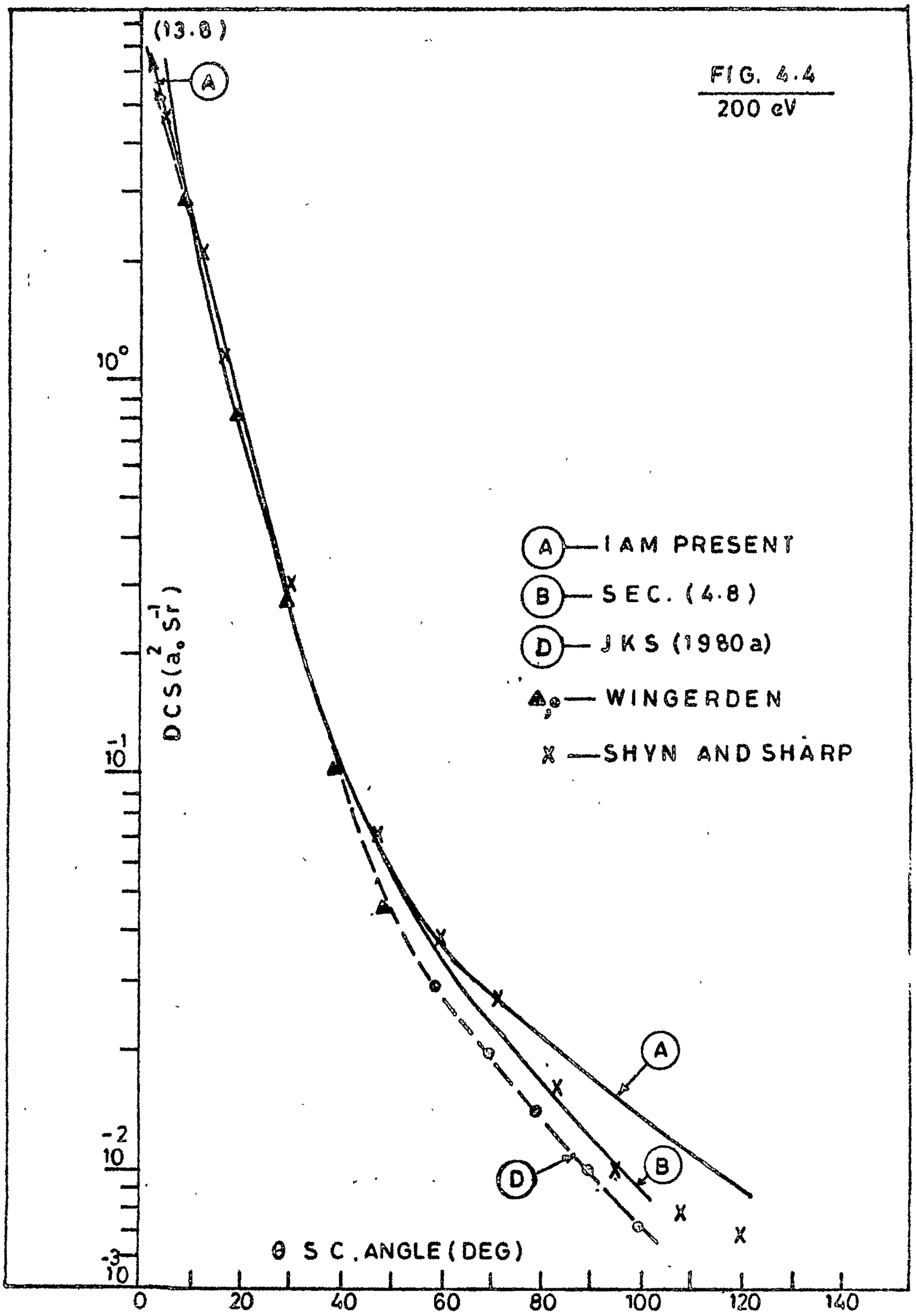
FIG. 4.4
200 eV
(13.8)
A
10°
10^{-1}
10^{-2}
10^{-3}
DCS(a_o^2 Sr^{-1})
θ SC. ANGLE (DEG)
0
20
40
60
80
100
120
140
A — IAM PRESENT
B — SEC. (4.8)
D — JKS (1980a)
▲,⊙ — WINGERDEN
X — SHYN AND SHARP
A
B
D

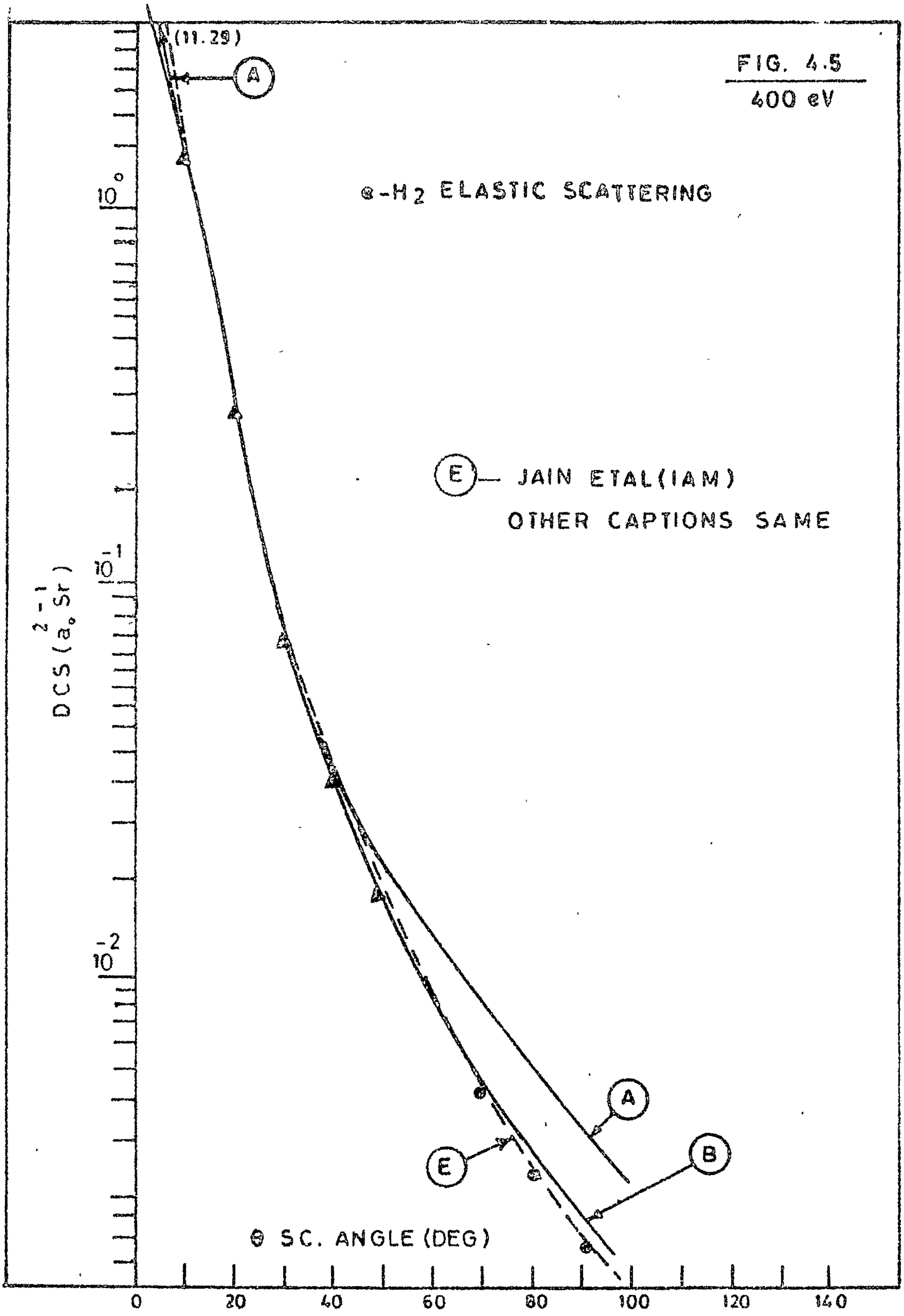
FIG. 4.5
400 eV
e-H_2 ELASTIC SCATTERING
E — JAIN ETAL(IAM)
OTHER CAPTIONS SAME
(11.29)
A
A
B
E
$DCS\ (a_0^2\ Sr^{-1})$
10^0
10^{-1}
10^{-2}
θ SC. ANGLE (DEG)
0
20
40
60
80
100
120
140

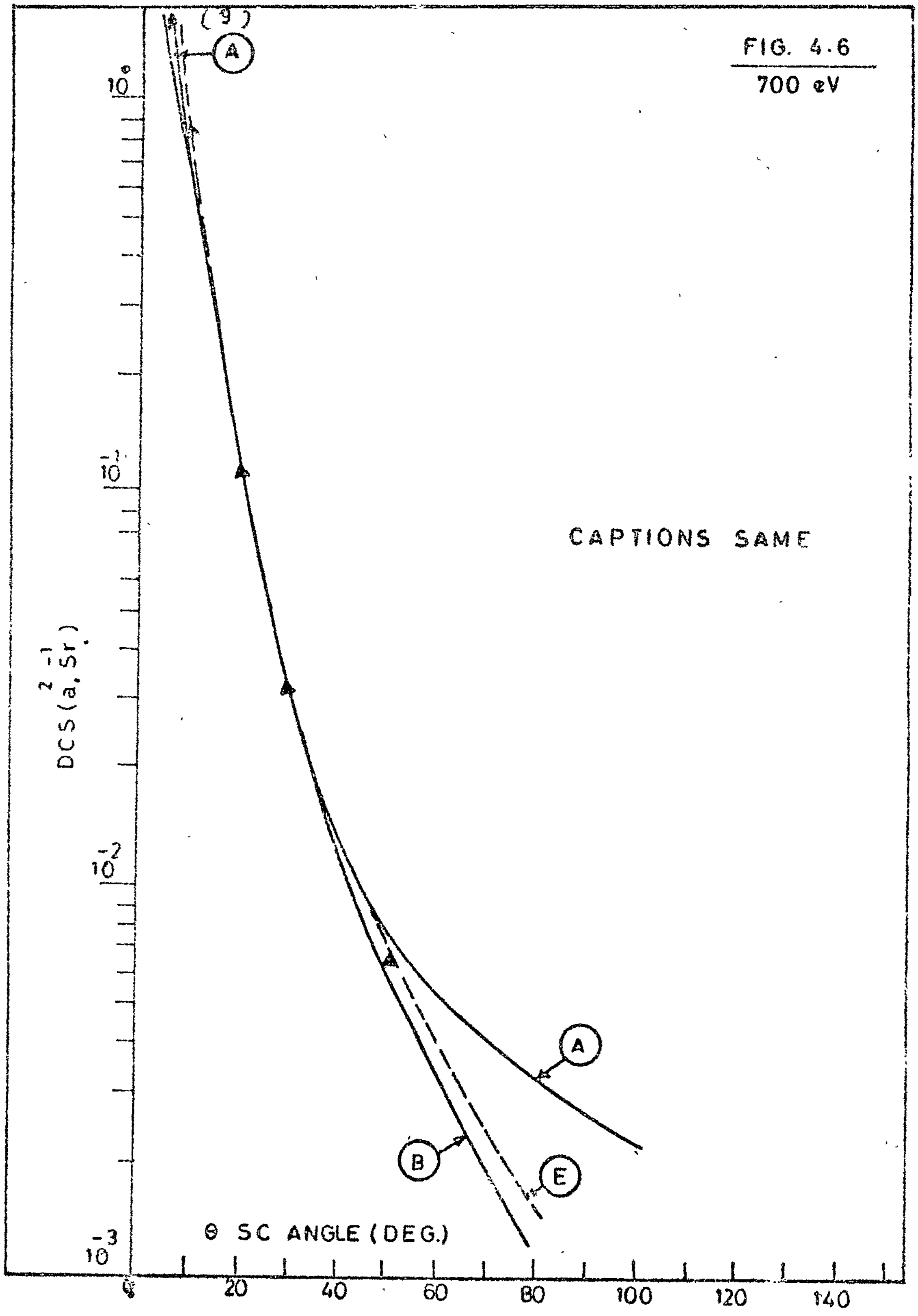

FIG. 4.6

700 eV

CAPTIONS SAME

2. The IAM formulation for e-H_2 system is actually valid above, say, 200 ev. But the present results confirm the earlier conclusion that it can give reliable results even at 100 and 200 ev. It has been shown (Jhanwar et al 1980 b) that the model begins to overestimate below 75 ev. This indicates that the breakdown of the model is slow. Further, at high energies it is quite reliable good.

3. It is our impression that the experimental data for molecular hydrogen are more reliable than the atomic hydrogen data, because of the purity and stability of molecular hydrogen. Hence, these experimental results can be considered as an excellent standard to judge the theory. However, the measurements of Van Wingerden et al (1977) and of Shyn and Sharp (1981) are somewhat at variance, with each other, as may be seen from figs. 4.3 and 4.4.

4. At once, we observe that the characteristics of the HHOB atomic scattering amplitude are reflected in the e-H_2 results. At small and medium angles, the present DCS are in a very good accord with experimental as well as other theoretical data. For all energies, whenever $\theta > 60^\circ$, the present DCS are overestimating. The reason lies in the behaviour of the second term

$O(k_i^{-2})$ of the real part of the present second Born amplitude and it needs to be rectified.

5. The other calculations done with IAM show a satisfactory agreement with measurements at all angles. However, one point is worth mentioning. We have seen in the prece~~e~~ding chapter that there is an appreciable difference in the results of the EBS and the MG theories, for electron hydrogen atom scattering, at least upto 200 ev. The UEBS calculation (Byron et al 1982) exhibits this difference even at 400 ev. But the difference in the EBS and the MG results for the e-H_2 case is not that much. At least that is what appears from the published graphical results of Jain et al (1979) and Jhanwar et al (1980 b). These two groups of authors have taken the variational parameter of the IAM α as 1.193 and 1.2005 respectively. Our purpose in studying the DCS with both these values of Z was (see fig. 4.2) to see if it makes a substantial difference. Our fig. 4.2 shows that the difference is only marginal. Further in these two calculations the method of including the exchange is also different, but that should not matter appreciably ~~at large angles~~. Thus, a substantial difference must come from the higher order terms included in the MG formulation. But as just mentioned, this does not come out to be the case. The reason for this remains

obscure.

6. Considering the e-H_2 measurements as standard, the IAM can be used (Van Wingerden et al 1977) to invert the data to obtain e-H cross-sections.However, we find from eqn. (4.14) that because of the parameter $Z > 1$ and also due to exchange term in the equation, the result obtained upon 'inverting' the IAM, will not be truely e-H DCS. All the same, it may not be very bad at high energies. Therefore, we have tried to obtain the e-H 'data' from the e-H_2 data of Van Wingerden et al (1977) in this way. Referring to fig. 3.5 of chapter three the results obtained in this way are indicated by dotted circles. There is an underestimation at small angles indicating the valance-bond effect, as just mentioned. The agreement with HHOB is not bad at intermediate angles.

7. At 1000 ev and above (not shown) the difference between the first Born and the improved results persists hardly upto 5° scattering angle, as expected. This discussion naturally leads us to modify the present calculations so as to yield better results. The modifications in the present e-H_2 calculations fall into two catagories, (a) the improvement of the atomic scattering amplitude, and (b) improvements in the IAM formulation itself.

4.5 The IAM with an Improved HHOB Amplitude

The atomic scattering amplitude in the HHOB can be improved by one of the methods discussed in the last chapter. Particularly, the behaviour of this approximation being unsatisfactory at large angles, we have corrected the same by replacing 'Re 2' with 'Re f_{w2}~~2~~' at large angles. Thus for $q > k_i$, we take

$$\text{Re } 2 \doteq \text{Re } f_{w2} \qquad (4.18)$$

This, as we have seen, is plausible since the difference between these two terms lies in the fact that the average excitation energy, $\bar{W} = 0$ for Re f_{w2}. Presently, calculations are done with the HHOB corrected for 'Re 2' and employed in the IAM; these are shown graphically at 100 ev in the fig. 4.7. The correction proves to be very good and the results are satisfactorily in accord with the data of Van Wingerden et al (1977). The DCS obtained in this manner will be quite reliable at all energies considered presently. The other improvement consists in writing the atomic scattering amplitude as,

$$f_{MG1} = f_{B1} + i \text{ Im } f^{(2)}_{HEA} + \text{Re } 1 + \sum_{n \geq 3} f_{Gn} \qquad (4.19)$$

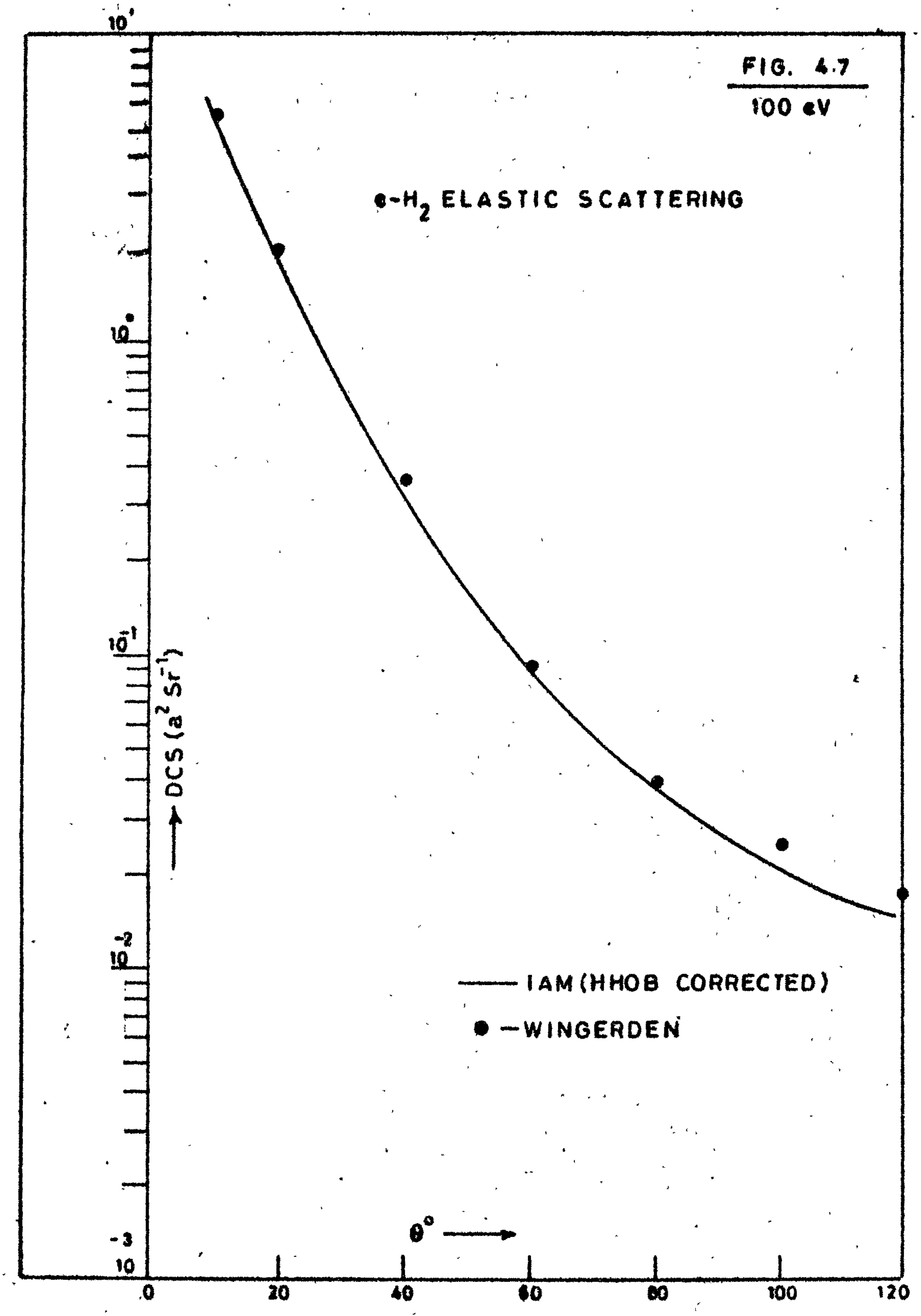
FIG. 4.7
100 eV
e-H_2 ELASTIC SCATTERING
IAM (HHOB CORRECTED)
● —WINGERDEN
→ DCS (a^2 Sr^{-1})
θ° →
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
0
20
40
60
80
100
120

Briefly, this amplitude surves three purposes simultaneously, viz. (i) it gives the imaginary part of the second term which is finite at $\theta = 0$, (ii) it has an inherent real part of the second term, $O(k_i^{-1})$ to account for target polarization, and (iii) the higher order terms ($n \geq 3$) of the Glauber series are also included. This expression differs from Gien's (1977) modified Glauber approximation basically in the manner of including the second Born term. The amplitude of eqn. (4.19) is theoretically more satisfying. This approach can be taken up within the IAM also, i.e. we can obtain the amplitude of the eqn. (4.19), with the effective charge $Z = 1.2005$ for the hydrogen atom and convert into elastic e-H_2 DCS, using eqn. (4.14). We may call them 'MG1' results, as against the 'MG' results of Jhanwar et al (1980 b) in the IAM. These two would differ slightly in the large-angle region. But comparing even the EBS (Jain et al 1979) results and the MG results (Jhanwar et al 1980b) the difference is hardly discernible. This fact discourages us to calculate for the MG1 results. To see the effect of higher order terms, we have simply converted the e-H results ($Z = 1$) of the UEBS method (Byron et al 1982) at 400 ev into the e-H_2 DCS. These are shown in table 4.5. Note that after taking the valance-bond correction,

Table 4.5

Elastic e-H_2 DCS in the IAM using the UEBS amplitudes (Z = 1)

θ_{deg}	DCS (a_o^2 sr^{-1})	Data of Wingerden
20	3.95 - 01	3.28 - 01
40	3.12 - 02	3.3 - 02
60	9.9 - 03	1.0 - 02
80	3.1 - 03	3.5 - 03
100	1.49 - 03	1.7 - 03
120	1.02 - 03	-
140	7.53 - 04	-
160	5.8 - 04	-

the DCS would be still lower than the data of Van Wingerden et al (1977).

From the previous paragraphs, one can appreciate the need of an accurate amplitude of electron-atom scattering, to be used in the IAM. Apart from this, there are some other aspects of the formulation of the independent atom model itself which can be modified to make it more realistic. Such modifications are described in the next section.

4.6 Modifications in the IAM Formulation

A realistic independent-atom model for the elastic electron-molecule collisions must include the following physical aspects.

1. The molecular binding or valance-distortion effect.
2. An accurate atomic scattering amplitude, incorporating polarization and absorption distortion effects.
3. The exchange effect.
4. The multiple scattering effects.
5. The effect of intramolecular vibrations.
6. The anisotropy of molecular potentials.

Of these, the first three aspects are already covered in our previous discussion. Although, in (2) above, one must also include the effect of projectile

-distortion, espectially at lower energies. Now, the two points mentioned in (4) and (5) lead to changes in the basic assumptions of the IAM itself.

(A) Multiple scattering effects

We now discuss the repeated interactions of an incident electron successively with different atoms of a molecule. Consider the single and double scattering from two identical atoms A and B, separated by $R = | \underline{r}_a - \underline{r}_b |$, as shown in figs. 4.1(b) and 4.1(c). An incident electron scatters from A to B, so that the incident waves on B include the plane waves plus waves scattered from A to B, and this consideration also applies to scattering from B to A. The total scattered waves consist of singly and doubly scattered electrons, neglecting further multiple scattering. We follow Massey (1969) to write for the amplitude of the total scattered waves as,

$$\begin{aligned} F = {} & f(\underline{n}_o, \underline{n}_1) [1 + \exp ik_i (\underline{n}_o - \underline{n}_i) . \underline{R}) \\ & + R^{-1} e^{ik_i R} (e^{-ik_i \underline{n}_i . \underline{R}} f(\underline{n}_o, \underline{R}) f(\underline{R}, \underline{n}_1) \\ & + e^{-ik_i \underline{n}_o . \underline{R}} f(\underline{n}_o - \underline{R}) f(- \underline{R}, \underline{n}_1)] \end{aligned} \tag{4.20}$$

where, $\underline{n}_o$ and $\underline{n}_1$ are the unit vectors along the initial and final direction of the incident electron. The first term of eqn. (4.20) shows single scattering. The second term corresponds to an incident electron first scattered from A to B along R and finally from 'B' it is scattered in the direction $\underline{n}_1$. A similar situation, starting from B, is represented by the last term of (4.20). The first term of eqn. (4.20) gives the single scattering amplitude of the simple IAM, in terms of the atomic amplitude $f(\underline{n}_o, \underline{n}_1)$, i.e.,

$$f_1 = 2\langle f(\underline{n}_o , \underline{n}_1) \cos (\underline{q}. \underline{R}/2) \qquad (4.21)$$

which leads to the averaged DCS of eqn. (4.10). Now from (4.20) and (4.21),

$$\begin{aligned} |F|^2 = |f_1|^2 &+ 2 \operatorname{Re} f_1 \langle R_1^{-1} e^{-ik_iR} [e^{-ik_i\underline{n}_1 . \underline{R}} \\ &f^* (\underline{n}_o, \underline{R}) f^*(\underline{R}, \underline{n}) + e^{ik_i\underline{n}_o . \underline{R}} \\ &f^* (\underline{n}_o, \underline{R}) f^*(-\underline{R}, \underline{n}_1)]\rangle + O(R^{-2}) \qquad (4.22) \end{aligned}$$

or

$$|F|^2 = |f_1|^2 + \delta I \qquad (4.23)$$

Thus, we have to evaluate the second term of (4.23) i.e. δI. The evaluation of this double scattering term was first attempted by Hoerni (1956) for a hypothetical U_2 molecule. Even for such a heavy molecule, the effect of intramolecular scattering was found to be negligible at a very high energy of 40 Kev. Later Yates and Tenny (1972) used the Glauber approximation to investigate the multiple scattering effect in e-N_2 elastic scattering. In both these studies the valance bond effect was not taken into account. Most of the recent studies (e.g. Jain 1982) are made on heavy molecules like N_2, in which cases, it is not possible, as it stands today to include the valance-bond effect. Presently, let us work with the first Born approximation for simplicity but include the variational parameter 'Z' for the H_2 molecule, thus taking the valance-distortion into account. The double scattering term δI consists of four terms, of which a typical one is written below.

$$\delta I1 = 2R^{-1} f(\underline{n}_0, \underline{n}_1)\, f(\underline{n}_0, \underline{R})\, f(\underline{R}, \underline{n}_1)$$

$$X \cos(k_i R - k_i\, \underline{n}_1 \cdot \underline{R}) \qquad (4.24)$$

This is obtained from eqns. (4.22) and (4.23). Now, to obtain the DCS overaged over all orientations of the molecular axis, we require, e.g.

$$\delta I1 = \frac{2}{4\pi R} \int_0^{2\pi} \int_0^{\pi} d\phi_R \sin\theta_R \, d\theta_R \, f(\underline{n}_0, \underline{n}_1)$$

$$f(\underline{n}_0, \underline{R}) \times f(\underline{R}, \underline{n}_1) \cos(k_i R - k_i \underline{n}_1 . \underline{R}) \qquad (4.25)$$

Here, the angular integrations are made difficult by the three directions $\underline{n}_0$, $\underline{n}_1$ and $\underline{R}$ required to be considered. The ϕ_R -integration is possible to be done analytically and the θ_R-integration has been presently done by us, numerically. The present results are shown in the tables 4.6 and 4.7. The double scattering term δI is tabulated ~~t~~ at 50, 200 ev in tables 4.6 and 4.7. The single and double scattering contributions, to the e-H_2 DCS are compared at 100 ev. These calculations lead to the following conclusions.

1. The effect of double scattering (DS) is relatively very small for the H_2 molecule, e.g. at 50 ev, the DCS in the forward direction is about 15 to 20 a_0^2 Sr^{-1}, while the DS contribution is -0.096 a_0^2 Sr^{-1}. The DS effect is practically nil above 100 ev i.e. the region where the IAM results are quite reliable.

2. It is interesting to note that the DS contribution is negative at 50 ev for all angles but has either sign

Table 4.6

The double scattering contribution in the IAM for e-H_2 scattering

Scattering angle deg	50 ev	200ev
05	- (9.6 - 02)	4.6 - 03
10	- (9.4 - 02)	4.2 - 03
20	- (8.8 - 02)	3.4 - 03
30	- (8.3 - 02)	2.6 - 03
40	- (7.7 - 02)	1.9 - 03
60	- (6.8 - 02)	1.3 - 03
80	- (6.5 - 02)	9.0 - 04
100	- (6.6 - 02)	8.5 - 04

Table 4.7

Comparison of the single (I_S) and double (I_D) scattering DCS (a_o^2 sr^{-1}) at 100 ev

Scattering angle deg	I_S (a)	I_D (b)
5	8.8 + 00	-(9.6 - 04)
10	5.2 + 00	-(8.7 - 04)
20	2.0 + 00	-(5.8 - 04)
40	3.7 - 01	+ 1.8 - 04
60	1.0 - 01	+ 1.5 - 04

above 50 ev. In particular, at intermediate angles, the contribution is positive. The relative magnitude of the DS term is more appreciable towards small angles.

3. It is thus seen that the DS contribution to e-H_2 cross-sections is not appreciably large, and can be neglected. But it is not the case with larger molecules like N_2, O_2, CO etc. The task of calculating the DS contribution in these molecules is quite involved. Let us show here a simple method of estimation.

For cases like N_2, O_2 etc. first we ignore the valance-bond correction. To estimate the DS contribution, in the first Born approximation, we have to evaluate the equation like (4.25), for which we need the first Born term of the atomic scattering amplitude. Now, using the static potentials of Cox and Bonham (1967), the first Born amplitudes are easily expressed. Thus, we need to evaluate, for a homonuclear diatomic molecule containing the atoms of atomic number 'Z',,

$$\delta I1 = \frac{16Z^3}{4\pi R} \sum_{i,j,k} \int_0^{2\pi} \int_0^{\pi} d\emptyset \sin \theta_R \, d\theta_R$$

$$\gamma_i \, \gamma_j \, \gamma_k \times \frac{\cos (k_i R - k_i \, \underline{n}_1 . \underline{R})}{(Q_1^2 + \lambda_i^2)(Q_2^2 + \lambda_j^2)(Q_3^2 + \lambda_k^2)} \qquad (4.26)$$

where, considering the single and double scattering, we have to define properly the momentum-transfers $\underline{Q}_1$, $\underline{Q}_2$ and $\underline{Q}_3$. This approximate procedure can also prove to be simpler upto molecules like O_3, H_2O etc. Some relevant details regarding the multiple scattering are also discussed in section (4.10).

(B) The effect of nuclear vibrations

Previously in section (4.2) we have assumed the two nuclei of a diatomic molecule to be fixed at the equilibrium separation R. However, this is unphysical. The effect of molecular vibrations though very small, can be considered in the IAM in a simple way by assuming the vibrations of the atomic nuclei to be simple harmonic. Thus, from the eqn. (4.9) we are required to obtain for harmonic vibrations,

$$\bar{I}(\theta) = \sum_{i,j} f_i^* f_j \int_0^{\infty} \left(\frac{\alpha}{\pi}\right)^{1/2} e^{-\alpha(r-R)^2} \frac{\sin qr}{qr} \, dr \qquad (4.27)$$

where α is related to the mass and the vibrational frequency of the nuclei. It can be shown that this amounts to replacing 'R' of the IAM formula (4.10) by the term $(R^2 + (1/2\,\alpha))^{1/2}$. Here '$\alpha$' being large, the correction is quite small.

Khare and DeoRaj (1982) have used the following formula in their treatment of $e-CO_2$ elastic scattering, to account for the nuclear vibrations,

$$\bar{I}\ (\theta) = \overline{\sum_{i=j=1}^{N} |f_i|^2 + \sum_{i \neq j} f_i f_j^*} \quad e^{-lg^2 q^2/2} \quad \frac{\sin qr_{ij}}{qR} \qquad (4.28)$$

with the symbols of Massey (1969). This equation takes into account the anharmonicity of nuclear vibrations and hence it is more realistic. In these calculations, it is difficult to judge the role of molecular vibrations i.e. their relative effect on the ~~d~~ DCS. It appears from the expression (4.28) that the effect of vibrations must be large at small 'q'. As yet, no systematic study has been done. However, Hermann et al (1976) have noted that the effect of nuclear vibrations is smaller than that of experimental errors, for N_2.

4.7 $e-H_2$ Elastic Scattering Using Molecular Wave Functions

We now turn to the collision theories treated in the molecular frame-work. If one wants to start with a molecular wavefunction to calculate the scattering cross-sections, there are at least two problems encountered. Firstly, the exact wave functions are not available and the existing accurate wave functions are often complicated to work with. Secondly, problems are there with the multicentre nature of molecular system itself. While the first one is unavoidable, the second one is simplified by the use of the one-centre wave function. Again~~st~~ here our focus is on the H_2 molecule for which approximate wave functions have been reasonably successful. The accuracy of a wave function lies in how closely it predicts the ground-state energy and other properties like the quadrupole moment, for example For the H_2 molecule, the following wave functions are considered as highly accurate. (i) Two-centre wave function of Kolos and Wolniewitz (1965), (ii) the wave function given by Davidson and Jones (1965) and (iii) single-centre wave function of Hayes (1967).

Even the first Born calculations can be difficult with an accurate wave function. Earlier on, Hara (1967) had used a simple two centre wave function of H_2 mainly for low-energy treatment. Liu and Smith (1973) and Ford and Browne (1973) used two-centre wave functions to obtain the first Born approximation for the e-H_2 system. The highly accurate one-centre wave function of H_2 molecule given by Hayes (1967) is a 57-term expansion in the Slater-type orbitals. This was employed by Gupta and Khare (1978) to obtain the first Born e-H_2 amplitudes. It is observed that a small difference between these calculations and the ones using highly accurate two-centre wave function, just mentioned, is found, that too only for small q ($< 0.5\ a_o^{-1}$) beyond which there is complete agreement. Here, we have compared the DCS obtained using Hayes' wave function (Gupta and Khare, 1978) with those using the IAM, both in the first Born approximation (see fig. 4.8). The IAM first Born DCS, with Z = 1.2005 are found to be higher than those obtained by any molecular wave function, at small 'q'. The difference between the IAM and the DCS with Hayes' wave function persists upto nearly $q = 4\ a_o^{-1}$, beyond which there is complete agreement. In our present work the first Born amplitudes of e-H_2 scattering calculated by Gupta and Khare (1978) using Hayes' (1967) wave function are utilized. Now, Jhanwar et al (1980 a) have determined the exchange amplitudes for e-H_2 system with the single-centre wave function of Hayes. Further to account for the target polarization effect a semiempirical potential was employed by Gupta and Khare (1978). When one uses such potentials, a clearcut advantage is that one does not

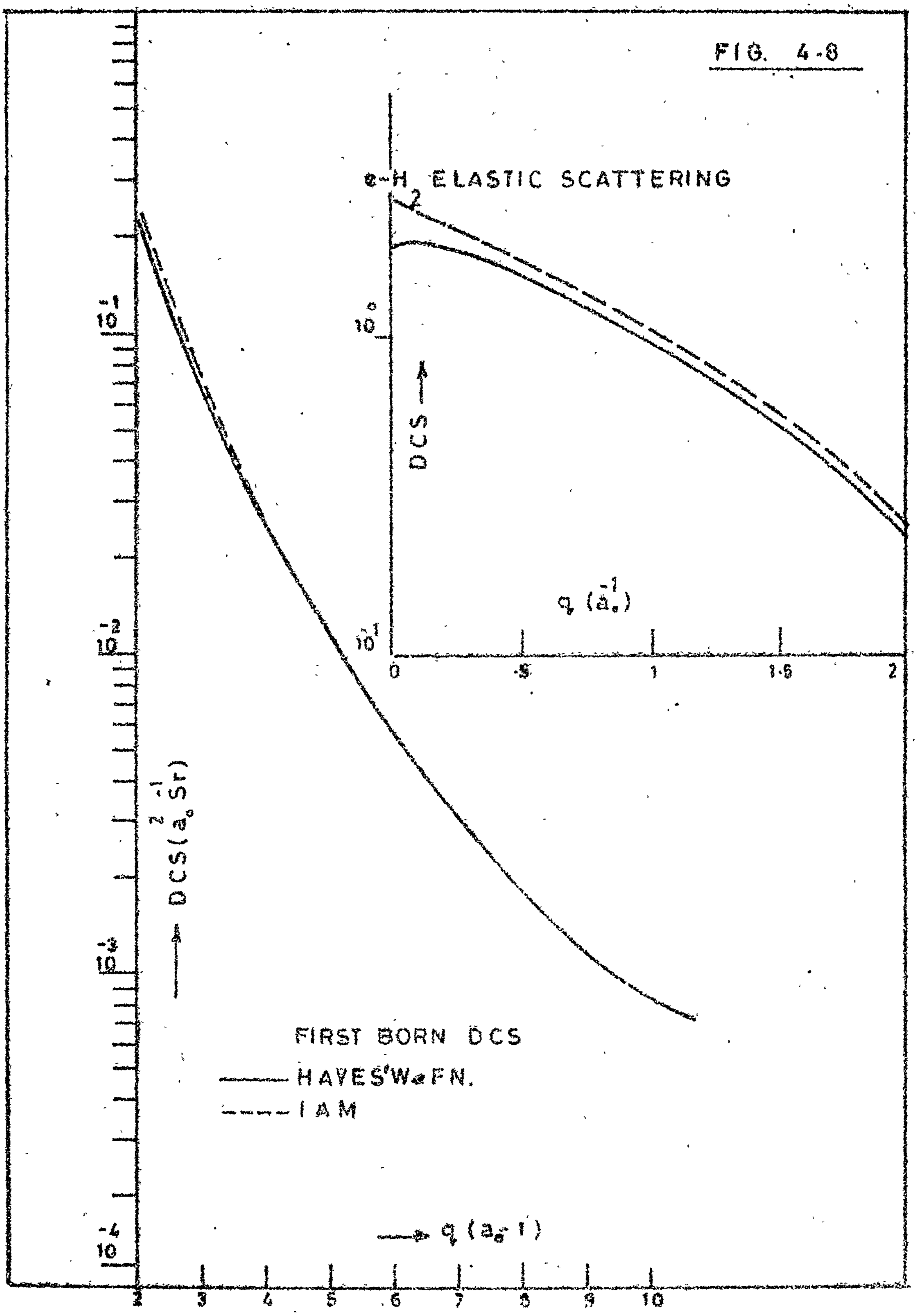

FIG. 4-8

e-H2 ELASTIC SCATTERING
DCS
q (a₀⁻¹)
10⁰
10¹
0
·5
1
1·5
2
10⁻¹
10⁻²
10⁻³
10⁻⁴
DCS(a₀² Sr⁻¹)
q (a₀⁻¹)
2
3
4
5
6
7
8
9
10
FIRST BORN DCS
HAYES' W. FN.
IAM

have to bother about wave functions. A realistic polarization potential must be dependent on the energy of the projectile. Gupta and Khare (1978) obtained satisfactory results with such a potential for the Hydrogen molecule.

It is interesting to compare the following molecular polarization potential with the atomic one given in chapter 3, through eqn. (3.91).

$$V_{dp}(r) = -\frac{\alpha_d\, r^2}{(r^2+d^2)^3} - \frac{\alpha_d'\, r^2}{(r^2+d^2)^3} \times P_2(\cos\theta) - \frac{\alpha_q\, r^4}{(r^2+d^2)^5} \qquad (4.29)$$

where d, α_d and α_q are related to the properties of the molecule, The anisotropic term $P_2(\cos\theta)$ is typical of any molecule. The absorption effect for H_2 molecule has also been considered in the optical potential formalism (Khare et al 1977). There is hardly any attempt to consider the projectile distortion in elastic e-H_2 scattering at intermediate energies.

It is well known that the real and imaginary parts of the second Born approximation correspond to these effects respectively. Thus, one must calculate the second Born amplitude for the e-H_2 problem which implies the need of a wave function of the target. Now, with an accurate wave function, to calculate even the first Born term itself is an involved task, so that the second Born calculations would be well nigh impractical. Fortunately, simple and spherically symmetric wave functions for the H_2 molecule are available, and their use in the second Born calculations does not introduce any serious error at the energies of our interest.

4.8 The HHOB Amplitude Using Carter's Wave function

Let us now discuss the second Born amplitude in the HHOB of Yates (1979) for e-H_2 elastic scattering, employing the wave function of Carter et al (1958) given by,

$$\Psi(r_1, r_2) = \phi(r_1)\,\phi(r_2) \tag{4.30}$$

with,
$$\phi(r) = \frac{N}{\sqrt{\pi}}\left(e^{-\alpha_1 r} + C e^{-\alpha_2 r}\right) \tag{4.31}$$

where,
$$N = 1.15098 \qquad C = -0.45073$$
$$\alpha_1 = 1.07315 \qquad \alpha_2 = 3.92868 \tag{4.32}$$

Carter's wave function has already been employed (Jhanwar et al 1980 a) to study the second Born approximation for the e-H_2 system. With this wave function the calculations are similar to the e-He problem. However, the terms depending on the internuclear separation $\underline{R}$ can still cause considerable trouble; we return to this point shortly.

Now, considering the molecular midpoint as the origin, the potential of interaction between a projectile electron and the hydrogen molecule is,

$$V(\underline{r}, \underline{r}_1, \underline{r}_2, \underline{R}) = -\frac{1}{|\underline{r} - \underline{R}/2|} - \frac{1}{|\underline{r} + \underline{R}/2|} + \sum_{i=1}^{2} \frac{1}{|\underline{r} - \underline{r}_i|} \qquad (4.32)$$

where $\underline{r}_i$ $(i = 1, 2)$ are the coordinates of the two target electrons and $\underline{r}$ is that of the incident electron. $\underline{R}$ is the internuclear vector, initially assumed to be fixed. Writing the wave function of the target as in eqn.(4.30), let us attempt to evaluate first the imaginary part of the second Born amplitude in HHOB i.e. eqn. (3.43) of the previous chapter,

$$\text{Im}\, f^{(2)}_{\text{HEA}} = \frac{4\pi^3}{k_i} \int d\underline{p} \, \langle \psi(r_1, r_2) \, | \bar{V}_1 \bar{V}_2 | \, \psi(r_1, r_2) \rangle \qquad (4.33)$$

where, the quantities

$$\bar{\bar{V}}_1 = \bar{V}_1 (\underline{p} + \underline{p}_z) \quad (4.34a)$$

and

$$\bar{V}_2 = \bar{V}_2 (\underline{q} - \underline{p} + \underline{p}_z) \quad (4.34b)$$

are the Fourier transforms of the potential of eqn. (4.32). The Fourier variables are introduced in chapter 3. Further let us introduce,

$$\underline{R} = \underline{B} + \underline{Z} \quad (4.35)$$

Now it is not necessary to write the explicit forms of eqn. (4.34a) and (4.34b). The Fourier transform of the first two terms in the potential, eqn. (4.32), is given below,

$$F(R) = \frac{-1}{2\pi^2 (p^2 + p_z^2)} \times \cos \left(\underline{p}.\frac{\underline{B}}{2} + p_z \frac{Z}{2}\right) \quad (4.36)$$

It is instructive to consider the first term in eqn. (4.33) that arises out of the product of these Fourier transforms; we consider for example,

$$\mathrm{I1} = \frac{1}{\pi k_i} \int \frac{d\underline{p}}{(p^2+\beta^2)(|\underline{q}-\underline{p}|^2 + \beta^2)} \iint d\underline{r}_1 \, d\underline{r}_2$$

$$\times \; |\psi(r_1, r_2)|^2 \times 4 \cos\left(\underline{p}\cdot\frac{\underline{R}}{2} + \beta \frac{Z}{2}\right)$$

$$\times \; \cos\left((\underline{q} - \underline{p})\cdot \frac{\underline{R}}{2} - \beta \frac{Z}{2}\right) \qquad (4.37)$$

This is the ~~m~~ nuclear term of Fourier transforms of interaction potential. Referring to the appendix, we find that the $\underline{p}$-integral of the last equation is far more difficult than the kind of integrals we have come across in the HHOB theory of the electron-atom cases (see chapter 3). In this type of calculations, whenever the nuclear terms containing $\underline{R}$ are involved, this difficulty is encountered. This amply speaks of difficulties in handling the molecular problems, which possess an axial symmetry. Note that the IAM avoids this difficulty of treating the $\underline{R}$-dependent terms. Also note that the difficulty would not arise with R = 0, i.e. in the He-atom (united atom) limit of the H_2 molecule. A similar problem is discussed by Jhanwar et al (1982b). They have started with a two-centre wave function for the H_2 molecule and after approximations, a resort is taken to the He-atom limit. This problem is attempted here in a different way.

Basically, consider the second Born amplitude of the HHOB, for elastic scattering from the ground state.

$$f^{(2)}_{HEA} = \frac{i}{2\pi k_i} \sum_{n=0}^{\infty} \int d\underline{r}\; e^{i\underline{q}.\underline{r}} \langle 0 | V\,(\underline{r}, \underline{x}) | n \rangle \int_{-\infty}^{\infty} dz'\, e^{-i\beta_{in}\, z'} \; H(z') \left(1 + \frac{iz'}{2k_i} \nabla^2_{z'}\right) \langle n | V\,(\underline{r} - \underline{z}', \underline{x}) \,|\, 0 \rangle \qquad (4.38)$$

where, $| 0 \rangle$ stands for the wave function of eqn. (4.30). Consider the matrix element,

$$\langle 0 \,| V\,(\underline{r}, \underline{x}) \,|\, n \rangle = \langle 0 \,|\, V^N \delta_{no} + V^e \,|\, n \rangle \qquad (4.39)$$

where V^N = the nuclear part of the interaction potential (4.32),

$$V^N = - \frac{1}{|\underline{r} - \underline{R}|2|} - \frac{1}{|\underline{r} + \underline{R}|2|} \qquad (4.40)$$

And,

v^e = the electronic part of the interaction potential.

$$= \sum_{i=1}^{2} \frac{1}{|\underline{r} - \underline{r}_1|} \qquad (4.41)$$

Note the Kronecker delta function, δ_{no}, with the nuclear part. This term does not contain the target -electron coordinates, hence for $n \neq 0$, the orthogonality of the target wave functions will leave that part of eqn. (4.39) to zero. And this also applies to the other matrix element of eqn. (4.38). There lies the trick ! If we drop the first term $n = 0$, from the sum over states in the second Born amplitude eqn. (4.38), we can get rid of the troublesome task of evaluating the nuclear-coordinate terms. Bonham (1971) introduced this procedure in a different context. The idea perhaps was that the polarization of the charge-cloud of the target is a virtual 'excitation' and the absorption corresponds to inelastic channels, hence in the sum over the states, $n = 0$ term may be dropped. Recently, Jhanwar et al (1980a) have also omitted $n = 0$ term and have successfully obtained the e-H_2 elastic DCS. However, $n = 0$ term corresponds to 'static' contribution in the second Born amplitude which can affect the large angle scattering.

Presently, our task is simplified by dropping the $n = 0$ term from the sum over states in the eqn. (4.38). Our second approximation is now to define the average energy parameter through,

$$\beta_{in} \doteq \beta = \bar{W}/k_i \qquad (4.42)$$

For the hydrogen molecule, $\bar{W}$ = 1.08 rydbergs. Due to eqn. (4.42) the sum over in eqn. (4.38) only affects the matrix elements, so that,

$$\sum_{n\neq 0}^{\infty} \langle 0 | V^e (\underline{r}, \underline{x}) | n \rangle \langle n | V^e (\underline{r} - \underline{z}', \underline{x}) | 0 \rangle$$

$$= \langle 0 | V^e (\underline{r}, \underline{x}) \; V^e (\underline{r} - \underline{z}', \underline{x}) | 0 \rangle$$

$$- \langle 0 | V^e (\underline{r}, \underline{x}) | 0 \rangle \langle 0 | V^e (\underline{r} - \underline{z}', \underline{x}) | 0 \rangle \qquad (4.43)$$

In arriving at this, the sum rule has been employed. Clearly then, we have to deal with the electronic terms only. Further from eqn. (4.43) we go for the usual procedure of the HHOB i.e. taking the Fourier representation etc. described in the chapter three. The present second Born amplitude splits up into real and imaginary terms, The resulting expressions are given below.

The expressions for the second Born terms in HHOB, obtained using the wave function of Carter et al (1958) for the H_2 molecule,

$$F_{B2} = i \,\mathrm{Im}\, F_{B2}^{HEA} + \mathrm{Re}\, F_{B2}^{HEA} \qquad (4.44)$$

$$\mathrm{Re}\, F_{B2}^{HEA} = \mathrm{Re}\, 1 + \mathrm{Re}\, 2, \qquad (4.45)$$

where, Re 1 and Re 2 are the terms of the real part of the second Born term, respectively of order $1/k_i$ and $1/k_i^2$.

$$\mathrm{Im}\, F_{B2}^{HEA} = \frac{8N^2}{\pi k_i} I_1 (\beta^2, 0) \sum_{i=1,3} (-D_i) \frac{a_i}{(q^2 + \lambda_i^2)}$$

$$- \frac{32N^4}{\pi^2 k_i} \sum_{\substack{i=1,3\\j=1,3}} a_i \, a_j \, D_i \, D_j \frac{1}{\lambda_i^2 \lambda_j^2} \Big[I_1(\beta^2, 0)$$

$$- I_1 (\beta^2, \lambda_i^2) - I_1(\beta^2, \lambda_j^2) + I_1(q^2, \lambda_i^2, \lambda_j^2) \Big] \qquad (4.46)$$

$$\mathrm{Re}\, 1 = - \frac{8N^2}{\pi^2 k_i} I_2 (\beta^2, 0) \sum_{i=1,3} (-D_i) \frac{a_i}{(q^2 + \lambda_i^2)}$$

$$+ \frac{32N^4}{\pi^2 k_i} \sum_{\substack{i=1,3\\j=1,3}} a_i \, a_j \, D_i \, D_j \frac{1}{\lambda_i^2 \lambda_j^2} \Big[I_2(\beta^2, 0)$$

$$- I_2 (\beta^2, \lambda_i^2) - I_2 (\beta^2, \lambda_j^2)$$

$$+ I_4 (q, \lambda_i^2, \lambda_j^2) \Big] \qquad (4.47)$$

$$\mathrm{Re}\ 2 = -\frac{4N^2}{\pi^2 k_i^2} D_B\ I_3\ (\beta^*, 0) \sum_{i=1,3} (-D_i) \frac{a_i}{(q^2 + \lambda_i^2)} + \frac{16N^4}{\pi^2 k_i^2} D_B \sum_{\substack{i=1,3\\ j=1,3}} a_i a_j\ D_i D_j\ (1/\lambda_j^2)$$

$$\left[I_2\ (\beta^*, \lambda_i^2) - I_4\ (q, -\lambda_i^2, \lambda_j^2)\right] \qquad (4.48)$$

Here, $a_1 = 1$, $a_2 = C^2$, $a_3 = 2C$

$$\lambda_1 = 2\alpha_1, \ \lambda_2 = 2\alpha_2, \ \lambda_3 = (\alpha_1 + \alpha_2). \qquad (4.49)$$

Further, $D_B = \frac{\partial}{\partial\beta}$ $\qquad D_k = \frac{\partial}{\partial\lambda_k}$

The constants of the wave function are from eqn. (4.32). The integrals I_1, I_2, I_3 and I_4 are defined by Rao and Desai (1981). Presently they are given in the appendix.

Having thus evaluated the amplitudes, we combine them with the exchange amplitudes 'g' in the Ochkur approximation and we employ the accurate first Born approximation obtained with the Hayes' (1967) wave function. The DCS for a particular orientation (θ_R, ϕ_R) of the molecule are given by,

$$I(\theta, \phi, \theta_R, \phi_R) = \left| F_{B1} - g + F_{B2} \right|^2 \qquad (4.50)$$

Lastly, the DCS averaged over all the molecular orientations,

$$\bar{I}(\theta) = \frac{1}{4\pi} \int I(\theta, \phi, \theta_R, \phi_R) \sin\theta_R \, d\theta_R \, d\phi_R \qquad (4.51)$$

4.9 Discussion of results obtained with the molecular wave function

The elastic e-H_2 DCS are obtained by us (Joshipura and Desai, 1983a) in the manner described, in the range of energy from 100 ev to 1000 ev. Already in ~~a~~ the figs. (4.3) through (4.6), the present DCS are plotted as curves marked 'B'. Also in fig. (4.4), at 200 ev the DCS of JKS (Jhanwar et al 1980a) obtained in a similar way, have been shown by curve 'D'. Additionally, our DCS are compared with the accurate first Born results (Hayes wave function) at 1000 ev in table 4.8. In that table, the data of Wingerden (1977) at 1000 ev are also given for comparison. On comparing various results we find that, (i) the results of JKS, curve D, are quite good at and above 200 ev (ii) the present work as well as that of JKS fails to incorporate the following two important aspects.

a) The term corresponding to ground state (n = 0) as the intermediate state is neglected. Although, it is true that it leads here to simplifications, the neglect

Table 4.8

Elastic e-H_2 DCS (a_0^2 Sr^{-1}) at 1000ev using Carter's wave function

Scattering angle (deg)	Present DCS	First Born DCS	Data of Wingerden
0	2.3 + 00	1.9 + 00	-
5	1.4 + 00	1.05 + 00	1.4 + 00
10	5.2 - 01	5.0 - 01	5.0 - 01
20	7.5 - 02	6.8 - 02	6.7 - 02
30	2.0 - 02	1.8 - 02	1.8 - 02
60	1.7 - 03	1.4 - 03	1.3 - 03

of this term can affect the DCS especially at large angles. We have already remarked about this prior to our derivation. In fact in the electron-atom theories, (e.g. Byron and Joachain, 1977) there have been attempts to consider the separate ('on shell') contribution of such a term in the second Born amplitude. This is done as given below.

$$f_{B2} = \overset{n=0}{f_{B2}}(\bar{W} = 0) + \overset{n\neq 0}{f_{SB2}}(\bar{W}) - \overset{n=0}{f_{B2}}(\bar{W}) \qquad (4.52)$$

The symbols are self-explanatory.

Now, from our results of curve 'B', it is seen that the DCS at 100 and 200 ev, near small angles tend to underestimate the experimental data. At first sight, it may seem that our results are good at large angles. But let us recall that the usual HHOB theory overestimates at large angles. Presently this overestimation is diluted by the absence of the term $n = 0$. The results of JKS, on the other hand agree with experimental data at all angles, while, from the prece~~e~~ding remarks, one should expect some underestimation, in these results also.

b) In an EBS approach, the amplitude must contain the third order term i.e., F_{G3}, which is missing in both the aforesaid calculations. In evaluating F_{G3}, even with Carter's wave function, the difficulties associated with the

R -dependent terms would also arise. Further, the contribution of the third and the higher order amplitudes is negative and its inclusion can reduce the cross-section. This has been mentioned in our e-H calculations also.

In view of this discussion, we conclude that looking to the complexity of handling molecular anisotropic terms, the methods related to the IAM will continue to play an effective role at intermediate and high energies.

4.10 The TCS, TECS and MTCS of e-H_2 Scattering

In the case of e-H_2 scattering a good amount of data for total cross-sections (TCS), total elastic cross-sections (TECS) and momentum transfer cross-sections (MTCS) is available. For a most recent piece of work, reference is made of Deuring et al (1983) for total e-H_2 cross-sections. Once, the DCS are known, the other cross-sections can be obtained by their definitions, given in the first chapter. The DCS provide the best test of the theory. Experimentally, the forward DCS are not obtainable. The TCS can tell us about the accuracy of the imaginary part of the forward elastic scattering amplitude Further, the TECS depend on the DCS values near the forward direction, mostly within 10 - 20^0 scattering angle. The MTCS depend on the small as well as large angle scattering. The tables 4.9 to 4.11 show respectively, the TCS,

Table 4.9

Total cross-sections (a_0^2) for e-H_2 scattering

Energy ev	Present results (a)	Present IAM results (b)	Hoffman et al[+] (experimental)
100	12.0	10.8	(9.8)* 9.14
200	7.20	6.30	5.96
400	4.10	3.57	3.57
700	2.30	2.22	-

*100 ev experimental results of Dalba et al (1980)

(a) in Carter's wave function, see section 4.8

(b) IAM, see section § 4.3

\+ quoted by Jhanwar et al (1982b)

Table 4.10

Total elastic cross-sections ($\times 10^{-16}$ cm^2)

Energy ev	Present results		Van Wingerden et al	Shyn and Sharp
	(a)	(b)		
100	0.72	0.85	0.88	0.77
200	0.40	0.41	0.51	0.39
400	0.14	0.16	0.15	-
700	0.085	0.085	0.073	-

(a) in Carter's wave function, see section 4.8

(b) IAM, see section 4.3

Table 4.11

Momentum transfer cross-sections ($\times 10^{-16}$ cm^2)

Energy ev	Present results		Shyn and Sharp
	(a)	(b)	
100	0.19	0.20	0.15
200	0.056	0.061	0.060
400	0.013	0.017	-
700	0.0077	0.0088	-

(a) in Carter's wave function, see section 4.8

(b) IAM, see section 4.3.

Table 4.12

The IAM results (a_0^2 units)

Energy ev	Total cross-section σ_{tot}	Total elastic cross-section σ_{el}	Total inelastic cross-section σ_{inel}
100	10.8	3.04	7.76
200	6.3	1.43	4.87
400	3.57	0.57	3.00
700	2.22	0.31	1.91

TECS and MTCS of the present calculations. For the TCS, we make use of a recent result (Jhanwar et al 1982b) which relates the scattering amplitude of the H_2 molecule with that in the united atom (He-atom) limit. The relation is given by,

$$f_{B2}^{H_2} = \cos (\underline{q} \cdot \underline{R}/2) \; f_{B2}^{He} (Z) \qquad (4.53)$$

This leads to the averaged DCS, for the H_2 molecule.

$$\bar{I}(\theta) = \frac{1}{2} \mid f^{He} (Z) - g^{He}(Z) \mid^2 (1 + \frac{\sin qR}{qR}) \qquad (4.54)$$

Presently, we have calculated the forward scattering amplitude with the H_2 molecule wave function by taking $R = 0$. The TCS are obtained via optical theorem. In the tables 4.9 to 4.11 the present results under (a) employ the molecular wave function and those under (b) employ the IAM (section 4.3) calculations.

In the IAM the imaginary part of the forward elastic e-H_2 scattering amplitude is obtained from the atomic amplitude as follows,

$$\mathrm{Im}\, f_{HEA}^{(2)} (q = 0) = \frac{4}{Z^2 k_i} (\ln (4Z\, k_i) - \frac{1}{4}) \qquad (4.55)$$

The imaginary part next to this in the HHOB, is of order

k_i^{-3} and it does not have an appreciable contribution. All the same, the higher order terms in the MG formulation can reduce the TCS, especially at the lower side of the present energy range.

A comparison of all these cross-sections is made mainly with measurements of Van Wingerden et al (1977) and Shyn and Sharp (1981). The table 4.9 includes the experimental values of Hoffman et al (see Jhanwar et al 1982b) and Dalba et al (1980). Considering the small differences in various data, we find that our results are satisfactory. The results employing Carter's wave function are at variance with the other results. The MTCS are generally used for low energy work and this quantity is quite small at high energies, but since data at 100 and 200 ev are available, the calculations are made for comparison. Lastly, table 4.12 shows total cross-sections, together with total elastic and inelastic cross-sections.

4.11 Elastic Scattering of Electrons from Molecules Other than H_2

Apart from H_2 some of the other molecules for which the elastic electron-scattering is studied are, N_2, O_2, CO, CO_2, CH_4, etc. Mention has been made about some of them in our previous discussion. Remarkably, for almost all cases the Independent Atom Model has been used. This is necessitated by the problem of molecular wave functions in the cases other than H_2. In principle the wave functions can be constructed by linear combination of atomic orbitals but in practice, they are computationally quite tedious. Even with the IAM the very first problem is of valance-bond correction, no simple method is known to account for the valance-distortion. The valance-bond correction in the IAM also implies consideration of terms in the scattering amplitude showing the overlap of atomic orbitals in the molecule. The overlap integrals are difficult to handle. And the situation worsens for big molecules with a relatively small bond-length e.g. N_2, for which the overlap is considerable. Finally in such cases, the multiple scattering is also considerable. We know from the e-H_2 results that neglect of the valance distortion leads to somewhat higher cross-sections. The other corrections are certainly more effective in other molecules than in H_2. Keeping this in mind we proceed for simple calculations.

The amplitude (f_M) of the electron-molecule scattering is related to the corresponding electron-atom amplitude (f_A) for homonuclear diatomic molecules, as given below,

$$f_M = 2 \cos (\underline{q} \cdot \underline{R}/2)\, f_A \qquad (4.56)$$

This can be used to estimate the total cross-sections. From our previous results (chapter 3) for the TECS of Carbon, Nitrogen and Oxygen atoms, obtained with the Cox-Bonham potentials, we estimate the TCS of various relevent molecules. In general, these results can be expected to be good at high energies, when the static potentials dominate. Towards lower energies the present results are higher due to reasons mentioned.

Take for example the e + LiH scattering in which multiple scattering may be small enough to be neglected at and above 100 ev. The TECS for LiH are shown in Table 4.13. Here, the valance-correction for H-atom (Z = 1.2005) as done in the H_2 molecule, is retained, in an attempt to mock the effect. The total elastic cross-sections for O_2 molecule are shown in the table 4.14. A comparison is made with the results of Khare and Raj (1982) who employed the static and polarization potentials along with partial waves in the IAM. Also in the table 4.14 we have shown the TECS of electron scattering by Ozone gas, which is of atmospheric interest. In O_3, the bond length is large so that the overlap may be small hence the simple IAM can be expected to be more justified (see also table 4.1). To our information, no data, either theoretical or experimental, are available on e + O_3 collisions. The table 4.15

Table 4.13

Total elastic cross-sections for e-LiH scattering

Energy ev	TECS (a_o^2)
100	11.5
200	5.9
400	2.81
700	1.57

Table 4.14

Total (elastic) cross-sections (a_0^2) using the IAM

Energy ev	Oxygen O_2		Ozone (O_3)
	(a)	(b)	(a)
100	44	-	66
200	23	-	35
300	15.7	10.7	23
400	12	8.5	18
500	9.6	7.2	14
700	7.0	-	10
1000	5.0	-	7.5

(a) with Cox-Bonham potentials

(b) Khare and Raj (1982)

Table 4.15

Total (elastic) cross-sections for N_2 and CN (a_o^2 units)

Energy ev	N_2 (a)	N_2 (b)	Cynogen CN
100	42	-	41
200	22	-	21
300	15	10.3	14.6
400	11.4	8.37	11
500	9.00	7.15	8.8
700	6.5	-	6.3
1000	4.6	-	4.4

(a) with Cox-Bonham potentials

(b) Khare and Raj (1982)

shows the TECS for the N_2 molecule, for which the double scattering effect is expected to be considerable. If I_m and I_a are molecular and free-atom cross-sections respectively, then from eqn. (4.10),

$$\frac{I_m}{2I_a} = 1 + \frac{\sin qR}{qR} \qquad (4.57)$$

Hermann et al (1976) experimentally obtained $I_m/2I_a$ for Nitrogen at different angles and incident energies. They found that the ratio agreed with the theoretical value, eqn. (4.57) at high energies. At 100 and 200 ev the agreement was found only after 30° angle, showing the multiple scattering and valance-bond effects in N_2. In table 4.15, we have estimated the TECS for e + CN system. The Cynogen (CN) molecule is of astrophysical interest. We have not found any data in this case also for comparison.

It is instructive to draw an analogy between the Born or the Glauber multiple scattering approach and the multiple scattering within the molecule which we discuss presently. In the former case, the projectile hits the same target ~~ap~~ repeatedly, and in the process excites its virtual states. The multiple or 'intramolecular' scattering in the present context, is a process in which the projectile is tossed, so to say, repeatedly among the different atoms within the molecule. In our eqn. (4.24) or (4.25), the treatment is of first order for the atomic amplitudes and of the second order (double scattering) for the intramolecular collisions. Hence, the virtual excitation does not appear. Mention must be made of a recent interesting analysis in this regard (Jhanwar et al 1982b). Here, considering H_2 as composed of atoms A and B, the second Born amplitude is obtained in the form,

$$f_{B2}^{H_2} = f_{AA} + f_{BB} + f_{AB} + f_{BA} \qquad (4.58)$$

The first two terms represent the double scattering from each of A and B, typical of the second Born term. The last two terms correspond to the 'intra molecular' or double scattering (DS) between A and B in the second Born approximation. The following eqn. clarifies the point further,

$$f_{AB} = \frac{1}{32\,\pi^4} \sum_n \int \frac{d\underline{K}}{K^2 - k_n^2 - i\epsilon}$$

$$\langle 0\,,\,\underline{k}_f \,|\, V_A \;\; n,\,\underline{K} \rangle \langle n,\,\underline{K} \,|\, V_B \,|\, 0,\,\underline{k}_i \rangle \qquad (4.59)$$

where, V_A and V_B are the atomic potentials. This has been evaluated, after approximations, by using the Feynmann technique. Alternatively, we may employ the

Green's function expansion.

Hayashi and Kuchitsu (1976) employ static potentials and write the electron-molecule elastic scattering cross-section as a multiple scattering series,

$$\bar{I}(\theta) = I_S + I_{SS} + I_{SD}^{(1)} + I_{SD}^{(2)} + I_{DD}^{(0)} + \ldots \qquad (4.60)$$

Here, the first two terms are those of eqn. (4.10). The subscript 'SD' stands for 'single-double' scattering, 'DD' for double-double scattering, etc. These authors find that $I_{SD}^{(1)}$, the leading correction reduces the cross-sections by 20 to 60 % at 100 ev and 10 - 15 % at 500 ev for N_2. On the average, the IAM DCS are found to be reduced by 1/3 at 100 ev. These investigations are extended recently by A. Jain (1982), with both the short-range and the long range potentials, for the isoelectronic systems N_2 and CO between 40-800 ev. Later, this method is also employed in the case of e-CO_2 collisions (Jain and Tayal, 1982). The anisotropic part of the long range potential is not considered. The DS contribution is found to be appreciable at and below 100 ev and can be as high as 25 % of the IAM values. All these multiple scattering treatments are excluding the valance-bond correction. In discussing the elastic scattering of electrons from heavy molecules, we must mention a recent measurement on SO_2 molecule in the range 12-200 ev by Orient et al (1982).

4.12 Chapter Summary, Further Prospects

The present chapter has covered the study of elastic electron-scattering by molecules, in the energy range 100-1000 ev. The study is carried out in two ways viz., using the independent atom model and using a molecular wave function, with an aim to bring about the merits and demerits of the two approaches. It can be noticed that such a study is presently possible for e-H_2 system only. The IAM is a high energy formulation and its suitability depends on the interatomic separations in the molecule. Therefore, we have estimated the limit of applicability of the IAM, for a few molecules, as regards the incident energy. However, for H_2 molecule, the IAM results are found to be good even at 100 ev. The most important correction to IAM for e-H_2 scattering is found to be that due to valance-distortion. Presently, the HHOB amplitudes of e-H scattering are employed with valance-bond correction, Z = 1.2005. All the characteristics of the atomic amplitude are reflected in the IAM results. Therefore, a correction required in the HHOB atomic scattering amplitude is applied. With this, the IAM calculations can yield reliable results for e-H_2 system, at all angles and energies, considered here. A simple calculation of the double scattering within the molecule, is attempted. For H_2, this is insignificant, but the calculations help us in making predictions about other molecules. The second important effect is that due to nuclear vibrations. It is to be noted that in the whole study of molecular scattering, covered in the thesis, the vibrational ground state has been assumed. At least for the e-H_2 case again, the effect is unimportant.

If one proceeds, on the other hand, to calculate the second Born amplitude using a molecular wave function, then the double scattering is included in two ways, i.e. it includes the repeated collisions with the same atom and also the successive collisions with different atoms. Here, we have shown the calculation of the second Born amplitude in the HHOB, employing Carter's wave function. The DCS results are found to be satisfactory above 200 ev. Further, the other cross-sections are also obtained and comparison with the available data are made.

Finally, we have attempted the total cross-sections for molecules like LiH, N_2, O_2, CN and O_3 from our previouss results for the atomic cross-sections. The discrepancies in our results are attributed to the valance-bond and multiple scattering effects.

Towards further prospects in the treatment of elastic scattering of electrons by molecules, we note the following :

1. The strength of the IAM depends on the atomic scattering amplitudes used. In this regard the modified Glauber formulation of Gien (1977) has been successful both in the e-H and the e-H_2 scatterings. But the MG formulation needs a firm theoretical background. Ideally a theory should be able to 'generate' physical effects of polarization, absorption and multiple scattering without any problems of divergence etc. Since researches are going on in this direction, accurate amplitudes thus obtained should be incorporated in the IAM to derive the molecular cross-sections.

2. Atleast in the energy range 50-200 ev, the projectile distortion is considerable. For heavy targets the upper limit can be higher. Several attempts have been made, (e.g. Junker 1975, Kingston and Walters 1980), to account for this distortion in the case of e-H scattering. The effect must be analysed explicitly for molecular targets. For molecules like H_2, N_2, etc. we can try to analyse the distortion produced by the long-range quadrupole potentials of these molecules.

3. The simple IAM in the limit $R \longrightarrow \infty$ goes over to the separated atom approximation. The actual

molecule, say a diatomic one, is a system somewhere between this limit and the other extreme, viz. the united atom limit. Considerations like this might be guiding in determining the valance-distortion effect in heavy molecules. In the absence of a thorough analysis it is useful to be able to have a semi-empirical way of estimating the valance-bond corrections over the cross-sections, e.g. in employing the atomic amplitude in the IAM, the polarization potential of electron-atom interaction may be modified, say by properly redefining the average excitation energy. Also when two atoms combine to form the molecule, the electron-density distribution changes, hence the parameters of Cox-Bonham (1967) static potentials should be modified.

4. The IAM canbe extended to polar molecules like O_3, CN, LiH, SO_2, etc. The interaction between an electron and a polar molecule may be expressed as

$$V = V_{st} + V_L + V_{pol} \qquad (4.61)$$

where V_{st} and V_{pol} are the static and induced polarization potentials, which may be treated in the IAM. The permanent long-range dipole interaction V_L, which carries the anistropic properties of the molecule, may be treated within the first Born or, the Glauber approximation. Particularly, Lithium Hydride being a light molecule, only next to H_2, the effect of multiple scattering may be neglected. Drawing analogy from eqn. (4.14), we can write the IAM formula for e + LiH scattering,

$$\bar{I}(\theta) = \left(|f_{Li} - \tfrac{1}{2} g_{Li}|^2 + |f_H - \tfrac{1}{2} g_H|^2 \right) \times \left(1 + \frac{\sin qR}{qR}\right) \qquad (4.62)$$

5. The IAM will continue to play an important role in studying the scattering of electrons by molecules. It will also be worthwhile to apply this approach for other projectiles such as positrons, protons, etc.