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Atomic Scattering Amplitudes for Electron Diffraction*

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Scattering amplitudes for 40 keV. electrons have been computed from the partial waves scattering theory for selected atoms and for scattering angles between 0° and 28°. The Thomas–Fermi potential was used in these calculations; in some instances Hartree potentials were also used and the results from the different potentials are compared.

1. Introduction

The atomic scattering amplitudes $f(\theta)$ which are required in the electron-diffraction determination of the molecular structure of gases have in the past been estimated by the first Born approximation,

$$f(\theta) \approx f^B(\theta) = \frac{2k\alpha}{Ze^2}\int_0^\infty V(r)\frac{\sin sr}{sr}r^2dr\,. \qquad (1)$$

Here k is $2\pi/\lambda$, α is $-Ze^2/\hbar v$, s is $2k\sin(\theta/2)$, θ is the scattering angle (twice the Bragg angle), v the velocity of the electron, and $V(r)$ is the potential energy of the incident electron in the atomic field. The X-ray form factor $F(\theta)$ is related to $f^B(\theta)$ by

$$f^B(\theta) = (-2k\alpha/s^2)(1-F(\theta)/Z)\,. \qquad (2)$$

Recent work (Schomaker & Glauber, 1952; Glauber & Schomaker, 1953) has shown that the first Born approximation, which is theoretically justified only for $-\alpha \to 0$, fails at the voltages used in electron-diffraction studies and leads, for example, to apparent asymmetry in the structures of molecules containing both heavy and light atoms. The atomic scattering amplitude actually is complex and, on the assumption that the molecular amplitude is simply a superposition of atomic amplitudes, the intensity scattered by a molecule is proportional to

$$\sum_{i,j}{}' |f_i(\theta)||f_j(\theta)|\cos[\eta_i(\theta)-\eta_j(\theta)]\frac{\sin sr_{ij}}{sr_{ij}}\,, \qquad (3)$$

where $\eta(\theta) = \arg f(\theta)$ and r_{ij} is the distance between atoms i and j. Complex atomic scattering amplitudes have recently been computed by the partial waves scattering theory for U and F atoms at 40 and 11 keV., and the scattering of the UF_6 molecule, predicted from these results, was found to be in good agreement with experiment (Hoerni & Ibers, 1953). In this paper we extend these calculations to other atoms and to a wider range of scattering angles at 40 keV.

2. Theory

The solution to the problem of elastic scattering of a beam of particles by a central potential is given by

$$f(\theta) = (2ik)^{-1}\sum_{l=0}^{\infty}(2l+1)(\exp[2i\delta_l]-1)P_l(\cos\theta)\,. \qquad (4)$$

When $\delta_l \ll 1$, the partial phases δ_l can be computed from the formula

$$\delta_l^0 = \frac{k\alpha\pi}{Ze^2}\int_0^\infty V(r)J^2_{l+\frac{1}{2}}(kr)r\,dr\,. \qquad (5)$$

For large values of δ_l we have shown (Hoerni & Ibers, 1953) that the WKB method can be applied and that there results approximately

$$\delta_l = \frac{k\alpha}{Ze^2}\int_{(l+\frac{1}{2})/k}^\infty V(r)[k^2-(l+\tfrac{1}{2})^2/r^2]^{-\frac{1}{2}}dr\,. \qquad (6)$$

When the atom is very light (e.g. $Z < 10$) the second Born approximation can be used. This approximation, which is more convenient to apply but valid only when $|f(\theta)| \approx f^B(\theta)$ and $\eta(\theta)$ is small, gives

$$\eta(\theta) = (k/4\pi f^B(\theta))\int f^B(\mathbf{k}', \mathbf{k}'')f^B(\mathbf{k}'', \mathbf{k})d\Omega_{\mathbf{k}''}\,, \qquad (7)$$

where $\mathbf{k}$ and $\mathbf{k}'$ refer to the directions of incidence and scattering, respectively, and $\mathbf{k}''$ is integrated over the sphere $|\mathbf{k}''| = k$ (Glauber & Schomaker, 1953).

3. Procedure and results

The choice of $V(r)$ is limited. It would be most desirable to use the Hartree–Fock potentials for all atoms. These calculations, however, have not been carried out for neutral atoms above calcium, and above krypton the Hartree calculation has been made only for tungsten and mercury (Hartree, 1946). We have therefore adopted the Thomas–Fermi potential in the approximate form of Rozental (1936):

$$V(r) = -\frac{Ze^2}{r}\sum_{i=1}^{3}a_i\exp[-b_ir/a] \qquad (8)$$

where $a_1 = 0{\cdot}255$, $a_2 = 0{\cdot}581$, $a_3 = 0{\cdot}164$, $b_1 = 0{\cdot}246$,

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Table 1. *Values of* $\eta(\theta)$

(Values in radians.)

$\theta =$ Z	0°	1°	2°	4°	6°	8°	10°	12°	16°	20°	24°	28°
1	$0{\cdot}00_5$	0·01	0·04	0·06	0·07	0·08	0·09	0·10	0·11	0·12	0·12	0·13
3	0·02	0·04	0·08	0·14	0·18	0·21	0·23	0·25	0·27	0·30	0·33	0·35
6	0·03	0·08	0·14	0·23	0·30	0·36	0·41	0·44	0·51	0·56	0·60	0·64
9	0·05	0·11	0·19	0·31	0·41	0·50	0·57	0·63	0·72	0·79	0·85	0·91
12	0·06	0·13	0·23	0·39	0·52	0·62	0·72	0·80	0·92	1·02	1·10	1·16
15	0·07	0·15	0·27	0·46	0·61	0·74	0·85	0·95	1·11	1·23	1·32	1·40
18	0·08	0·17	0·31	0·52	0·70	0·86	0·98	1·09	1·28	1·43	1·54	1·63
22	0·10	0·20	0·35	0·60	0·82	0·99	1·14	1·27	1·50	1·68	1·81	1·92
26	0·12	0·22	0·39	0·68	0·91	1·12	1·29	1·44	1·70	1·91	2·07	2·20
32	0·14	0·26	0·45	0·77	1·05	1·29	1·50	1·68	1·98	2·24	2·45	2·61
38	0·17	0·28	0·50	0·86	1·17	1·45	1·69	1·89	2·24	2·54	2·78	2·98
44	0·19	0·31	0·54	0·93	1·28	1·59	1·86	2·09	2·48	2·81	3·07	3·31
50	0·21	0·33	0·57	1·00	1·38	1·72	2·01	2·26	2·69	3·05	3·35	3·62
56	0·22	0·35	0·60	1·07	1·47	1·84	2·15	2·43	2·90	3·29	3·61	3·90
62	0·24	0·36	0·63	1·13	1·57	1·95	2·28	2·58	3·08	3·50	3·85	4·16
68	0·25	0·38	0·65	1·19	1·65	2·05	2·41	2·72	3·26	3·71	4·09	4·40
74	0·26	0·39	0·68	1·24	1·72	2·14	2·52	2·85	3·43	3·88	4·30	4·63
80	0·27	0·41	0·70	1·28	1·78	2·23	2·63	2·98	3·58	4·07	4·50	4·85
86	0·28	0·42	0·72	1·32	1·84	2·31	2·73	3·09	3·73	4·25	4·68	5·07
92	0·29	0·43	0·73	1·35	1·89	2·38	2·82	3·20	3·86	4·42	4·86	5·27
98	0·30	0·44	0·74	1·38	1·94	2·45	2·90	3·30	4·00	4·58	5·04	5·46

Table 2. *Values of* $|f(\theta)|$

(Values in Ångström units.)

$\theta =$ Z	0°	1°	2°	4°	6°	8°	10°	12°	16°	20°	24°	28°
1	4·4	0·62	0·222	0·066	0·031	0·018	0·012	0·008	0·005	0·003	0·002	0·002
3	5·5	1·45	0·570	0·186	0·088	0·054	0·034	0·024	0·014	0·009	0·006	0·005
6	7·9	2·35	0·991	0·344	0·167	0·102	0·068	0·048	0·028	0·018	0·013	0·009
9	9·1	3·12	1·36	0·500	0·243	0·150	0·100	0·070	0·041	0·027	0·019	0·014
12	9·9	3·78	1·68	0·629	0·314	0·194	0·129	0·092	0·054	0·035	0·025	0·019
15	10·6	4·36	1·97	0·750	0·382	0·236	0·157	0·113	0·067	0·044	0·031	0·023
18	11·2	4·87	2·23	0·860	0·445	0·275	0·183	0·132	0·079	0·052	0·037	0·028
22	12·0	5·50	2·55	1·00	0·521	0·323	0·218	0·157	0·094	0·062	0·044	0·034
26	12·6	6·07	2·84	1·12	0·593	0·367	0·250	0·179	0·109	0·072	0·051	0·039
32	13·3	6·81	3·22	1·29	0·688	0·425	0·292	0·211	0·128	0·085	0·060	0·046
38	13·9	7·44	3·56	1·43	0·770	0·477	0·328	0·239	0·146	0·096	0·069	0·053
44	14·5	7·98	3·87	1·55	0·842	0·524	0·361	0·264	0·163	0·107	0·077	0·059
50	14·9	8·46	4·14	1·66	0·904	0·568	0·391	0·287	0·179	0·118	0·085	0·065
56	15·4	8·89	4·36	1·76	0·956	0·607	0·418	0·308	0·192	0·128	0·092	0·071
62	15·6	9·28	4·58	1·84	1·00	0·641	0·443	0·328	0·205	0·138	0·099	0·076
68	15·9	9·63	4·78	1·91	1·04	0·671	0·466	0·347	0·217	0·147	0·106	0·081
74	16·2	9·94	4·96	1·97	1·08	0·696	0·486	0·363	0·228	0·155	0·113	0·086
80	16·4	10·22	5·13	2·04	1·12	0·718	0·503	0·378	0·238	0·164	0·120	0·091
86	16·6	10·49	5·28	2·10	1·15	0·736	0·518	0·391	0·246	0·172	0·128	0·096
92	16·8	10·73	5·44	2·15	1·18	0·751	0·532	0·403	0·253	0·179	0·135	0·101
98	16·9	10·95	5·58	2·21	1·21	0·763	0·546	0·413	0·260	0·185	0·140	0·105

$b_2 = 0{\cdot}947$, $b_3 = 4{\cdot}356$, and a, the screening radius, is $0{\cdot}4685/Z^{1/3}$ in Ångström units.* Equation (8) allows analytic integration of (5), (6) and (7).

Tables 1 and 2 give the values of $\eta(\theta)$ and $|f(\theta)|$ computed from (8) for selected values of Z and θ at 39·47 keV. (This voltage corresponds to a wavelength of 0·06056 Å, the calibration wavelength used in the UF_6 studies.) It is interesting that even for very light atoms the $\eta(\theta)$ differ appreciably from zero. Comparison of $|f(\theta)|$ with $f^B(\theta)$, however, indicates a maximum difference occurring at high Z of only about 30% over the range of Z and θ considered.†

Some remarks are perhaps in order regarding the actual calculation. It is convenient to improve the convergence of (4) in the following way. For the real part of $f(\theta)$ we subtract term by term from (4) the series

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* This form is a better approximation to the potential than the fit of Molière (1947) which we used in our previous paper.

† The maximum difference for argon is about 4%. This relative reliability of $f^B(\theta)$ accounts for the satisfactory agreement found by Bartell & Brockway (1953) between the X-ray form factor for argon calculated from the Hartree–Fock potential and that obtained by use of the Born approximation from electron-intensity data.

Table 3. *Calculations from Hartree potentials*

Z	$V(r)$
9	$V(r) = -(Ze^2/r)\,[1\cdot133\ e^{-4\cdot248r}-0\cdot133\ e^{-127\cdot5r}-r(6\cdot173\,e^{-16\cdot51r}+\ 10\cdot50\,e^{-71\cdot43r})]$ (a)
18	$V(r) = -(Ze^2/r)\,[1\cdot315\ e^{-3\cdot923r}-0\cdot315\ e^{-88\cdot25r}-r(7\cdot874\,e^{-9\cdot634r}+\ 20\cdot21\,e^{-44\cdot22r})]$ (b)
74	$V(r) = -(Ze^2/r)\,[0\cdot1573\,e^{-1\cdot878r}+0\cdot6520\,e^{-7\cdot451r}+\ 0\cdot1804\,e^{-31\cdot56r}+0\cdot0103\,e^{-233\cdot4r}]$ (c)
80	$V(r) = -(Ze^2/r)\,[0\cdot1208\,e^{-1\cdot997r}+0\cdot4613\,e^{-5\cdot405r}+\ 0\cdot3644\,e^{-16\cdot33r}+0\cdot0536\,e^{-78\cdot69r}]$ (d)

$\eta(\theta)$

$\theta =$ Z	0°	1°	2°	4°	6°	8°	10°	12°	16°	20°	24°	28°
9	0·09	0·10	0·13	0·24	0·34	0·43	0·50	0·56	0·65	0·72	0·77	0·82
18	0·14	0·17	0·24	0·47	0·66	0·80	0·93	1·03	1·22	1·37	1·51	1·63
74	0·23	0·38	0·62	1·13	1·61	2·03	2·41	2·74	3·30	3·78	4·17	4·51
80	0·28	0·41	0·65	1·18	1·69	2·13	2·52	2·87	3·48	3·95	4·36	4·72

$|f(\theta)|$

$\theta =$ Z	0°	1°	2°	4°	6°	8°	10°	12°	16°	20°	24°	28°
9	2·1(e)	1·8(e)	1·22	0·508	0·251	0·148	0·098	0·070	0·042	0·028	0·020	0·015
18	4·8	3·8	2·28	0·825	0·423	0·265	0·184	0·135	0·080	0·054	0·039	0·029
74	15·2	8·7	4·33	1·93	1·07	0·688	0·483	0·363	0·228	0·157	0·115	0·091
80	13·4	8·6	4·80	2·01	1·10	0·705	0·496	0·375	0·236	0·166	0·122	0·097

(*a*) Brown, 1933.
(*b*) Hartree & Hartree, 1938.
(*c*) Manning & Millman, 1936.
(*d*) Hartree & Hartree, 1935.
(*e*) For very low θ, the values of $|f(\theta)|$ are uncertain owing to insufficient knowledge of the asymptotic behavior of the Hartree potentials.

$$k^{-1}\sum_{l=0}^{\infty}(2l+1)\delta_l^0 P_l(\cos\theta)\,, \tag{9}$$

and add $f^B(\theta)$, since substitution of (5) into (9) yields (1). For the imaginary part of $f(\theta)$ we subtract term by term the asymptotic form of $(1-\cos 2\delta_l)$ for large l, namely $2\delta_l^2$. Using (8) we have

$$2\delta_l^2 \sim (\alpha^2 a_1^2/b_1)\pi ka(l+\tfrac{1}{2})^{-1}\exp[-2(l+\tfrac{1}{2})b_1/ka] = g(l+\tfrac{1}{2})\,, \tag{10}$$

and we have for the resultant sum

$$(2k)^{-1}\sum_{l=0}^{\infty}(2l+1)g(l+\tfrac{1}{2})P_l(\cos\theta) = \frac{(\alpha^2 a_1^2\pi a/b_1)\exp[-b_1/ka]}{(1-2\exp[-2b_1/ka]\cos\theta+\exp[-4b_1/ka])^{\frac{1}{2}}}\,. \tag{11}$$

When the summations are made in this way, negligible errors arise from termination of the series for both the real and imaginary parts at $l = 100$, except for $\theta = 0°$, but here an exact correction can be applied.

In order to check the reliability of the Thomas–Fermi potential, we have fitted the Hartree–Fock potentials for F and A and the Hartree potentials for W and Hg in the form

$$V(r) = -\frac{Ze^2}{r}\sum_i \alpha_i r^{n_i}\exp[-\beta_i r]\,. \tag{12}$$

Equation (12) also allows analytic integration of (5) and (6).

Values of $\eta(\theta)$ and $|f(\theta)|$ for these potentials at 39·47 keV. are given in Table 3. It can be seen that $|f(\theta)|$ is relatively insensitive to the potential used, except at low angles. We find, as would be expected, that the relative differences in the values of $\eta(\theta)$ computed from the Hartree potentials and from the Thomas–Fermi potential increase with decreasing Z; yet, the absolute differences do not increase. Furthermore, our limited comparison indicates that the Hartree values differ from the Thomas–Fermi values by amounts which depend somewhat on θ but relatively little on Z. Since it is the absolute error in $\Delta\eta_{ij} = \eta_i-\eta$, according to equation (3), which affects the accuracy of the calculation of scattered intensities, it seems best to use the Thomas–Fermi potential for all atoms rather than to use the Hartree potentials, where available, in conjunction with the Thomas–Fermi potential.

It is extremely difficult to give an estimate of the accuracy of the results presented in Tables 1 and 2. The actual numerical details, i.e. function values, summation, problems of convergence, etc., have all been adequately handled. We cannot be so confident of the theoretical details. No corrections have been made for polarization, electron exchange, or electron spin. The first two effects are presumably important only at very low l and the extra labor involved in the use of the Dirac equations is not justified. The WKB method is itself an approximation; however, previous investigators have found it to be reliable under comparable circumstances (Bartlett & Welton, 1941; Gunnersen, 1952). (We employ an approximate WKB equation, (6), which we have shown gives magnitudes

Table 4. *Actual and transformed values for* $Z = 60$

V (keV.)	θ (°)	$\eta(\theta)_{\text{act.}}$ (radians)	$\eta(\theta)_{\text{tran.}}$ (radians)	$\lvert f(\theta)\rvert_{\text{act.}}$ (Å)	$\lvert f(\theta)\rvert_{\text{tran.}}$ (Å)	$f^B(\theta)$ (Å)
55	2	0·647	0·640	3·91	3·70	4·63
	8	1·91	1·92	0·506	0·470	0·644
	16	2·97	2·98	0·153	0·148	0·188
	24	3·65	3·67	0·076	0·074	0·067
25	2	0·590	0·576	5·46	5·75	6·85
	8	1·90	1·90	0·826	0·914	1·19
	16	3·08	3·09	0·274	0·294	0·373
	24	3·91	3·92	0·136	0·148	0·108

and arguments differing by not more than about 3% from those computed from the more exact equation.*)

The principal source of error in the calculation probably lies in our uncertain knowledge of the atomic potentials $V(r)$, which is in fact so uncertain as to justify all our other approximations. Altogether, we feel that Tables 1 and 2 are sufficiently reliable to allow molecular structures, regardless of the atoms present, to be determined as accurately as is presently possible for compounds containing atoms of approximately the same atomic number. To be sure, the approximation of equation (3), i.e. the neglect of valence distortion, plural scattering, and the like, may not be adequate: indeed it is more doubtful for the actual atomic scattering with phase shift than for that without phase shift given by the first Born approximation. In practice, however, this approximation seems to be satisfactory.

We note that complex atomic scattering amplitudes cannot generally be used to calculate the diffraction from single crystals (Hoerni, 1954). Analogous to the X-ray case (Coster, Knol & Prins, 1930), complex f-values used in the kinematical theory may lead to different intensities for the reflections hkl and $\bar{h}\bar{k}\bar{l}$ in a crystal lacking a center of symmetry. At the same time, however, dynamical interactions arise among a number of diffracted beams in the crystal, so that even with complex f-values the range of validity of the kinematical theory is limited to extremely small crystals.

4. Extension to other voltages

Our results are directly applicable only for $V = V_o = 39{\cdot}47$ keV. For voltages V not too different from V_o, the following transformations might prove useful:

$$\eta(Z, \theta, V) \approx \eta(Z', \theta', V_o) \quad \text{if}$$
$$Z' = Z(v_o/v),\ \sin(\theta'/2) = (Z'/Z)^{1/3}(k/k_o)\sin(\theta/2)\,, \quad (13)$$

$$|f(Z, \theta, V)| \approx |f(Z'', \theta'', V_o)| \quad \text{if}$$
$$Z'' = Z(kv_o/k_ov)^3,\ \sin(\theta''/2) = (Z''/Z)^{1/3}(k/k_o)\sin(\theta/2)\,, \quad (14)$$

where $v_o = 1{\cdot}1148 \times 10^{10}$ cm.sec.$^{-1}$ and $k_o = 103{\cdot}75$ Å^{-1} refer to 39·47 keV. In Table 4 results computed for $Z = 60$ for 25 and 55 keV. using (4) are compared with the values deduced from Tables 1 and 2 using (13) and (14). These transformations were suggested by the fact that they hold rigorously both for $f^B(\theta)$ and, if one assumes the simple screened-Coulomb field $-Ze^2e^{-r/a}/r$ and the second Born approximation, for $\eta(\theta)$ (Glauber & Schomaker, 1953). The agreement exhibited in Table 4 for $\eta(\theta)$ is remarkable but we do not imply that such agreement can be obtained in all cases; the agreement for $|f(\theta)|$ is not as good but the indication is that $|f(\theta)|_{\text{transformed}}$ are more reliable than $f^B(\theta)$.

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* The use of equation (6) together with the differences in the form of the approximate fit of the Thomas–Fermi potential and the use of a convergence factor for the imaginary part of $f(\theta)$ account for the differences in the values for U given here and given previously.