

## Spin Polarization of Low-Energy Electrons Scattered Elastically from Atoms and Molecules\*

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The  $Z$  dependence of total spin polarization is systematically ascertained by tracing the trajectory of a particular zero of the scattered amplitude as a function of atomic number. The incident electron energy corresponding to 100% polarization is shown to increase linearly with increasing atomic number. In addition, it is found that total polarization is confined to a relatively narrow angular range for varying  $Z$ . Further calculations on the independent-atom model representation of electron spin polarization for electron-molecule collisions are given. Arguments leading to the improbability of obtaining enhanced polarization over the atomic case are presented. The most significant result of these calculations is the relative insensitivity of the spin polarization to the molecular parameters.

### I. INTRODUCTION

A search of the literature<sup>1-14</sup> of recent years shows a new resurgence of interest in the spin polarization of low-energy (less than 2000 eV) electrons scattered elastically from atomic and molecular targets.

Some workers<sup>6,13</sup> have suggested that the corresponding angular distributions may serve as very useful tools in obtaining more information about atomic and molecular potentials than is possible with the cross sections. With the advent of large computers, it has become possible to obtain accurate self-consistent-field (SCF) wave functions, and hence, greatly improved atomic potentials.<sup>15-17</sup> The experiments of Eitel, Jost, and Kessler<sup>7</sup> have shown that, for the energy range of 100–2000 eV and scattering angles of from 30° to 150°, no serious discrepancies exist between experiment and theory, as given by the calculations of Bunyan and Schonfelder,<sup>10</sup> and Holzwarth and Meister.<sup>9</sup> These workers used relativistic Hartree potentials determined by SCF calculations using the Dirac equations and imposing the Hartree assumptions.

The production of highly polarized electron beams is of considerable importance for the study of many processes, e.g., nuclear reactions and exchange scattering. High polarization effects for large atoms and low incident electron energies were predicted as early as 1941 by Massey and Mohr,<sup>18</sup> who also noted the diffraction minima in the angular distribution of the cross section, which are observed when the wavelength of the incident electron is comparable to atomic dimensions. Recently Buhning<sup>12</sup> analyzed the features exhibited by spin-polarization curves by considering the complex zeros of the scattered amplitude; whereupon it was predicted that total polarization can, in principle, be obtained for elements as light as neon. One aim of the present paper is to report results of calculations of combinations of energies and angles which lead to total polarization, and to follow these points as a function of atomic number. The particular advantage of our calculation to that described by Buhning is the use of better atomic fields which have been described in an earlier paper.<sup>19</sup>

The second part of this work is to report additional calculations using a model presented in a recent brief report<sup>14</sup> which describes the spin polar-

ization of electrons scattered elastically from molecular targets, the first experimental results of which, have been reported by Hilgner and Kessler.<sup>6</sup> In the following section, we give the Mott relations for scattering from a central field, and briefly sketch Buhning's analysis, followed by the results from the atomic calculations. Section III contains a detailed description of the independent atom model for electron spin polarization following electron-molecule collisions. The Appendix gives an abbreviated description of the numerical procedure used in the calculations.

### II. SPIN POLARIZATION: ATOMS

#### A. Theory

The wave equation for target atom plus incident electron can be written as

$$\left(H_0 + H - \frac{Z}{r_0} + \sum_{i=1}^N \frac{1}{r_{0i}}\right) \Psi(\vec{r}_0, \vec{r}_1, \dots, \vec{r}_N),$$

$$= (W + E_0) \Psi(\vec{r}_0, \vec{r}_1, \dots, \vec{r}_N), \quad (2.1)$$

where the undisturbed  $N$ -electron atomic system is represented by

$$H\Phi_m(\vec{r}_1, \dots, \vec{r}_N) = E_m \Phi_n(\vec{r}_1, \dots, \vec{r}_N), \quad (2.2)$$

where  $H$  is the time-independent Dirac Hamiltonian given by

$$H = \sum_i \left( c \vec{\alpha}_i \cdot \vec{p}_i + \beta_i mc^2 - \frac{Z}{r_i} \right) + \sum_{i < j} \frac{1}{r_{ij}}, \quad (2.3)$$

$$\text{and } H_0 = c \vec{\alpha}_0 \cdot \vec{p}_0 + \beta_0 mc^2, \quad (2.4)$$

where  $\alpha_{xi}$ ,  $\alpha_{yi}$ ,  $\alpha_{zi}$ , and  $\beta_i$  are the  $4 \times 4$  Dirac matrices, and  $W$  is the total energy of the incident electron,  $E_0$  is the total energy eigenvalue for the atom in its ground state.

A number of calculations have been made using relativistic Hartree fields,<sup>20</sup> i.e., ignoring electron exchange and correlation effects for the atomic electrons. However, an equation for the scattered electron which includes exchange effects can be derived by employing the Hartree-Fock (HF) scheme. The nonrelativistic treatment for electron-atom scattering in the HF approximation has been given elsewhere,<sup>21,22</sup> so only a rough sketch outlining the principal differences between relativistic and non-relativistic treatments will be given here.

The four-vector  $\Psi(\tilde{\mathbf{r}}_0, \tilde{\mathbf{r}}_1, \dots, \tilde{\mathbf{r}}_N)$  can be expanded in eigenstates of the complete Hamiltonian

$$\Psi(r_0, r_1, \dots, r_N) = \sum_{m=0}^{\infty} \Psi^m(\tilde{\mathbf{r}}_0, \tilde{\mathbf{r}}_1, \dots, \tilde{\mathbf{r}}_N), \quad (2.5)$$

where the  $\Psi^m$  are to be approximated by single Slater determinants of one-electron central-field wave functions

$$\Psi^m(\tilde{\mathbf{r}}_0, \tilde{\mathbf{r}}_1, \dots, \tilde{\mathbf{r}}_N) = [(N+1)!]^{-\frac{1}{2}} \times \begin{vmatrix} \psi^m(\tilde{\mathbf{r}}_0) & \psi^m(\tilde{\mathbf{r}}_1) & \dots & \psi^m(\tilde{\mathbf{r}}_N) \\ \varphi_1^m(\tilde{\mathbf{r}}_0) & \varphi_1^m(\tilde{\mathbf{r}}_1) & \dots & \varphi_1^m(\tilde{\mathbf{r}}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N^m(\tilde{\mathbf{r}}_0) & \varphi_N^m(\tilde{\mathbf{r}}_1) & \dots & \varphi_N^m(\tilde{\mathbf{r}}_N) \end{vmatrix}, \quad (2.6)$$

where  $\psi^m(\tilde{\mathbf{r}}_0)$  is the wave function of the scattered electron. It should be remembered that each one electron function is itself a four vector. The assumption is now made that  $\psi^m(\tilde{\mathbf{r}}_0)$  and  $\varphi_i^m(\tilde{\mathbf{r}}_j)$  are both solutions of the relativistic Fock Hamiltonian arising from the  $(N+1)$  electron system represented by (2.6), but in addition, it is also necessary to assume the  $\varphi_i^m(\tilde{\mathbf{r}}_j)$  are eigenfunctions of the  $N$ -electron relativistic atomic Fock Hamiltonian. The extent of these approximations and the connection of the  $N$ - and  $(N+1)$ -electron problem has been discussed by Bonham.<sup>22</sup>

A one-electron Hamiltonian for the scattered electron can now be obtained by substituting (2.5) into (2.1), multiplying by the atomic wave function for the  $p$ th state, i.e.,

$$\Psi_A^p = (N!)^{-\frac{1}{2}} \times \begin{vmatrix} \varphi_1^p(\tilde{\mathbf{r}}_1) & \varphi_1^p(\tilde{\mathbf{r}}_2) & \dots & \varphi_1^p(\tilde{\mathbf{r}}_N) \\ \varphi_2^p(\tilde{\mathbf{r}}_1) & \varphi_2^p(\tilde{\mathbf{r}}_2) & \dots & \varphi_2^p(\tilde{\mathbf{r}}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N^p(\tilde{\mathbf{r}}_1) & \varphi_N^p(\tilde{\mathbf{r}}_2) & \dots & \varphi_N^p(\tilde{\mathbf{r}}_N) \end{vmatrix}, \quad (2.7)$$

and integrating over the atomic coordinates. By making use of the appropriate orthonormality conditions, simplifying, and discarding the inelastic and non-exchange terms (we ignore the terms corresponding to exchange between the incident and atomic electrons, but not exchange between atomic electrons), we obtain

$$\left( H_0 - W - \frac{Z}{r_0} + \int \frac{d\tilde{\mathbf{r}}' \rho(\tilde{\mathbf{r}}')}{|\tilde{\mathbf{r}}_0 - \tilde{\mathbf{r}}'|} \right) \psi(\tilde{\mathbf{r}}_0) - \sum_{i=1}^N \int d\mathbf{r}' \frac{\varphi_i(\tilde{\mathbf{r}}') \psi(\tilde{\mathbf{r}}') \varphi_i(\tilde{\mathbf{r}}_0)}{|\tilde{\mathbf{r}}_0 - \tilde{\mathbf{r}}'|} = 0, \quad (2.8)$$

where  $\rho(r)$  is the relativistic electron charge density

$$\rho(\tilde{\mathbf{r}}) = \sum_j \varphi_j^*(\tilde{\mathbf{r}}) \varphi_j(\tilde{\mathbf{r}}) \quad (2.9)$$

with the summation index running over all occupied orbitals. The exchange term in (2.8) can be

replaced by Gaspar's average value<sup>23</sup> to get

$$[H - W + V(r)]\Psi(\tilde{\mathbf{r}}) = 0, \quad (2.10)$$

where the zero subscript has been dropped, with

$$rV(r) = -Z + \int_0^r 4\pi r'^2 \rho(r') dr' + r \int_r^\infty 4\pi r' \rho(r') dr' - \frac{r}{\pi} [3\pi^2 \rho(r)]^{1/3}. \quad (2.11)$$

Equation (2.10) is the usual Dirac equation for a central field and can be separated to give the following radial equation in Schrödinger form<sup>24</sup> for the scattering problem in atomic units as

$$\frac{d^2 g_l(r)}{dr^2} + \left( k^2 - \frac{l(l+1)}{r^2} - U_l(r) \right) g_l(r) = 0, \quad (2.12)$$

where

$$-U_l(r) = 2\gamma V(r) + \alpha^2 V^2(r) + \frac{l+1}{r} \frac{\eta'}{\eta} + \frac{1}{2} \frac{\eta''}{\eta} - \frac{3}{4} \left( \frac{\eta'}{\eta} \right)^2, \quad (2.13)$$

with  $\eta = (1+\gamma)/\alpha + \alpha V(r)$ , and where  $\gamma$  is the relativistic correction factor,  $\alpha$  is the fine-structure constant, and  $k^2 = (\gamma^2 - 1)/\alpha^2$  is the square of the magnitude of the incident wave vector.

The spin polarization caused by the interaction of the electron with a central potential is given by

$$P(\theta) = i(fg^* - f^*g)/I(\theta), \quad (2.14)$$

where  $f(\theta)$  and  $g(\theta)$  are the scattering amplitudes, and  $I(\theta)$  is the differential cross-section,

$$I(\theta) = |f|^2 + |g|^2, \quad (2.15)$$

with

$$f(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} [(l+1)(e^{2i\delta_l} - 1) + l(e^{2i\delta_{l-1}} - 1)] P_l(\cos\theta), \quad (2.16a)$$

and

$$g(\theta) = \frac{1}{2ik} \sum_{l=1}^{\infty} (e^{2i\delta_{l-1}} - e^{2i\delta_l}) P_{l-1}(\cos\theta), \quad (2.16b)$$

where  $\delta_l$  and  $\delta_{l-1}$  are the Dirac phase shifts.

For the energies in which we are interested, large values of the polarization occur only in a very narrow angular range around a minimum in the cross section curve. A minimum in the cross section is thus due primarily to one of the complex zeros,  $z_0 = a + ib$ , of  $f(z = \cos\theta)$  situated near the real axis. Buhning considered this and has written

$$f(x) = [x - (a + ib)] A(x), \quad (2.17)$$

$$\text{and } g(x) = d(x) A(x) e^{-i\varphi(x)}, \quad (2.18)$$

where  $z = x$  corresponds to physical values, and  $d(x) > 0$ . Then, on substitution into (2.14) and (2.15) to get relations for  $P(x)$  and  $I(x)$ , and assuming  $A$ ,  $g$ ,  $\varphi$ , and  $d$  to be constant in the neighborhood of a minimum in the cross section, one arrives at the following condition for total polarization:

$$b = \pm d \cos\varphi. \quad (2.19)$$

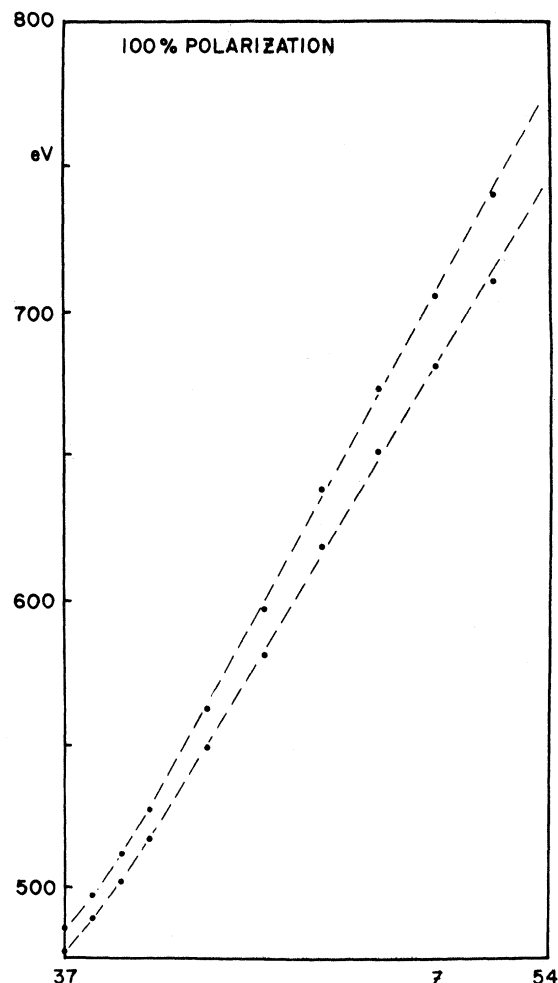


FIG. 1. Points of total spin polarization plotted as incident electron energy versus atomic number. The upper curve refers to positive polarization values and the lower to negative values.

### B. Results

Our calculations for atoms have been confined to determining combinations of energies and angles which give rise to total polarization as a function of atomic number. The results of these calculations are given in Figs. 1 and 2. It should first be remarked that these curves were computed by tracing the path of a particular zero of  $f(z)$  as a function of the nuclear charge. Two sets of points are plotted in Fig. 1 (distinguished by the dashed curves), the upper set corresponding to 100% positive polarization as defined by (2.14), and the lower points for the case in which the polarization is in the opposite direction. The most striking fea-

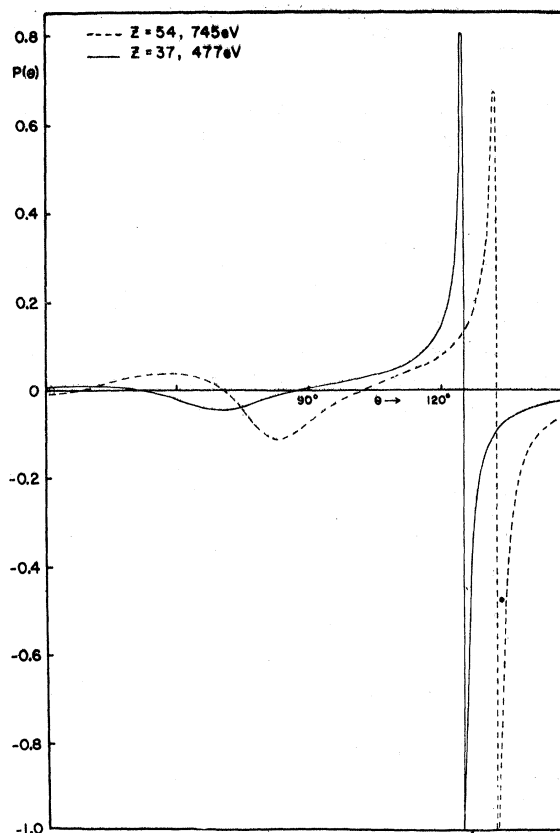


FIG. 2. Total negative spin polarization for  $Z=37$  and 54, for incident electron energies of 477 eV and 745 eV, respectively.

ture of the  $Z$  dependence is the near-linearity for increasing atomic number, which, of course, infers that additional points may be obtained by extrapolation. As shown, the energy separation of total positive and negative polarization increases with increasing atomic number. Figure 2 gives the angular distributions for  $Z=37$  and 54, and shows how the features of the curves are shifted to larger angles with increasing atomic numbers. It was also found, at least for the zero we chose to follow, that the large peaks were confined to an angular range of  $120^\circ$  to  $135^\circ$ . A large number of other calculations were made for smaller atoms which were in complete agreement with the general aspects of Buhring's discussion of total polarization for target atoms lighter than mercury. For  $Z < 7$  energy values corresponding to total polarization are all inside 30 eV, and as has been shown in an earlier paper,<sup>19</sup> the present description of the scattering process breaks down due to the increasing importance of incident and atomic electron exchange.

## III. SPIN POLARIZATION: MOLECULES

### A. Theory

As pointed out in an earlier paper,<sup>14</sup> if we consider a molecule, consisting of  $N$ -spherically symmetric atoms, and invoke the independent-atom model, then a very simple expression for the polarization resulting from electron-molecule collisions can be determined. By linear superposition the total scattering amplitudes,  $F(s)$  and  $G(s)$  are given by

$$(a) F(s) = \sum_{i=1}^N f_i(s) e^{i\vec{s} \cdot \vec{r}_i} \text{ and (b) } G(s) = \sum_{i=1}^N g_i(s) e^{i\vec{s} \cdot \vec{r}_i}, \quad (3.1)$$

where  $\vec{s} = \vec{k}_i - \vec{k}_f$  is the momentum transfer vector, i.e., the difference between the initial and final momentum vectors, and  $\vec{r}_i$  is the position vector relating the  $i$ th nucleus to the center of mass;  $f_i$  and  $g_i$  are defined by (2.16). Thus, by comparison with (2.14), the polarization in this case is

$$P(s) = \frac{i\langle FG^* - F^*G \rangle}{\langle |F|^2 + |G|^2 \rangle} = \frac{i\langle \sum_i (f_i g_i^* - f_i^* g_i) + \sum_{i \neq j} (f_i g_j^* - f_j^* g_i) e^{i\vec{s} \cdot \vec{r}_{ij}} \rangle}{\langle \sum_i (|f_i|^2 + |g_i|^2) + \sum_{i \neq j} (f_i f_j^* + g_i g_j^*) e^{i\vec{s} \cdot \vec{r}_{ij}} \rangle}, \quad (3.2)$$

where the brackets denote rotational and vibrational averages. Now if the effect of the collision of a beam of electrons with a molecule, initially in the ground state, is to excite all the rotational and vibrational states associated with that state, then (3.2), as a result of closure arguments<sup>25,26</sup> may be written as

$$P_m(s) = \frac{i \sum_i (f_i g_i^* - f_i^* g_i) + \sum_{i \neq j} (f_i g_j^* - f_j^* g_i) e^{-\frac{1}{2} l_{ij}^2 s^2} j_0(sr_{ij})}{\sum_i (|f_i|^2 + |g_i|^2) + \sum_{i \neq j} (f_i f_j^* + g_i g_j^*) e^{-\frac{1}{2} l_{ij}^2 s^2} j_0(sr_{ij})}$$

$$= \frac{2 \sum_i |f_i| |g_i| \sin(\eta_i^g - \eta_i^f) + \sum_{i \neq j} |f_i| |g_j| \sin(\eta_i^g - \eta_j^f) e^{-\frac{1}{2} l_{ij}^2 s^2} j_0(sr_{ij})}{\sum_i (|f_i|^2 + |g_i|^2) + \sum_{i \neq j} |f_i| |f_j| \cos(\eta_i^f - \eta_j^f) + |g_i| |g_j| \cos(\eta_i^g - \eta_j^g) e^{-\frac{1}{2} l_{ij}^2 s^2} j_0(sr_{ij})}$$

where the  $\eta_j$  are defined by  $f_j = |f_j| \exp(i\eta_j^f)$ , the  $l_{ij}$  are the amplitudes of vibration, and  $j_0$  is a spherical Bessel function of the first kind, and order zero.

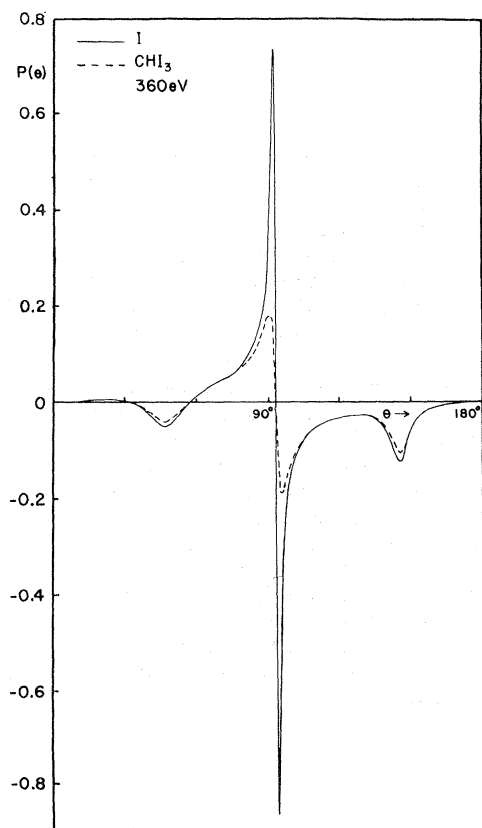


FIG. 3. Electron spin polarization curves for atomic iodine and  $\text{CHI}_3$ , for incident electron energies of 360 eV.

## B. Results and Discussion

Because of the simultaneous variations of the phase differences and  $j_0$ , as a function of  $s$ , it is not possible to make an exact statement with respect to the enhancement of polarization for electron-molecule collisions over electron-atom collisions without a complete definition of  $f_i$  and  $g_i$  as functions of energy and atomic number. However, as a result of a very large number of calculations on several systems over a wide range of energies, it seems apparent that enhancement is not possible; but if it can occur for molecular configurations not considered here, then it must occur for  $s < 2$ , for only in this region are the molecular terms (double sums) in (3.3) large enough to appreciably influence the magnitude of the polarization. Figures 3-5 show three such calculations.  $\text{CHI}_3$  and  $\text{AsBr}_3$  were chosen as examples since both molecules have large molecular-atomic ratios, i.e., the ratio of the double sum to the single sum in the denominator of (3.3). Also,  $\text{CHI}_3$ , owing to the large differences in atomic number of the constituent atoms, causes the  $\cos(\eta_i - \eta_j)$  factors to pass through zero, significantly reducing the polarization. The corresponding curve for  $\text{AsBr}_3$  would be expected to give results very nearly those of Br. In Fig. 3 the polarization curves for C and H are not given, since the magnitudes are less than  $10^{-2}$  throughout the entire angular range. This set of curves clearly shows the dilution effect of carbon and hydrogen on atomic iodine. The calculations for  $\text{AsBr}_3$  are more descriptive of the model, and are given for energies where very high peaks for both As and Br occur. Figures

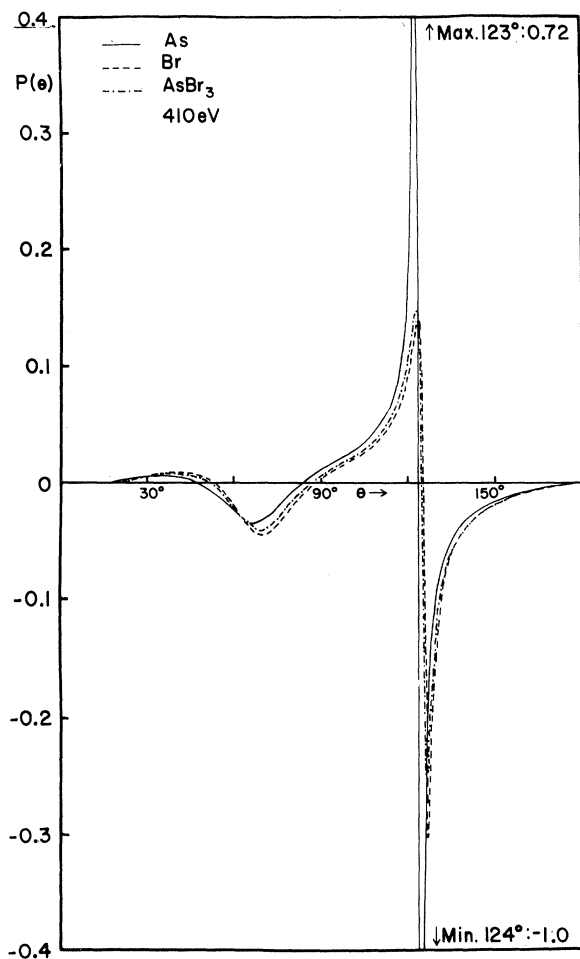


FIG. 4. Spin polarization curves for atomic As and Br, and for  $\text{AsBr}_3$ , for incident electron energy of 410 eV.

4 and 5, like the curves for  $\text{CHI}_3$ , show that the polarization due to the molecular collision is point by point less than that of the atom having the largest polarization at that point. Note that, as expected, the curves for  $\text{AsBr}_3$  follow very closely those of Br. In Fig. 4 the effect of As is to increase the polarization in the vicinity of the large peaks, where in Fig. 5, the effect is just the opposite. One of the more significant results of these calculations has been to show that with the appropriate combinations of energy and atomic numbers, the peaks for the molecule can be made slightly broader than the corresponding ones for the atoms. This can be made clear by noting the slight broadening of the peaks (at half height) for  $\text{AsBr}_3$ . Figures 3–5 together with equation (3.3) completely describe the model.

Hilgner and Kessler<sup>6</sup> have suggested that measurements of spin polarization of electrons scattered from molecules might be useful in determining molecular structure. The sensitivity of the polarization to the molecular description can be determined, for the present approximation, by varying the molecular parameters<sup>27</sup> defined in the preceding sub-section. The result of varying the I-to-I distances in  $\text{CHI}_3$  and the Br-to-Br distances in

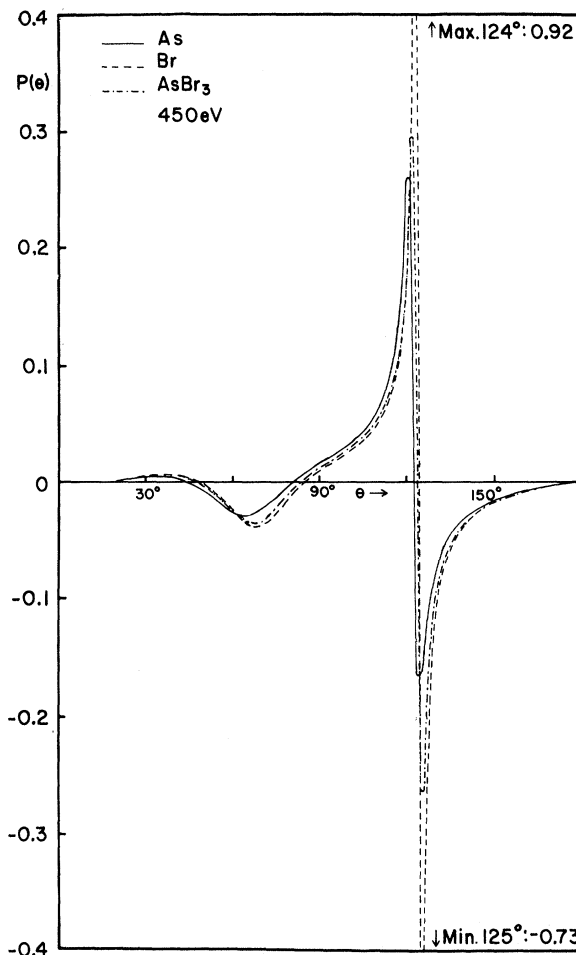


FIG. 5. Spin polarization curves for atomic As and Br, and for  $\text{AsBr}_3$ , for incident electron energy of 450 eV.

$\text{AsBr}_3$  by 0.1 Å are given for selected values of  $\theta$  in Tables I and II. Also given in the tables are the corresponding percentage deviations of the molecular cross-section [given by the denominator of (3.3)]. The most notable feature is that the polarization is highly sensitive to the bond distances in the vicinity of a zero of the polarization distribution. This effect is due to the slight shift of the curve (a few tenths of a degree) and its steepness. An overall comparison leads to the conclusion that the cross-section is more sensitive to the model than is the polarization. In any case, it appears that until the accuracy of the polarization measurements are considerably improved, the sensitivity is not enough to provide information about the molecule as accurate as that obtained from other measurements.

#### IV. CONCLUSIONS

A systematic approach to determining the behavior of total polarization as a function of atomic number was undertaken and the results of this investigation have been given in Sec. II.B. Using the best atomic fields which are presently available, a large number of combinations of energies and angles over a wide range of  $Z$  corresponding to to-

Table I. Change in polarization and differential cross section for  $\text{AsBr}_3$  for a variation of  $0.1\text{\AA}$  in the Br-to-Br nonbonded distance for 450-eV electrons. The angle  $\theta$  is in degrees,  $s = 2k \sin \frac{1}{2}\theta$ , and  $\Delta I$  and  $\Delta P_m$  are given as percentage differences in the absolute magnitudes.

$\theta$	$s$	$\Delta I(\theta)$ (%)	$\Delta P_m(\theta)$ (%)
5	0.95	6.73	0.47
6	1.14	8.42	<0.01
7	1.33	7.27	2.32
8	1.52	2.38	4.31
9	1.71	2.38	2.97
10	1.89	4.23	0.55
11	2.08	3.98	1.91
12	2.27	3.01	5.21
13	2.46	2.18	12.81
14	2.65	2.02	>100
15	2.84	2.52	8.61
16	3.03	3.11	1.35
17	3.21	2.98	1.01
18	3.40	1.71	1.62
19	3.59	0.58	1.49
20	3.78	3.42	1.10
21	3.96	6.20	0.68
22	4.15	8.08	0.31
34	6.36	6.86	0.28
35	6.54	5.41	0.65
36	6.72	2.79	0.94
37	6.90	0.15	0.98
38	7.08	1.56	0.69
39	7.26	2.07	0.14
40	7.44	1.78	0.58
41	7.61	1.35	1.35
42	7.79	1.38	1.98
43	7.97	1.98	2.27
44	8.14	3.02	1.98
45	8.32	3.84	0.92
46	8.49	3.76	1.11
47	8.67	2.45	5.34
48	8.84	0.59	51.10
49	9.02	2.85	8.95
50	9.19	5.56	3.22
51	9.36	7.32	1.26
52	9.53	7.47	0.32
53	9.70	5.63	0.11
81	14.12	0.38	1.21
82	14.26	2.56	1.38
83	14.41	4.52	1.50
84	14.55	5.89	2.12
85	14.69	6.39	0.34
86	14.83	5.86	0.51
87	14.97	4.31	0.36

Table II. Change in polarization and differential cross section for  $\text{CHI}_3$  for a variation of  $0.1\text{\AA}$  in the I-to-I nonbonded distance for 360-eV electrons. The angle  $\theta$  is given in degrees,  $s = 2k \sin \frac{1}{2}\theta$ , and  $\Delta I$  and  $\Delta P_m$  are given as percentage differences in the absolute magnitudes.

$\theta$	$s$	$\Delta I(\theta)$ (%)	$\Delta P_m(\theta)$ (%)
5	0.85	5.53	0.36
6	1.02	7.20	1.70
7	1.19	7.27	4.67
8	1.36	4.51	6.91
9	1.53	0.41	5.73
10	1.69	2.16	3.30
11	1.86	2.60	1.40
12	2.03	1.69	0.12
13	2.20	0.23	0.84
14	2.37	1.16	1.65
15	2.54	1.95	2.28
16	2.71	1.60	2.48
17	2.87	0.09	1.92
18	3.04	2.60	0.75
19	3.21	4.77	0.28
20	3.38	5.59	0.62
21	3.54	4.85	0.35
22	3.71	2.93	0.25
23	3.88	0.41	0.99
24	4.04	2.15	1.95
25	4.21	4.20	3.01
26	4.37	5.18	4.12
27	4.54	4.59	4.95
28	4.70	2.38	4.84
29	4.87	0.71	2.87
30	5.03	3.37	6.20
31	5.20	4.54	36.32
32	5.36	3.95	30.78
33	5.52	2.02	14.40
34	5.69	0.53	9.85
35	5.85	3.02	7.42
36	6.01	4.80	5.58
37	6.17	5.28	3.77
38	6.33	4.11	1.86
50	8.22	4.41	1.22
51	8.37	3.40	1.93
52	8.52	1.87	1.79
53	8.68	0.41	0.72
54	8.83	0.42	1.18
55	8.98	0.39	4.01
56	9.13	0.35	10.55
57	9.28	1.42	15.66
58	9.43	2.34	0.03
59	9.58	2.67	2.65
60	9.72	2.13	3.73
90	13.75	2.71	0.18
91	13.87	2.49	0.61
92	13.99	1.86	0.89
93	14.10	1.94	38.42
94	14.22	3.10	8.86
95	14.34	3.73	2.85
96	14.45	3.05	0.62

tal polarization were found, not all of which have been given here. These points of varying atomic number can be assigned to particular zeros of the scattered amplitudes. The general conclusion hence, is that the energies of 100% polarization [due to the trajectory of some predetermined zero

of  $f(\cos\theta)$  approaches linearity as a function of  $Z$  with increasing  $Z$ . For very small values of  $Z$  (e.g.  $Z < 10$ ), the half-widths of the large peaks are only a few tenths of a degree and would go unobserved by recent measurements<sup>7</sup> quoting angular resolutions of  $\pm 1^\circ$ . One further aspect of this sequence of calculations is that throughout the range of  $Z$ , the large peaks resulting from the same root of  $f(\cos\theta)$  are restricted to a relatively narrow angular range.

The description of spin polarization for electron-molecule collisions afforded by the independent atom model has so far proved to be an excellent approximation in regard to quantitative agreement between theory and experiment.<sup>14</sup> However, as has been shown in the preceding section, it appears that the precision of these measurements has not reached the level which would offer any serious competition to established methods of structure determination, e.g., intensity measurements in electron diffraction, positions of absorption or emission bands in spectroscopy, etc. But

the possibility of peak broadening in the angular regions corresponding to large values of the polarization should add considerably to the possibility of producing highly polarized beams of intensity higher than that previously obtained. It should also be clear from Figs. 3–5 what overlap of the atomic curves would induce high polarization or peak broadening for the corresponding molecule.

Finally it should be noted that, although the present description is capable of giving good results for some molecular configurations it might be expected to fail for molecules such as  $Sb_4$  or  $N_2$ , where intramolecular multiple scattering and binding effects, respectively, are thought to be quite important.

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#### APPENDIX

The phase shifts  $\delta_l$  defined by the asymptotic solution of (2.12),

$$g_l(r) \rightarrow (kr)^{-1} \sin(kr - \frac{1}{2}l\pi + \delta_l), \text{ as } r \rightarrow \infty,$$

are determined as usual by integrating the radial Dirac equation out to a point  $r=a$ , where  $V(a) \approx 0$ , and subsequently matching to the field-free solution.<sup>28</sup> This may be done using the summed form of the Noumerov algorithm.<sup>29,30</sup>

$$\Delta \xi_i = (h^2 A_i + h^4 A_i^2 / 12) \xi_i, \quad (\xi_{i+1} - \xi_i) = (\xi_i - \xi_{i-1}) + \Delta \xi_i, \quad \xi_{i+1} = (\xi_{i+1} - \xi_i) + \xi_i, \quad (A1)$$

where  $h$  is the integration step size, and  $\xi_i$  is given by

$$\xi_i = [1 - h^2 A_l(r_i)] g_l(r_i) = B_l(r_i) g_l(r_i), \quad (A2)$$

$$\text{with } A_l(r_i) = -k^2 + l(l+1)/r_i^2 + U_l(r_i). \quad (A3)$$

Using the field-free solutions, and matching logarithmic derivatives at  $r=a$ , the phase shift can be calculated from

$$\tan \delta_l = \frac{\{[1 - a\omega_l(a)] B_l(a) + a B_l'(a)\} j_l(ka) + ka B_l(a) j_l'(ka)}{\{[1 - a\omega_l(a)] B_l(a) + a B_l'(a)\} n_l(ka) + ka B_l(a) n_l'(ka)}, \quad (A4)$$

where  $\omega = \xi_l'/\xi_l$ , and  $j_l$  and  $n_l$  are spherical Bessel functions of the first and second kind, respectively, and the prime on the Bessel function denotes the first derivative with respect to the argument  $ka$ . Note that  $B_l$  in (A4) corresponds to the field-free case.

A step-size of 0.001 assures six stable figures in the  $l=0$  phase shift, using the scheme outlined above. The calculations can be performed on the CDC 3600 at the rate of 1 phase shift/sec.

The series given by Eq. (2.16) were summed directly up to terms for which  $|\delta_l| < 10^{-6}$  rad.

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## Rotational Excitation of Polar Molecules by Electrons

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Rotational excitation of polar molecules is calculated in the approximation that the electron transit time is short compared with rotational periods with the result of an  $E^{-1}$  behavior of the cross section. Diffusion cross sections are calculated for  $\Delta l = 0, 1, 2$ . Significant corrections to the Born approximation are obtained for large dipole moments. The range (in energy) of applicability of the result is discussed in terms of the energy dependence of the corrections, and a novel energy dependence of these corrections is encountered and explained.

### I. INTRODUCTION

The full problem of electron scattering by a general atomic or molecular target is much too complex a problem for an exact solution to be even attempted. However, for some values of the incident energy there are solvable approximation schemes which are valid. For example, for low-enough energies it is known that electron-atom scattering is usefully parametrized in terms of the long-range parts of the potential.<sup>1</sup> Similarly for scattering by polar molecules, we can find an energy range of the incident electron in which a solvable approximation scheme is valid.

If the electron moves fast compared with the rotational motion of the molecule, then we may describe the process in terms of electron scattering from a molecule of fixed orientation<sup>2</sup> and subsequently average over the orientation. If,

further, the electron has low-enough energy so that its wave function does not probe the inner structure of the molecule, i. e., the scattering is dominated by the long-range potential, then we may further approximate the molecule by a point dipole. Thus the scattering in this energy range, which is bounded from above and below, may essentially be described as the scattering of an electron by a fixed point dipole. The numerical solution of this problem has been previously given.<sup>3</sup> It is used in the next section to obtain rotational excitation diffusion cross sections. In the third section the approximations described above are treated in more detail. It is found that the domain of applicability is most seriously restricted from below and that the restriction is more severe the greater the dipole moment. If the dipole moment is greater than the critical value the method breaks down. This is discussed briefly in the fourth section.

### II. DERIVATION AND NUMERICAL RESULTS

The scattering problem of an electron on a molecule is most conveniently described by the integral equation