XVIII

SCATTERING OF SLOW ELECTRONS AND POSITRONS BY COMPLEX ATOMS

1. The Ramsauer and Townsend effects

As was shown in Chap. XVI, § 5, Born's first approximation is not applicable to low-velocity collisions of electrons with atoms, and the experimental results obtained in this region show clearly that a more elaborate theory is required.

In a preliminary investigation in 1921 of the free paths of electrons of very low energy (0·75 to 1·1 eV) in various gases, Ramsauer[†] found the free paths of these electrons in argon to be very much greater than that calculated from gas-kinetic theory. The extension of these observations to a wider range of velocities[‡] revealed a surprising variation in the cross-section. It was found that the effective cross-section (proportional to the reciprocal of the free path) of argon atoms increases with decreasing velocity until the electron energy becomes less than 10 eV. For electron energies below this value it decreases again to the low values found in the preliminary measurements. Independently, Townsend and Bailey[§] examined the variation of free path with velocity for electrons with energies between 0·2 and 0·8 eV by a different method, and showed that a maximum of the free path occurs at about 0·39 eV. This was confirmed by much later work of Ramsauer and Kollath.[||]

Since these classical experiments were carried out, the behaviour of a large number of gases and vapours has been examined over a wide voltage range.[††] The results obtained are illustrated in Fig. 89 for some monatomic gases and vapours. In these figures the variation of effective cross-section with velocity is illustrated. This is proportional to the reciprocal of the mean free path. For purposes of comparison the gas-kinetic cross-section is indicated on the figures.

The striking features of the cross-section–velocity curves are their wide variation in shape and size and also the marked similarity of

† *Ann. der Phys.* 64 (1921), 513. ‡ Ramsauer, ibid. 66 (1921), 545.
§ *Phil. Mag.* 43 (1922), 593; 44 (1922), 1033. || *Ann. der Phys.* 3 (1929), 536.
†† See, for example, the summaries by Kollath, *Phys. Zeits.* 31 (1931), 985; Brode, *Rev. Mod. Phys.* 5 (1933), 258; McMillen, ibid. 11 (1939), 84; Massey and Burhop, *Electronic and Ionic Impact Phenomena*, chap. i.

behaviour of similar atoms, such as those of the heavier rare gases and the alkali metal vapours. At the time of the earlier measurements no satisfactory explanation of the phenomena could be given, but on the introduction of quantum mechanics it was immediately suggested that
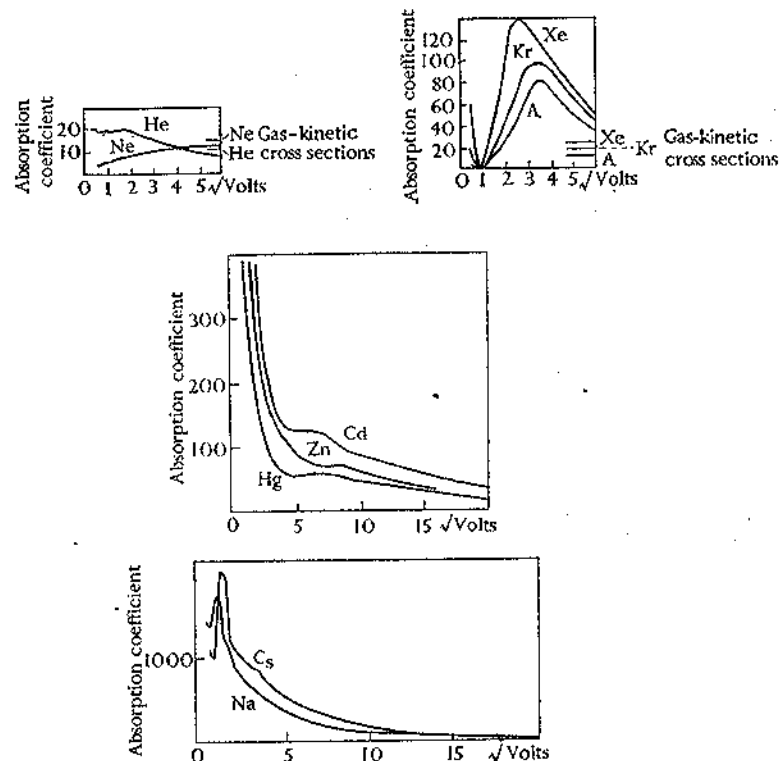

Fig. 89. Observed variation of effective cross-section with electron velocity.

the effect was a diffraction phenomenon. Thus Bohr[†] suggested in general terms how the minimum cross-section observed in the rare gases near 0·7 eV could be explained. The field of a rare gas atom falls off very much more rapidly with distance than that of any other atom, and might be expected to behave in much the same way as a spherical potential well, discussed in Chap. II, § 4. It was shown there that the well may be deep enough to introduce within its range one or more

† In conversation with Professor R. H. Fowler.

complete wave-lengths of zero angular momentum without affecting waves of higher angular momentum appreciably. An observer at a great distance from the atom will then fail to observe any scattering.
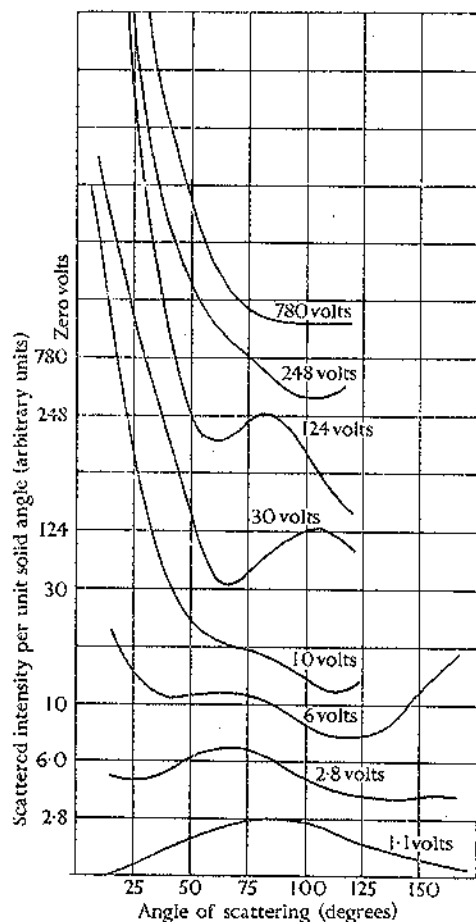

FIG. 90. Observed angular distributions of electrons scattered elastically by argon atoms.

Strong experimental evidence of the wave nature of the phenomena was afforded by measurements of the angular distributions of the elastically scattered electrons. These were first carried out for electrons of energy between 4 and 40 eV by Bullard and Massey for argon.[†]

† Proc. Roy. Soc. A, 130 (1931), 579.

Instead of the curves characteristic of Born's first approximation, showing a monotonic decrease of intensity with angle of scattering, the curves obtained by Bullard and Massey exhibit maxima and minima. In Fig. 90 a series of curves is given illustrating the variation in form of these curves, for argon, as the electron energy increases from 1·1 eV to 780 eV; they show the gradual transition to the curves predicted
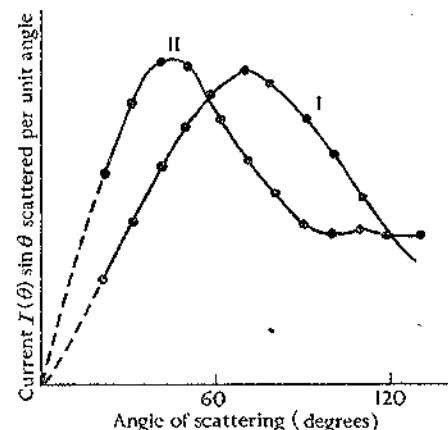

FIG. 91. The finite scattering through small angles. I. Curve for 6 volt electrons scattered by neon atoms. II. Curve for 7 volt electrons scattered by nitrogen molecules.

by Born's first approximation. The higher energy measurements (42–780 eV) are due to Arnot,[†] and at the lowest energies (1·1 and 2·8 eV) to Ramsauer and Kollath.[‡] These experiments have been carried out for a large number of gases over a wide range of electron energies, and it is found that in the majority of cases maxima and minima occur in some energy range.[§] For light gases, such as hydrogen and helium, this range is small (up to 15 eV in helium and 6 eV in hydrogen), while for mercury pronounced maxima and minima are observed up to the highest energies for which observations have been taken (800 eV). From these experiments it is obvious that the wave nature of the electron is important over a wider range than is apparent from the observation of effective cross-sections.

† Ibid. A, 133 (1931), 615.
‡ Ann. der Physik, 12 (1932), 529.
§ See McMillen, Rev. Mod. Phys. 11 (1939), 84, and Massey and Burhop, Electronic and Ionic Impact Phenomena, chap. ii.

It is of interest to examine the evidence from the angular distribution measurements as to the validity of the theoretical result (Chap. V, § 1.1) that the function $2\pi I(\theta)\sin\theta$, giving the number of electrons scattered per unit *angle* by a gas atom, tends to zero as θ tends to zero. In Fig. 91 two experimental curves representing scattering per unit angle are illustrated, and it is seen that the evidence is in favour of the theoretical conclusion.

2. The theory of the elastic scattering of low-velocity electrons

2.1. *Effective scattering potential*

In order to develop a theory of the scattering of low-velocity electrons by atoms, we must refer to the general theory of Chapter XII. The wave function Ψ, which in this case represents the system of atom+incident electron, was expanded in the form

$$\Psi = \left(\sum_n + \int\right)\psi_n(\mathbf{r}_a)F_n(\mathbf{r}), \qquad (1)$$

where $\psi_n(\mathbf{r}_a)$ is the wave function representing the nth excited state of the atomic system. It was then shown that the function $F_n(\mathbf{r})$ satisfies the equation

$$(\nabla^2+k_n^2)F_n = \frac{2m}{\hbar^2}\int V(\mathbf{r},\mathbf{r}_a)\Psi(\mathbf{r}_a,\mathbf{r})\psi_n^*(\mathbf{r}_a)\,d\tau_a,$$

where $V(\mathbf{r},\mathbf{r}_a)$ is the interaction energy between the incident and atomic electrons, and k_n is the wave number of the outgoing electron wave, equal to $mv_n/\hbar$.

If we neglect electron exchange, the elastic scattering is completely determined by the function F_0, which satisfies the equation

$$(\nabla^2+k^2)F_0(\mathbf{r}) = \frac{2m}{\hbar^2}\int V(\mathbf{r},\mathbf{r}_a)\Psi(\mathbf{r}_a,\mathbf{r})\psi_0^*(\mathbf{r}_a)\,d\tau_a. \qquad (2)$$

To solve (2) we must substitute some approximate form for Ψ on the right-hand side of (2). For instance, in obtaining Born's approximation in Chapter XII we neglected all the scattered waves and replaced Ψ by $\psi_0(\mathbf{r}_a)\exp(ikz)$. A less drastic approximation is to neglect all but the elastically scattered wave, and thus set on the right-hand side of (2)

$$\Psi = \psi_0(\mathbf{r}_a)F_0(\mathbf{r}).$$

We thus obtain
$$\left\{\nabla^2+k^2-\frac{2m}{\hbar^2}V_{00}(r)\right\}F_0(\mathbf{r}) = 0, \qquad (3)$$

where
$$V_{00}(r) = \int V(\mathbf{r},\mathbf{r}_a)\psi_0\psi_0^*\,d\tau_a.$$

This is the equation which represents the motion of the incident electron in the static field of the atom, V_{00} being just the potential of this field.

In fact the effect of the terms neglected in (3) can be represented by adding to V_{00} in (3) an interaction of non-local type as shown in Chap. XII, § 5.6. Furthermore, within a certain energy range this non-local interaction may be replaced approximately by an equivalent local interaction which may be energy dependent (Chap. VIII, § 1.42). The combination of this interaction with V_{00} is the so-called optical model potential (Chap. XII, § 4.1), which is real when the electron energy is below the threshold for inelastic scattering and complex otherwise. We may therefore survey the data on the elastic scattering of electrons with energy below this threshold by assuming an effective central potential V which, while generally similar to V_{00}, must not be expected to be equal to it.

This will be the first procedure we shall adopt. Having shown how the experimental data on total and differential elastic cross-sections may be understood in terms of this concept of an effective scattering potential we shall consider some cases, particularly those of helium, neon, argon, and sodium, in more detail, isolating the contribution from V_{00} and examining those which arise from electron exchange and atomic distortion or polarization.

The method required for this calculation is described in Chap. II, § 1. Since we shall have no further occasion to consider the inelastic scattering in this chapter, we shall drop the suffix 0 in F_0.

If we expand the function F in the form
$$F = \sum_l F_l(r)P_l(\cos\theta),$$

and substitute in (3), the function $F_l(r)$ satisfies the equation

$$\frac{d^2}{dr^2}(rF_l) + \left[k^2 - \frac{2m}{\hbar^2}V(r) - \frac{l(l+1)}{r^2}\right](rF_l) = 0.$$

As shown in Chapter II, the solution of this equation which is finite at the origin will have the asymptotic form

$$rF_l \sim A_l\sin(kr-\tfrac{1}{2}l\pi+\eta_l),$$

η_l being a phase constant. The amplitude $f(\theta)$ of the scattered wave was shown in Chapter II to be given by

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

and the differential cross-section for elastic scattering into the solid angle $d\omega$ is
$$I(\theta)\,d\omega = |f(\theta)|^2\,d\omega.$$

The total elastic cross-section Q is given by

$$Q = 2\pi \int_0^\pi I(\theta)\sin\theta \, d\theta;$$

we thus obtain

$$Q = \sum_l Q_l,$$

where

$$Q_l = 4\pi k^{-2}(2l+1)\sin^2\eta_l. \tag{5}$$

Born's first approximation holds only when η_l is small, so that $\sin\eta_l$ never passes through a maximum due to η_l reaching the value $\frac{1}{2}\pi$. Thus to this approximation one expects no oscillations in Q_l as a function of the energy. This is no longer the case if η_l may become greater than $\frac{1}{2}\pi$.

The classical approximation to $I(\theta)$ is never valid for electron scattering problems, but Jeffreys's method, particularly as modified by Langer (see Chap. V, p. 99), may usually be employed to obtain a good approximation to a phase η_l which is not too small.

It was shown in Chap. II, § 2, that, if

$$V(r) \ll \frac{l(l+1)}{r^2}\frac{\hbar^2}{2m},$$

for r given by

$$kr \sim \{l(l+1)\}^{\frac{1}{2}},$$

the contribution of all phases η_n with $n > l$ can be neglected. The convergence will thus be best for light atoms and slow electrons (see Chap. XVI, § 5).

Westin† has carried out an analysis, in terms of phase shifts, of the experimental data on the total and differential cross-sections for helium, neon, and argon. The 'observed' phases which he derives are illustrated in Figs. 92, 93, and 94. It must be remembered that analysis in terms of real phases is strictly correct only for electron energies below the excitation threshold, but it should be reasonably satisfactory at higher energies if the coupling with inelastic processes is not strong. Furthermore, the accuracy of much of the experimental data used by Westin is poor so that too much reliance should not be placed on the 'observed phases' which he derives. They may be taken as a valuable guide which could be made much more reliable if accurate experimental data were available. The reliability of phase-shift analyses for nuclear collisions (see Chap. XI, § 6.3, and Chap. XX, § 7.2) is much greater because of the relatively high precision of the observed data.

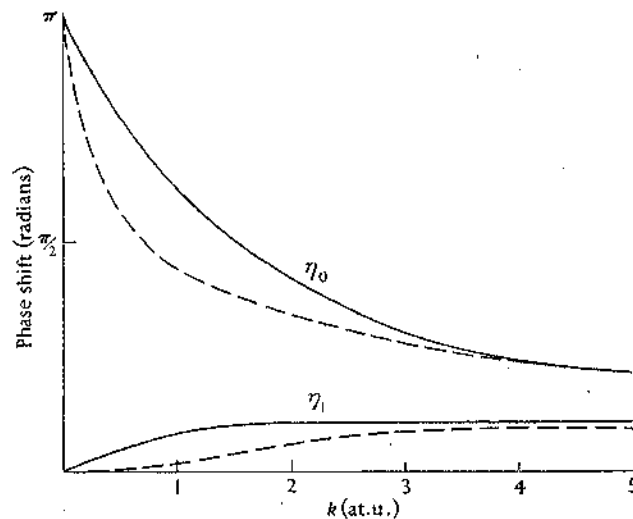† *Det. K. Norske Vidensk. Selskabs Skrifter*, 2 (1946–7).

FIG. 92. Phase shift for elastic scattering of electrons by helium atoms, derived from observed data by Westin.
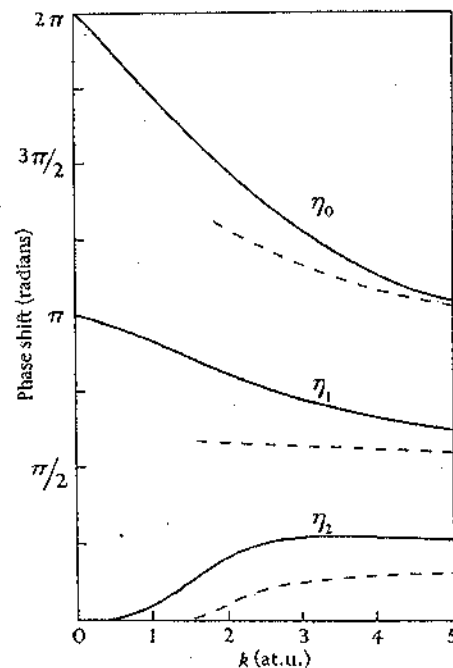- - - - calculated from the Hartree field without allowance for exchange.

FIG. 93. Phase shifts for elastic scattering of electrons by neon atoms, derived from observed data by Westin.
- - - - - - calculated from the Hartree field without allowance for exchange.
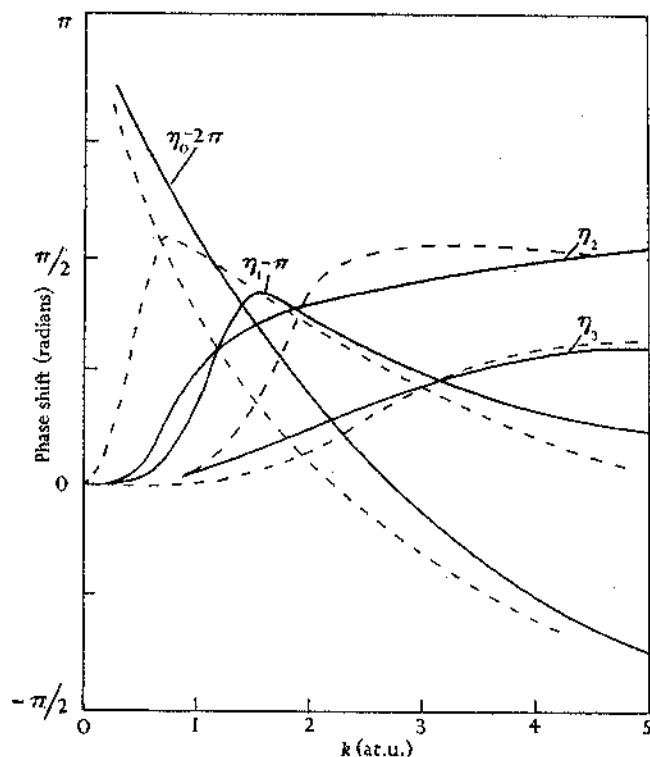
Fig. 94. Phase shifts for elastic scattering of electrons by argon atoms, derived from observed data by Westin.

- - - - - -   calculated from the Hartree field without allowance for exchange.

3. General application of the method of partial cross-sections

3.1. *Condition for existence of a Ramsauer–Townsend effect*

It has already been pointed out that a vanishing cross-section near the low-velocity limit can occur if the field is strong enough to introduce one or more additional wavelengths, i.e. one or more additional zeros of the wave function F_0 within the field. For this to be possible the field must be strong enough to introduce respectively one or more discrete energy-levels of zero angular momentum. The effect cannot occur with a repulsive field for the reasons discussed in Chap. II, § 5—the phase η_0 can only equal $s\pi$ for such a field if it eliminates s complete wavelengths which would exist if the field were not present. This is not possible

at low energies because the wavelength is then much greater than the range of the field. At higher energies it may occur, but then higher-order phases must be affected also and their contributions will prevent the total cross-section from becoming abnormally small.

Quantitative calculations, discussed in § 4, confirm this explanation of the Ramsauer–Townsend effect.

3.2. *Explanation of other general features*

We now give a general explanation of the following experimental facts:

1. The magnitude of the cross-section varies between wide limits, the maximum observed for the alkali metals being over 100 times that observed in neon.
2. The angular distributions of the scattered electrons show marked maxima and minima.
3. The cross-section–velocity curves have forms characteristic of the different columns of the periodic table.

In order to do this we make use of the following properties of the calculated phases:

(a) For any atomic field η_l decreases monotonically with l.

(b) η_l is small when, for r such that $kr \sim l + \frac{1}{2}$,

$$\frac{2m}{\hbar^2} V(r) \ll \frac{l(l+1)}{r^2}.$$

It follows from (b) that the series of partial cross-sections will converge quite quickly for low-velocity impacts; the major contribution will arise from the partial cross-sections Q_l of such an order that $\eta_l \simeq \frac{1}{2}\pi$. The maximum value of the contribution from a partial cross-section of order l is

$$Q_l^{\text{max}} = \frac{4\pi}{k^2} (2l+1).$$

We may therefore say at once that, the lower the velocity and the larger the value of l for which the phase η_l attains the value $\frac{1}{2}\pi$, the bigger will be the cross-section. Referring to the condition (b), we see that the biggest collision cross-sections will be those of atoms whose fields extend out to the greatest distances, viz. the alkali metals. If we use the empirical rules due to Slater[†] for the effective nuclear charges

† *Phys. Rev.* **36** (1930), 57.

of alkali atoms, and define the diameter of an atom as the distance at which the radial charge density $r^2|\psi|^2$ of the outer shell is a maximum, the following values of the radii r_0 of various atoms are obtained:

TABLE I

	r_0 in atomic units	kr_0	
		13 volts	0·5 volt
Li	2·3	2·3	0·46
Ni	4·1	4·1	0·82
K	6·1	6·1	1·22
Zn	3·1	3·1	0·62
He	0·6	0·6	0·12
Ne	0·7	0·7	0·14
A	1·3	1·3	0·26
Kr	1·7	1·7	0·34

Note. k is measured in units of $1/a_0$.

We give also the values of kr_0 corresponding to 13 and 0·5 eV electrons. Thus, using the criterion (5), we find that for potassium at least 7 harmonics are required, and the cross-section may be greater than† $50\pi a_0^2$, whereas one harmonic only is required for neon, and the effective area will not be greater than $10\pi a_0^2$. For $k = 0·2/a_0$ (0·54 eV), the area may be as great as $300\pi a_0^2$ for potassium, but still not much greater than $10\pi a_0^2$ for neon or helium. There is, then, clearly no difficulty in explaining the wide range in magnitude observed in the effective cross-sections. It is equally clear that the method indicates the possibility of maxima and minima in the angular distribution given by (4). Again the dominant effect arises from terms in the series such that $\eta_l \simeq \frac{1}{2}\pi$. The angular distribution, then, is roughly of the form

$$I(\theta) = \text{const.}\{P_l(\cos\theta)\}^2,$$

which has l minima. This will be especially marked for the lower velocity impacts, where only a few terms of the series (4) are required and the weight factor $2l+1$ is particularly effective. Thus for electrons of 30 eV energy in argon the angular distribution is given closely by $\{P_2(\cos\theta)\}^2$. Actually the calculated phase values at this velocity are

$$\eta_0 = 2\pi+0·885, \quad \eta_1 = 4·831, \quad \eta_2 = 1·983, \quad \eta_3 = 0·374, \quad \eta_4 = 0·159.$$

† The cross-sections obtained in this way will only be approximately correct when the field is sufficiently strong to produce large phase changes. For collisions of high-velocity electrons a large number of terms are required in the series, but each is small and the total cross-section small also.

It must be realized that these remarks are only illustrative, and the actual effects produced by the sum of a number of partial cross-sections may be very complicated, particularly for heavy atoms. The diffraction of waves by spherical obstacles is a much more complicated process than diffraction by a grating or other symmetrical arrangement.

It is not possible to explain the third feature listed above in such simple terms as the preceding. The quasi-periodic behaviour of the partial cross-sections must be due to the behaviour of $\sin\eta_l$. At low velocities, for the lightest atoms, only the zero-order phase is appreciable. An atomic field will behave qualitatively in a similar way to the potential well discussed in Chap. II, § 4. At a given velocity, for some atomic field, the phase η_0 will attain a value near $\frac{1}{2}\pi$, and for some heavier atom a value of $\frac{3}{2}\pi$ will be attained, giving an equal maximum of the zero-order cross-section, and so on. For some atom with intermediate properties η_1 will become appreciable, and so on. In this way some quasi-periodic behaviour of the cross-sections might be expected, but we still require to show from the theory that the periodicity follows that of the periodic table. This was first done by Allis and Morse† using a simplified model for the effective scattering potential of the form

$$V = \begin{cases} -Z\epsilon^2\left(\dfrac{1}{r}-\dfrac{1}{r_0}\right) & (r \leqslant r_0), \\ 0 & (r \geqslant r_0), \end{cases} \tag{6}$$

which makes possible an analytic solution of equation (3). In order to illustrate the periodic behaviour of the cross-sections two quantities, x and β, were defined such that

$$\beta^2 = Zr_0/2a_0, \qquad x = kr_0.$$

The first of these depends only on the atomic field, while the second is a function also of the incident electron velocity. Allis and Morse then showed that the cross-sections are quasi-periodic in β with period unity. This is illustrated in Fig. 95, where a number of partial cross-sections corresponding to different values of x are illustrated as functions of β.‡ If, now, the approximate atomic radii given by Slater are used (given above in Table I) and the constant Z above is adjusted to give as good agreement as possible of the form (6) for V with that obtained from Slater's values, it is found that a period of 1 in β is approximately a

† *Zeits. f. Physik,* 70 (1931), 567.

‡ Compare the behaviour of Q_0 as function of β for $x = 0$ with the corresponding behaviour of Q_0 as function of k_0 for $k = 0$ in Fig. 4 (a) of Chapter II.
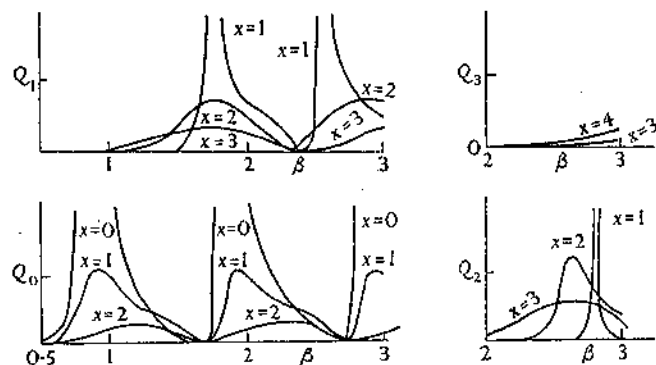
FIG. 95. Quasi-periodicity of partial cross-sections.

whole period in the periodic table. This may be seen from the following values of β:

TABLE II

Lithium	.	.	.	1·36	Helium .	.	.	0·77
Sodium	.	.	.	2·54	Neon .	.	.	1·73
Potassium	.	.	.	3·51	Argon .	.	.	2·68
					Krypton	.	.	3·66

The lighter elements are to some extent anomalous in this respect; this is also borne out by the observations (see Fig. 89 of this chapter).

4. Quantitative application of method of partial cross-sections

The first quantitative application of the theory was made by Holtsmark[†] for the scattering of electrons by argon; but we shall first consider the results obtained by Allis and Morse using their simplified model.

Having chosen the values of the parameter β and r_0, using Slater's rules (loc. cit.), it was usually found that a good approximation to the observed cross-sections is obtained with this model. In Fig. 96 the experimental curves are compared with calculated curves. The values of β and r_0 used in obtaining the latter are slightly different from those obtained from Slater's rules (loc. cit), but the differences are not great. In Table III the parameters which give the best fit with experiment are compared with Slater's values, both measured in atomic units.

The agreement obtained is very striking and leaves little doubt as to the correctness of the theoretical explanation of the Ramsauer–Townsend effect afforded by quantum mechanics. However, the field

† *Zeits. f. Physik*, 55 (1929), 437.

used gives only a rough approximation, particularly for very low velocity collisions. For such cases large effects may arise from the atomic field beyond the radius r_0. To allow for this Morse† extended the calculations to the interaction

$$V = - Z\epsilon^2 r^{-1} \exp(-2r/r_0),$$

and found that very similar results are obtained, the same quantities β and kr_0 being again important.
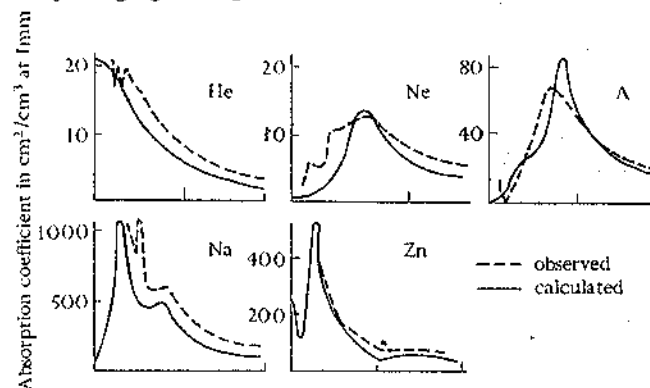

FIG. 96. Comparison of observed and calculated cross-section curves.

TABLE III

| Atom | β | | r_0 | |
	Slater	From cross-sections	Slater	From cross-sections
Helium	0·77	0·80	0·6	0·55
Neon	1·73	1·71	0·7	0·75
Argon	2·68	2·7	1·3	1·4
Sodium	2·54	2·55	4·1	4·25
Zinc	3·77	3·78	3·1	3·14

Holtsmark‡ obtained very good agreement with the observed cross-section for argon, including the Ramsauer–Townsend effect, by using for V the Hartree field modified by an empirical polarization correction and evaluating the phases η_l by numerical integration of the differential equations. Without the polarization modification the agreement is not good, the Ramsauer–Townsend effect not being found (cf. Fig. 104).

A much stricter test of the theory may be applied by comparing calculated and observed angular distributions. These are much more sensitive to inaccuracy in the theory. In Fig. 97 the angular distribution curves observed by Bullard and Massey and by Ramsauer and Kollath

† *Rev. Mod. Phys.* 4 (1932), 577.   ‡ Loc. cit.

for argon (loc. cit.) are compared with those calculated by using Holts-
mark's values of the phases η_l. The agreement for 30 and 12 volts is
found to be very good. It is of interest to note that at the lower voltages
the agreement with curves calculated from the simplified model of Morse
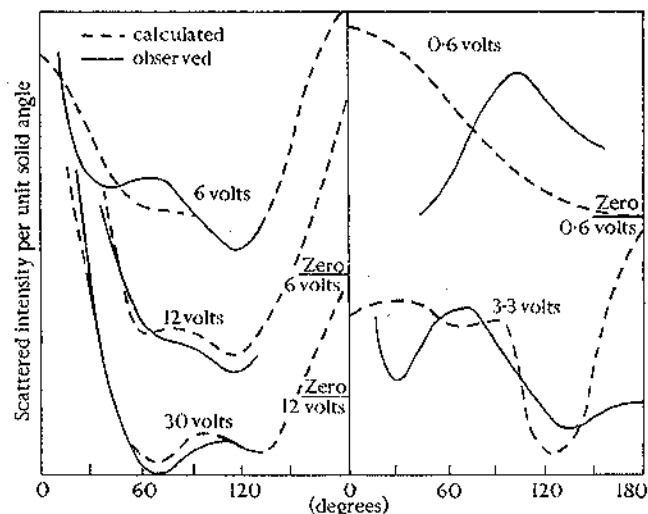

FIG. 97. Comparison of observed and calculated angular distributions of electrons
scattered by argon atoms.

and Allis discussed in § 3 is not nearly so satisfactory. At very low
velocities, however, the observations of Ramsauer and Kollath are no
longer in agreement even with Holtsmark's calculations, as seen from
the figure.

Holtsmark† carried out calculations for krypton similar to those for
argon, using the Hartree field modified by a polarization correction.
He obtained good agreement with observation, both in comparison with
observed total cross-sections and with the angular distributions measured
by Arnot‡ and by Ramsauer and Kollath§ except at very low electron
energies (less than 3 eV).

We now consider the problem of calculating the scattering directly
given the Hartree–Fock wave functions for the atomic electrons. As in
Chapter XVII we proceed first from the static field approximation (§ 5),
then allow for exchange (§ 6) and finally for atom distortion and polariza-
tion (§ 7).

† Zeits. f. Physik, 66 (1930), 49.   ‡ Proc. Roy. Soc. A, 133 (1931), 615.
§ Ann. der Physik, 12 (1932), 837.

---

5. Results obtained with the static field approximation

Calculations of the phase shifts for scattering by the Hartree or
Hartree–Fock fields have been carried out for various atoms, notably
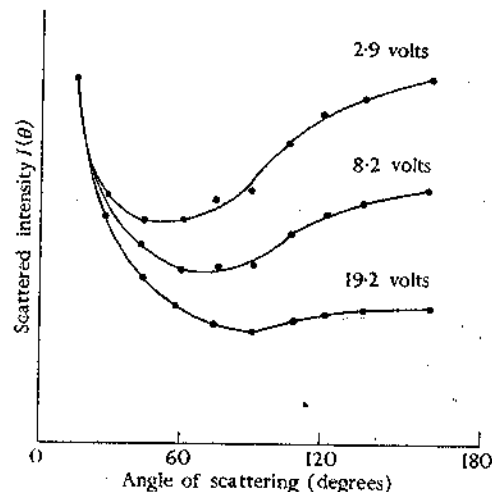helium,† neon,‡ argon,§ chlorine,‖ and oxygen.††

FIG. 98. Observed angular distributions of slow electrons scattered
elastically by helium atoms.

Results for argon are illustrated in Fig. 94. Apart from failure to
reproduce the behaviour required to give the Ramsauer–Townsend
effect the static field phase shifts are considerably in error at energies
below 30 eV ($ka_0 = 1\cdot5$). Similar quite considerable discrepancies are
seen for neon (Fig. 93).

The most obvious failure of the static atomic field as a representation
of the effective potential for slow collisions is presented by electron
scattering from helium atoms. At electron energies below 20 eV the
phase shifts η_l ($l \geqslant 1$) for scattering by the static field are all very small
(see Fig. 92) so the angular distribution should be uniform. However,
as shown in Fig. 98, the observed‡‡ curves exhibit a pronounced mini-
mum even for electron energies as low as 3 eV.

† MacDougall, Proc. Roy. Soc. A, 136 (1932), 549; La Bahn and Callaway, Phys. Rev.
135 (1964), 1539.   ‡ Thompson, Proc. Roy. Soc. A, in course of publication.
§ Westin, loc. cit.; Thompson loc. cit.
‖ Hartree, Kronig, and Petersen, Physica, 1 (1934), 901.
†† Bates and Massey, Proc. Roy. Soc. A, 192 (1947), 1.
‡‡ Bullard and Massey, Proc. Roy. Soc. A, 133 (1931), 637; Ramsauer and Kollath,
Ann. der Physik, 10 (1931), 143; 12 (1932), 529, 837.

For a number of other atoms calculations have been carried out in which the large phases were determined from Jeffreys's approximation (Chap. V, § 5) and the small ones from Born's approximation (Chap. V, § 2). To illustrate the kind of accuracy which may be attained in this way[†] Table IV gives the values of the phase shifts calculated for

TABLE IV

Calculated phase shifts for 54-volt electrons scattered by krypton atoms

Phase η_l l	From accurate solution	Jeffreys's approximation	Langer modification	Born approximation
0	9·696	··	9·597	··
1	7·452	7·710	7·540	··
2	4·469	4·748	4·505	··
3	1·238	1·410	1·355	0·779
4	0·445	0·557	0·535	0·414
5	0·143	0·190	0·174	0·144

54-volt electrons in krypton calculated by accurate numerical solution of the differential equation[‡] and by the approximate methods.[§] Values obtained by use of Langer's modification of Jeffreys's approximation are also included. It will be seen that for $\eta < 0.5$ Born's approximation is sufficiently accurate. For larger values of η Jeffreys's approximation is superior and is improved considerably for small-order phases by the Langer modification.

For mercury vapour Henneberg[||] and Massey and Mohr[††] carried out calculations in this way using the Thomas–Fermi field.[‡‡] The calculated angular distributions are compared with Arnot's observations in Fig. 99, good general agreement being revealed. Similar calculations have been carried out for potassium,[§§] zinc,[||||] cadmium,[||||] and bromine,[†††] reasonable agreement being obtained in all cases provided the electron energy is not too low.

6. Electron exchange in elastic collisions

In the discussion of § 4 the elastic scattering has been considered in terms of a semi-empirical model. At higher energies good results are obtained if the effective interaction assumed is taken to be the actual

---

† An empirical discussion of the effectiveness of these methods has been given by Arnot, *Proc. Camb. Phil. Soc.* 32 (1936), 161; see also Karle and Bonham, *J. Chem. Phys.* 40 (1964), 1396.   ‡ Holtsmark, *Zeits. f. Physik*, 66 (1930), 49.

§ Arnot and Baines, *Proc. Roy. Soc.* A, 146 (1934), 651.

|| *Zeits. f. Physik*, 83 (1933), 555.   †† *Nature*, 130 (1932), 276.

‡‡ Loc. cit.   §§ McMillen, *Phys. Rev.* 46 (1934), 983.

|||| Childs and Massey, *Proc. Roy. Soc.* A, 142 (1933), 509.
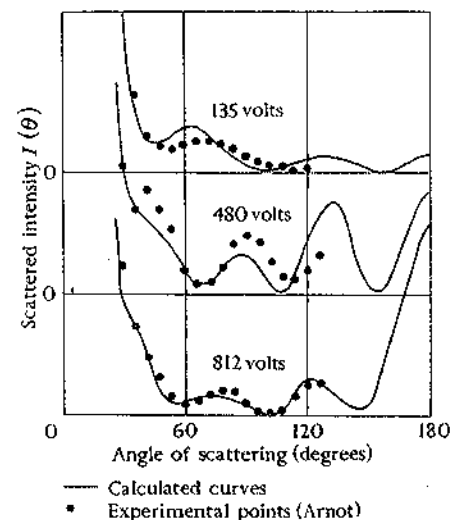
††† Shaw and Snyder, *Phys. Rev.* 58 (1940), 600.

FIG. 99. Comparison of observed and calculated angular distributions of electrons elastically scattered by mercury atoms.

mean static potential V_{00} of the atom or rather the Hartree or Hartree–Fock potential. For low energies, however, this is not adequate. Thus Holtsmark found it necessary to include an additional potential which had the asymptotic form $(-\alpha \epsilon^2/r^4)$ expected from a polarization effect but which otherwise was continued inwards to join smoothly to the Hartree field in an adjustable fashion so as to reproduce the observed results for argon and krypton, including the Ramsauer–Townsend effect. Even this empirical potential did not reproduce satisfactorily the observed angular distribution for electrons with energies below 4 eV.

The obvious failure of the static field as a representation of the effective potential for slow collisions presented by electron scattering from helium atoms has also been pointed out.

As discussed in Chap. XVII, § 2, the most important modification of the static field approximation in the theory of electron scattering by hydrogen atoms arises from electron exchange. It is natural, therefore, to examine the contribution which exchange makes to the scattering for other atoms.

The method used for including electron exchange in the one-body approximation for helium has already been outlined in Chap. XV, § 1.33. It involves the solution of integro-differential equations of the same