Complex Amplitudes for Electron Scattering by Atoms*

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The partial waves scattering theory has been applied to electron scattering by U and F atoms at 40 and 11 kev. The electron scattering by the UF_6 molecule, predicted from these results, is in good agreement with experiment.

I. INTRODUCTION

RECENTLY, Schomaker and Glauber[1] have pointed out that anomalies, e.g., apparent asymmetry, in the structures of molecules containing both heavy and light atoms as determined by electron diffraction can be removed by using complex atomic scattering amplitudes $f(\theta)$ and hence by rejecting the first Born approximation which gives only real amplitudes. This approximation, although theoretically justified only for $-\alpha=Ze^2/(\hbar v)$ small, has nevertheless been universally employed in investigations of the molecular structure of gases by electron diffraction. Using the second Born approximation, Glauber and Schomaker[2] evaluated the phase of the complex amplitude, $\eta(\theta)=\arg f(\theta)$, for the exponentially screened Coulomb potential $-Ze^2e^{-r/a}/r$; agreement was obtained for a large group of molecules at 40 kev. However, good agreement is not obtained for the UF_6 pattern at 11 kev,[3] and, in any case, the second Born approximation and the assumption of the screened Coulomb field are both uncertain, so that a more adequate calculation is desired. We describe below an application of the partial waves scattering theory to the problem of the scattering of electrons by atoms (U and F). The energies considered (11 and 40 kev) are sufficiently high so that electron exchange and polarization effects can be neglected.

II. THEORY[4]

The solution to the problem of the elastic scattering of a beam of particles by a central potential $V(r)$ is given by

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

where θ is the scattering angle, k is $2\pi/\lambda$, and the phases δ_l may be interpreted as the phase differences between the perturbed and unperturbed radial functions at large distances from the nucleus. The δ_l's can be evaluated in several ways for electron scattering. When $\delta_l\ll 1$, (1) can be rewritten as

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

and the δ_l's are given by

$$\delta_l{}^0=\frac{k\alpha\pi}{Ze^2}\int_0^{\infty}V(r)J_{l+\frac{1}{2}}{}^2(kr)rdr. \quad (3)$$

Substitution of (3) into (2) yields the first Born approximation for the scattering amplitudes, namely,

$$f^B(\theta)=\frac{2k\alpha}{Ze^2}\int_0^{\infty}V(r)\frac{\sin(sr)}{sr}r^2dr, \quad (4)$$

where $s=2k\sin(\theta/2)$. When the δ_l's are not small, they may be evaluated conveniently by the WKB method. Starting with the relativistic Schrödinger equation,

$$\nabla^2\psi+\kappa^2(r)\psi=0, \quad (5)$$

where

$$\kappa^2(r)=\frac{[E-V(r)]^2-m^2c^4}{\hbar^2c^2}=k^2+\frac{V^2(r)-2EV(r)}{\hbar^2c^2},$$

we obtain

$$\delta_l=\int_{r_1}^{\infty}G(r)dr-\int_{r_2}^{\infty}G_0(r)dr, \quad (6)$$

with

$$G(r)=\{\kappa^2(r)-[(l+\tfrac{1}{2})/r]^2\}^{\frac{1}{2}},\quad G_0(r)=\{k^2-[(l+\tfrac{1}{2})/r]^2\}^{\frac{1}{2}}.$$

Here, the energy E includes the rest energy, and $r_1, r_2>0$ are the zeros of the respective integrands. In accordance with the work of Langer,[5] we have replaced $l(l+1)$ by $(l+\frac{1}{2})^2$. The δ_l's may also be evaluated exactly. This has been done by Bartlett and Welton[6] with a differential analyzer for Hg at 100 and 230 kev starting with Gordon's solutions of the Dirac equation. Although the δ_l's from the WKB method are generally supposed to be reliable only when large, and hence only when l is small, Bartlett and Welton found these values to be in excellent agreement with the exact values over the entire range of l; they found the $\delta_l{}^0$'s to be reliable at large l.

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[1] V. Schomaker and R. Glauber, Nature **170**, 290 (1952).
[2] R. Glauber and V. Schomaker, Phys. Rev. **89**, 667 (1953).
[3] Preliminary results by G. Felsenfeld and J. Ibers.
[4] As a general reference, we give N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, 1949), second edition, particularly Chapter VII.
[5] R. E. Langer, Bull. Am. Math. Soc. **40**, 574 (1934); Phys. Rev. **51**, 669 (1937).
[6] J. H. Bartlett, Jr., and T. A. Welton, Phys. Rev. **59**, 281 (1941).

III. PROCEDURE AND RESULTS

We first compute the complex atomic scattering amplitudes for U and F at 40 and 11 kev and then apply these to the scattering by the UF_6 molecule. UF_6 was selected because it offers the most severe test (the molecule exhibits the largest apparent asymmetry[1]) and because only for it do we have electron diffraction photographs prepared at 11 kev as well as at the usual 40 kev.

For U we adopted the Thomas-Fermi potential, using the approximate form[7]

$$V(r)=-\frac{Ze^2}{r}\sum_{i=1}^{3}a_i e^{-b_i r/a}, \tag{7}$$

where $a_1=0.10$, $a_2=0.55$, $a_3=0.35$, $b_1=6.0$, $b_2=1.2$, $b_3=0.3$, and a, the screening radius, is $0.4685/Z^{\frac{1}{3}}$. For F we used the Hartree potential[8] in the approximate form

$$V(r)=-(Ze^2/r)(e^{-\beta_1 r}+cre^{-\beta_2 r}), \tag{8}$$

where $\beta_1=3.94$, $\beta_2=17.0$, and $c=-2.67$. Preliminary calculations indicated that the effect of electron spin would be important only for $l\leqslant 2$,[9] and since in the final summation (1) these terms are reduced in importance by the factor $2l+1$, we felt justified in adopting the relativistic Schrödinger equation (5). For small l, the δ_l's were calculated for 40 and 11 kev from the WKB expression (6); for large l ($\geqslant 25$), it was found that the δ_l^0's (3) and δ_l's (6) were in excellent agreement, as anticipated from the work of Bartlett and Welton.[6] With the δ_l's obtained in this way (Table I), we have evaluated the magnitudes $|f(\theta)|$ and the arguments $\eta(\theta)$ of the complex scattering amplitudes (Table II). The δ_l's for U can also be computed over the entire l range from the asymptotic expression (15) below. In this case, although the δ_l's differ from the above by as much as 8 percent at 40 kev and 15 percent at 11 kev, the resultant magnitudes and arguments in no case differ by more than 3 percent from those in Table II, the relative error increasing with increasing θ.

In the application of these results to the molecule UF_6, the assumption is made that multiple scattering and valence distortion are negligible. Then for visual data the following expression for the intensity function (specialized for the case of UF_6) is suitable:

$$\begin{aligned}I(s)K(s)=&(6/r_{U\text{-}F})\cos[\eta_U(\theta)-\eta_F(\theta)]\sin(r_{U\text{-}F}s)\\&+(|f_F(\theta)|/|f_U(\theta)|)\\&\times\{(12/r_{F\text{-}F})\{\exp[-(a_{F\text{-}F}-a_{U\text{-}F})s^2]\}\sin(r_{F\text{-}F}s)\\&+(3/r_{F\cdot F})\{\exp[-(a_{F\cdot F}-a_{U\text{-}F})s^2]\}\sin(r_{F\cdot F}s)\},\end{aligned} \tag{9}$$

where $I(s)$ is the modified scattering intensity, $K(s)$ is is a smoothly decreasing function of s, and $\exp(-a_{ij}s^2)$ is the temperature factor for the distance r_{ij} between atoms i and j.[1,10] Using our complex amplitudes and a symmetric UF_6 model,[11] we have evaluated the function $I(s)K(s)$ at 11 and 40 kev. Figure 1 compares the calculated and the visually estimated versions of this function. When one considers that the visual curves are significant only for comparisons of intensity over a small range of s (e.g., that one usually can compare the height of maximum n only with the average of the heights of maximum $n+1$ and maximum $n-1$), the agreement is excellent. For the present purpose, the most significant parts of the patterns are the very sensitive regions where $\eta_U(\theta)-\eta_F(\theta)=\pi/2$, and these are reproduced satisfactorily (Table III).

TABLE I. Selected values of δ_l.[a]

l	Uranium 40 kev	Uranium 11 kev	Fluorine 40 kev	Fluorine 11 kev
0	6.11	7.20	0.571	1.05
2	3.49	4.67	0.414	0.555
4	2.47	2.96	0.317	0.391
6	1.87	2.06	0.258	0.297
8	1.53	1.52	0.218	0.234
10	1.26	1.16	0.189	0.188
15	0.847	0.679	0.135	0.113
20	0.602	0.441	0.101	0.071
25	0.452	0.302	0.077	0.046
30	0.353	0.212	0.059	0.029
35	0.282	0.152	0.046	0.019
40	0.228	0.110	0.036	
50	0.155	0.059	0.022	
70	0.076	0.018		
100	0.028			

[a] The actual values used were 39.470 and 11.380 kev.

Table II also provides a comparison with the magnitudes $f^B(\theta)$ calculated by the first Born approximation[12] [using (18) and (19)] and the phase angles $\eta^B(\theta)$ for U calculated by the second Born approximation. For the latter it was necessary to extend the calculations of Glauber and Schomaker[2] to the potential for U used here. Their formula is

$$\eta^B(\theta)=\eta^B(\mathbf{k}',\mathbf{k})=\frac{k}{4\pi f^B(\theta)}\times\int f^B(\mathbf{k}'\mathbf{k}'')f^B(\mathbf{k}'',\mathbf{k})d\Omega_{\mathbf{k}''}, \tag{10}$$

[7] G. Molière, Z. Naturforsch. **2a**, 142 (1947).
[8] F. W. Brown, Phys. Rev. **44**, 214 (1933).
[9] See reference 4, Chap. IV, Eq. (23).
[10] Shaffer, Schomaker, and Pauling, J. Chem. Phys. **14**, 659 (1946).
[11] $r_{U\text{-}F}=2.00$A, $r_{F\text{-}F}=2.83$A, $r_{F\cdot F}=4.00$A, $a_{F\text{-}F}-a_{U\text{-}F}=2.2\times10^{-3}A^2$, $a_{F\cdot F}-a_{U\text{-}F}=0.75\times10^{-3}A^2$.
[12] It should be noted that $f^B(\theta)$ is related to $F(\theta)$, the x-ray form factor, by the relation

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

The $F(\theta)$ for U obtained from the corresponding $f^B(\theta)$ given in Table II agree to within 1½ percent with the Thomas-Fermi values given in *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (Gebrüder Borntraeger, Berlin, 1935), Vol 2, p. 573. The $F(\theta)$ for F agree to within 10 percent with those of R. W. James and G. W. Brindley [Phil. Mag. **12**, 81 (1931)], and to within 6 percent with the f of R. McWeeny [Acta Cryst. **4**, 513 (1951)]; our values being in general lower than those of McWeeny and higher than those of James and Brindley. We suspect these differences arise from differences in the models used.

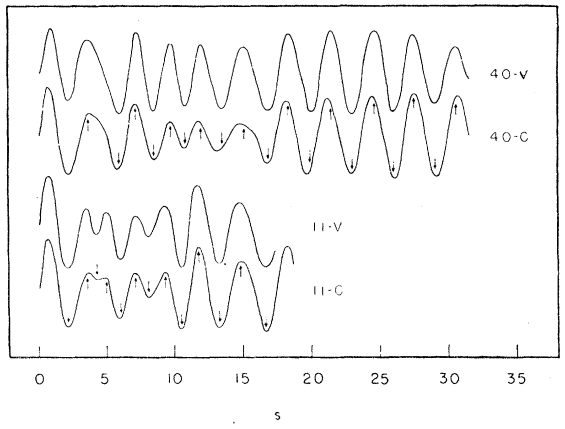

FIG. 1. Intensity curves for UF_6. 'V" visual, "C" calculated for "40" or "11" kev. Further photographs will be made both at 40 and 11 kev, and the visual curves (40 V is due to Dr. Otto Bastiansen and 11 V to Felsenfeld and Ibers (reference 3)) are not to be regarded as final.

where $\mathbf{k}$ and $\mathbf{k}'$ refer to the directions of incidence and scattering, respectively, and $\mathbf{k}''$ is integrated over the sphere $|\mathbf{k}''|=k$. When the potential (7) for U was inserted and the integration performed there resulted

$$\eta^B(\theta)=\frac{\alpha^2}{2kf^B(\theta)\cos(\theta/2)}\sum_{i,j=1}^{3}\frac{a_ia_j}{\mu_{ij}}\times\tanh^{-1}\frac{2\mu_{ij}\cos(\theta/2)}{g_{ii}g_{jj}-\cos\theta}, \quad (11)$$

$$g_{ij}=1+(b_i^2+b_j^2)/(4k^2a^2),$$

$$\mu_{ij}=\{[(b_i^2-b_j^2)/(4k^2a^2)]^2+[g_{ij}^2-\cos^2(\theta/2)]\tan^2(\theta/2)\}^{\frac{1}{2}},$$

which is in serious disagreement with the partial waves values and with experiment, as may be seen from Tables II and III. The good agreement with experiment obtained previously[2] must be due to a fortuitous cancellation of errors: For heavy atoms the exponentially screened Coulomb field is quite unsatisfactory and (10), even at 40 kev, is inadequate.

It is planned to extend the calculations for 40-kev electrons to other atoms with the hope of achieving a sufficiently general theoretical basis for electron diffraction studies of the molecular structures of gases.

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IV. APPENDIX—MATHEMATICAL DETAILS

The Phases δ_l and δ_l^0

When computing δ_l it is convenient to split up (6) as follows:

$$\delta_l=\int_{r_1}^{r_3}G(r)dr-\int_{r_2}^{r_3}G_0(r)dr+\int_{r_3}^{\infty}[G(r)-G_0(r)]dr$$
$$=I_1-I_2+I_3. \quad (12)$$

Here, r_3 is sufficiently large so that for $r>r_3$, $G(r)$ and $G_0(r)$ do not differ by more than 10 percent. Then I_3 reduces to

$$I_3=\frac{k\alpha}{Ze^2}\int_{r_3}^{\infty}[V(r)]/[G_0(r)]dr. \quad (13)$$

r_1 was evaluated graphically and I_1 was integrated numerically using Simpson's rule; I_2 can be integrated analytically. $I_3(13)$ can be expressed in terms of various power expansions and when $V(r)$ is given by (7), the following expression is convenient:

$$I_3=-\alpha\sum_{i=1}^{3}a_i\int_{r_3}^{\infty}[e^{-b_ir/a}]/[r^2-((l+\tfrac{1}{2})/k)^2]^{\frac{1}{2}}dr,$$
$$=-\alpha\sum_{i=1}^{3}a_i\left\{K_0(u_i)-e^{-u_i}\left[m-u_i\frac{m^3}{3!}+(3u_i^2-u_i)\frac{m^5}{5!}-(15u_i^3+u_i-15u_i^2)\frac{m^7}{7!}+\cdots\right]\right\}, \quad (14)$$

$$u_i=b_i(l+\tfrac{1}{2})/(ka), \quad m=\cosh^{-1}[(r_3k)/(l+\tfrac{1}{2})].$$

For large values of l ($\gtrsim 25$), it was found that $r_1\approx r_2\approx r_3$,

TABLE II. Magnitudes and arguments of the scattering amplitudes.

	Uranium								Fluorine					
	40 kev				11 kev				40 kev			11 kev		
θ	$\lvert f(\theta)\rvert$	$\eta(\theta)$	$f^B(\theta)$	$\eta^B(\theta)$	$\lvert f(\theta)\rvert$	$\eta(\theta)$	$f^B(\theta)$	$\eta^B(\theta)$	$\lvert f(\theta)\rvert$	$\eta(\theta)$	$f^B(\theta)$	$\lvert f(\theta)\rvert$	$\eta(\theta)$	$f^B(\theta)$
0	14.51	0.317	17.24	0.50	12.01	0.414	16.36	0.90	2.31	0.079	2.32	2.15	0.141	2.20
1	10.30	0.424	12.78		10.64	0.456	14.88		1.90	0.093	1.91	2.03	0.148	2.08
2	5.54	0.687	7.52		7.85	0.579	11.78		1.24	0.128	1.24	1.73	0.169	1.77
3	3.21	1.00	4.74	1.39	5.37	0.772	8.86	1.51	0.776	0.179	0.781	1.39	0.201	1.43
4	2.08	1.31	3.27		3.67	1.01	6.72		0.507	0.231	0.511	1.08	0.243	1.12
5	1.46	1.60	2.42		2.61	1.28	5.23		0.349	0.281	0.352	0.841	0.290	0.871
6	1.08	1.88	1.87	2.41	1.94	1.57	4.18	2.63	0.252	0.329	0.254	0.660	0.341	0.685
7	0.837	2.16	1.49		1.52	1.85	3.44		0.190	0.376	0.192	0.525	0.396	0.546
8	0.683	2.42	1.21		1.24	2.13	2.88		0.148	0.420	0.149	0.424	0.447	0.442
10	0.500	2.89	0.848	3.44	0.930	2.64	2.12	3.96	0.096	0.487	0.098	0.291	0.552	0.302
12	0.403	3.26	0.624		0.756	3.03	1.63		0.068	0.551	0.070	0.211	0.651	0.218
14	0.327	3.61	0.478		0.623	3.34	1.30		0.051	0.623	0.052	0.162	0.748	0.164
16	0.263	3.95	0.378	4.64	0.520	3.60	1.06	5.60	0.040	0.676	0.041	0.128	0.830	0.128

so that (12) reduces to

$$\delta_l = -\alpha \sum_{i=1}^{3} a_i K_0(u_i). \tag{15}$$

For the same potential, (3) becomes

$$\delta_l^0 = -\alpha \sum_{i=1}^{3} a_i Q_l\left[1+\frac{1}{2}\left(\frac{b_i}{ka}\right)^2\right]. \tag{16}$$

The Q_l's were computed for $0 \leqslant l \leqslant 10$, using the polynomial expansions,[13] for $l \geqslant 10$ they were evaluated using Watson's relation[14]

$$Q_l(\cosh\xi) \sim (\exp[-(l+\tfrac{1}{2})(\xi-\tanh\xi)])(\operatorname{sech}^{\frac{1}{2}}\xi) \times (K_0[(l+\tfrac{1}{2})\tanh\xi]) + O(e^{-l\xi}/l). \tag{17}$$

At $l=10$, (17) gave values in excellent agreement with the exact values and therefore its use was justified for higher l. When computing the phases for large l ($\geqslant 25$), only the term for $i=3$ is of importance in (7). Since the corresponding ξ is much less than unity, (17) reduces very nearly to

$$K_0[(l+\tfrac{1}{2})\xi] = K_0[(l+\tfrac{1}{2})(b_3/(ka))],$$

so that the δ_l's and δ_l^0's are in close agreement.

Corresponding quantities for the F potential (8) can be readily obtained: Integrals involving a term of the form $cre^{-\beta r}$ are obtained by differentiating with respect to β the integrals already obtained for terms of the form $ce^{-\beta r}$ (the U potential).

The Scattering Amplitudes

In summing (1), the convergence of the real part is improved by subtracting $f^B(\theta)$ as given by its series expansion (2) and adding it as obtained by the integration of (4). The integrated expressions are respectively, for U and F,

$$f^B(\theta) = -2k\alpha a^2 \sum_{i=1}^{3} a_i (b_i^2 + a^2 s^2)^{-1}; \tag{18}$$

and

$$f^B(\theta) = -2k\alpha[(\beta_1^2+s^2)^{-1} + (2c\beta_2)(\beta_2^2+s^2)^{-2}]. \tag{19}$$

By substituting the following asymptotic expressions:[15]

$$K_0(x) \sim (\tfrac{1}{2}\pi/x)^{\frac{1}{2}} e^{-x}, \tag{20}$$

and

$$P_l(\cos\theta) \sim \sqrt{2}(\pi l \sin\theta)^{-\frac{1}{2}} \sin[(l+\tfrac{1}{2})\theta + \pi/4] \leqslant \sqrt{2}(\pi l \sin\theta)^{-\frac{1}{2}}, \tag{21}$$

into the respective expressions for the real and the imaginary parts of $f(\theta)$, it was shown that negligible errors would arise from termination of the summation at $l=70$ for the real part and at $l=100$ for the imaginary part, for $\theta \geqslant 1°$. For $\theta = 0°$, $P_l(\cos\theta) = 1$ and an exact termination correction can be made.

The $P_l(\cos\theta)$ were obtained from the available tables up to $l=10$ and for $10 \leqslant l \leqslant 100$, $1° \leqslant \theta \leqslant 16°$, they were computed from the relation

$$P_l(\cos\theta) \sim (\theta/\sin\theta)^{\frac{1}{2}} J_0[(l+\tfrac{1}{2})\theta] \tag{22}$$

which may be derived from the corresponding asymptotic expressions.[16] Equation (22) was satisfactory for l as low as 5 over the whole range of θ indicated in Table II.

TABLE III. Values of s where $\eta_U(\theta) - \eta_F(\theta) = \pi/2$.

Voltage, kev	$s$observed	$s$partial waves	s2nd Born
40	10.7±0.6	10.9	7.7
11	6.6±0.6	7.1	3.8

[13] A. Cayley, Messenger Math. **17**, 21 (1887). The same polynomials with decimal coefficients are given by N. Rosen, Phys. Rev. **38**, 255 (1931).

[14] G. N. Watson, Messenger Math. **47**, 151 (1918).

[15] See, for example, E. Jahnke and F. Emde, *Funktionentafeln* (Dover Publications, New York, 1945), fourth edition, p. 138, noting that $K_0(x) = (\pi/2)iH_0^{(1)}(ix)$, and p. 117.

[16] Reference 15, pp. 117, 138; see also reference 7, p. 144.