THE ERRORS OF APPROXIMATION IN JEFFREYS'S PHASES

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The exact solution of the radial wave equation representing the motion of an electron in the field of a spherically symmetrical atom can be obtained only by a lengthy and laborious numerical integration. An approximate solution, which for many purposes is sufficiently accurate, can be rapidly obtained by a method originally due to Jeffreys*. Since this approximation has been used extensively in the past, and will undoubtedly prove useful in the future, it is clearly of importance to known just how good the approximation is, and where it is likely to fail.

Two years ago, with the assistance of Dr G. O. Baines, I made an investigation† of the errors occurring in Jeffreys's approximation for phases in krypton, for which gas a few exact phases were known. Since then a large number of exact phases for neutral chlorine have been calculated by Hartree, Kronig and Petersen‡, so making possible a far more extensive test of this approximation.

In this paper a large number of phases, calculated by Jeffreys's method, are compared with the exact phases. The source of the errors occurring in the approximate phases is discussed, and simple methods for correcting the errors are put forward, and their application to a number of phases is shown.

Jeffreys's approximation

The wave equation for an electron of energy E in a spherically symmetrical atomic field in which its potential energy is $V(r)$ is

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0, \tag{1}$$

of which the solutions are

$$\psi = \frac{P(r)}{r} P_l(\cos\theta), \tag{2}$$

where $P(r)$ satisfies the radial wave equation

$$P'' + \left[k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right] P = 0, \tag{3}$$

* Jeffreys, *Proc. Lond. Math. Soc.* 23 (1924), 437.

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

‡ Hartree, Kronig and Petersen, *Physica*, 1 (1934), 895.

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in which $k = 2\pi/\lambda = (8\pi^2 mE/h^2)^{\frac{1}{2}}$,

λ being the wave-length of the electron, and

$$-2Z_p/r = 8\pi^2 m\, V(r)/h^2,$$

where Z_p is the effective nuclear charge for potential, using the Hartree field. The dashes in (3) denote differentiation with respect to r.

We require to known the asymptotic behaviour of that solution of (3) which is zero at the origin. If $V(r)$ is zero this solution is a multiple of

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

and has the asymptotic behaviour

$$P \sim \sin(kr - \tfrac{1}{2}l\pi). \tag{4}$$

If $V(r)$ is not zero it is not possible to obtain an analytical solution of (3). But since $rV(r)$ tends to zero for large r, its asymptotic solution will differ from (4) only by a certain phase difference δ_l. Thus

$$P \sim \sin(kr - \tfrac{1}{2}l\pi + \delta_l). \tag{5}$$

A knowledge of these phase constants is required in all problems involving the scattering of electrons by atoms. For instance, the intensity of the elastically scattered current at an angle θ is given by

$$I(\theta) = \frac{1}{4k^2}\left|\sum_{l=0}^{\infty}(2l+1)\,[e^{2i\delta_l} - 1]\,P_l(\cos\theta)\right|^2.$$

The numerical integration of the radial wave equation (3) required to obtain these phases is a lengthy and laborious process. However, an approximate solution, originally due to Jeffreys, has been obtained in various ways by several authors, including Wentzel, Kramers and Brillouin.

Following Hartree, Kronig and Petersen* we notice that in the region in which

$$k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2} \tag{6}$$

is positive the radial wave function P is an oscillating function of r. We therefore write

$$P(r) = F(r)\sin\phi(r), \tag{7}$$

where $F(r)$ and $\phi(r)$ may be regarded as the local amplitude and phase of the oscillation at radius r. Substitution of (7) in (3) gives

$$\left[F'' + \left(k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right)F - (\phi')^2 F\right]\sin\phi + [F\phi'' + 2F'\phi']\cos\phi = 0.$$

Then choosing F and ϕ so that the coefficients of $\sin\phi$ and $\cos\phi$ are each zero we obtain

$$\left.\begin{aligned} \phi' &= \frac{k}{F^2}, \\ F'' + \left[k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right]F - \frac{k^2}{F^3} &= 0, \end{aligned}\right\} \tag{8}$$

* Hartree, Kronig and Petersen, *Physica*, 1 (1934), 895.

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where the arbitrary constant has been put equal to k. With this choice of the arbitrary constant, $F \to 1$, $F' \to 0$ as $r \to \infty$.

Jeffreys's approximation is obtained by neglecting F'', which is valid provided that

$$\frac{F''}{F\left[k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right]} \ll 1. \tag{9}$$

Neglecting F'' in (8) we obtain

$$\left.\begin{aligned} F &= k^{\frac{1}{2}}\left[k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right]^{-\frac{1}{4}}, \\ \phi &= \int \frac{k}{F^2}\,dr = \int\left[k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right]^{\frac{1}{2}} dr, \end{aligned}\right\} \tag{10}$$

and hence from (7)

$$P = k^{\frac{1}{2}}\left[k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right]^{-\frac{1}{4}} \sin\int\left[k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right]^{\frac{1}{2}} dr.$$

This expression for P is valid only over the range of r where (6) is positive. If (6) has a zero r_0 such that (6) is negative for $r < r_0$ and positive for $r > r_0$, then Jeffreys has shown that the asymptotic value of the phase is given by

$$P \sim \sin\left[\tfrac{1}{4}\pi + \int_{r_0}^{\infty}\left\{k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right\}^{\frac{1}{2}} dr\right]. \tag{11}$$

For $r < r_0$, P decreases exponentially, becoming zero at the origin. The term $\pi/4$ is the contribution to the phase from the exponential tail of the wave in the totally reflecting region $r < r_0$.

If $V(r)$ is zero we obtain in place of (11) the equation

$$P \sim \sin\left[\tfrac{1}{4}\pi + \int_{r_0'}^{\infty}\left\{k^2 - \frac{l(l+1)}{r^2}\right\}^{\frac{1}{2}} dr\right], \tag{12}$$

where r_0' is the zero of this integrand.

The phase constant δ_l in (5) is the phase difference between (11) and (12). Therefore we have

$$\delta_l = \int_{r_0}^{\infty}\left[k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right]^{\frac{1}{2}} dr - \int_{r_0'}^{\infty}\left[k^2 - \frac{l(l+1)}{r^2}\right]^{\frac{1}{2}} dr, \tag{13}$$

where r_0 and r_0' are the zeros of the respective integrands. In the special case of the δ_0 phase we must put $r_0 = r_0' = 0$, as has been pointed out by Arnot and Baines (*loc. cit.*).

Comparison of approximate and exact phase

Using the values of Z_p given by Hartree, Kronig and Petersen for the atomic field of neutral chlorine, a number of phases have been calculated from Jeffreys's approximate equation (13). These, together with the exact phases calculated by

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Hartree, Kronig and Petersen, are given in Table I. In the last column of the table the error in Jeffreys's approximate phase, being the difference between the two previous columns, is tabulated.

Table I. *Exact and approximate phases for chlorine*

k^2 volts	k^2 atomic units	k atomic units	Phase	Exact value	Jeffreys's approx.	Error
0	0	0	δ_0	9·425	10·464	1·039
1·356	0·1	0·316	δ_0	8·680	9·431	0·751
4·06	0·3	0·548	δ_0	8·210	8·926	0·716
6·78	0·5	0·707	δ_0	7·928	8·658	0·730
			δ_1	5·145	5·251	0·106
15·0	1·11	1·05	δ_0	7·417	8·121	0·704
			δ_1	4·892	4·985	0·093
			δ_2	0·650	1·206	0·556
30·0	2·22	1·49	δ_0	6·913	7·643	0·730
			δ_1	4·593	4·718	0·125
			δ_2	1·450	1·649	0·199
27·12	2·00	1·41	δ_3	0·197	0·184	−0·013
50·0	3·70	1·92	δ_0	6·503	7·231	0·728
			δ_1	4·327	4·439	0·112
			δ_2	1·750	1·821	0·071
54·24	4·00	2·00	δ_3	0·508	0·533	0·025
			δ_4	0·176	0·177	0·001
81·36	6·00	2·45	δ_3	0·725	0·779	0·054
			δ_4	0·300	0·301	0·001
100·0	7·40	2·72	δ_0	5·913	6·633	0·720
			δ_1	3·926	4·028	0·102
			δ_2	1·860	1·918	0·058
108·48	8·00	2·83	δ_3	0·860	0·901	0·041
			δ_4	0·405	0·408	0·003
216·00	16·00	4·00	δ_0	5·209	5·977	0·768
			δ_1	3·439	3·544	0·105
			δ_2	1·844	1·908	0·064
			δ_3	1·069	1·074	0·005
			δ_4	0·648	0·651	0·003
			δ_6	0·242	0·246	0·004
			δ_7	0·152	0·152	0·000

In using the equation (13) the two integrals are not summed independently. The procedure is to plot against r the value of

$$\left[k^2+\frac{2Z_p}{r}-\frac{l(l+1)}{r^2}\right]^{\frac{1}{2}}$$

from r_0 to r_0', and then continue the curve by plotting

$$\left[k^2+\frac{2Z_p}{r}-\frac{l(l+1)}{r^2}\right]^{\frac{1}{2}}-\left[k^2-\frac{l(l+1)}{r^2}\right]^{\frac{1}{2}}$$

from r_0' outwards until its value becomes zero, which occurs at $r=7{\cdot}0$ atomic units for chlorine.

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Owing to the rapid fall of the curves frequent changes of scale must be made. The curves were then integrated by an Amsler planimeter.

It will be seen from Table I that, with one exception, the error is always positive, i.e. Jeffreys's approximation gives too large a value for the phase. The exception occurs for δ_3 for $k = 1{\cdot}41$. The negative error in this phase has been checked by making two completely independent redeterminations of Jeffreys's value.

In considering the error in the approximate phases it should be noted that it is the actual error, and not the percentage error, that is of primary importance; since even multiples of π in any phase are of no consequence.

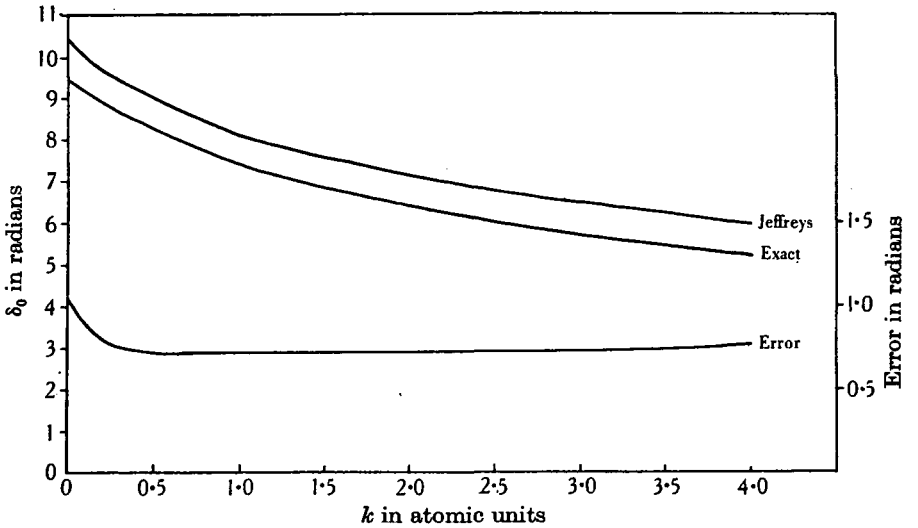


Fig. 1. Jeffreys's value and exact value for δ_0. Showing variation of the error with k.

The conclusions drawn in the paper by Arnot and Baines are confirmed here. Thus we see that (*a*) by far the largest error occurs in the phases of zero order; (*b*) with the exception of δ_2 for small values of k, the error decreases as the order of the phase increases at each value of k; (*c*) as k is increased the error in the zero order phase at first decreases rapidly and then becomes practically constant. This is illustrated in Fig. 1, where Jeffreys's phase, the exact phase and the error in Jeffreys's phase are plotted as functions of k.

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DISCUSSION OF THE ERROR IN JEFFREYS'S PHASE

(1) *Errors in phases of order greater than zero*

Jeffreys's value for δ_l is obtained by taking the difference between the phases

$$\tfrac{1}{4}\pi + \int_{r_0}^{\infty}\left[k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right]^{\frac{1}{2}} dr \qquad (14)$$

and

$$\tfrac{1}{4}\pi + \int_{r_0'}^{\infty}\left[k^2 - \frac{l(l+1)}{r^2}\right]^{\frac{1}{2}} dr, \qquad (15)$$

except in the case of δ_0 which will be discussed later. The expression (14) is the phase of the P-wave in the field of the atom, and (15) represents the phase it would have if the atom were absent, i.e. for $V(r)$ zero.

The error in (15) has been discussed by Arnot and Baines* who found that it is independent of the value of k, and has the value

$$[l + \tfrac{1}{2} - \sqrt{\{l(l+1)\}}^{\frac{1}{2}}]\frac{\pi}{2}$$

for all values of l greater than zero, the expression (15) being *greater* than the exact value by this amount. For $l=1$ this error amounts to 0·134; for $l=2$ it is 0·079; for $l=3$ it is 0·063; for $l=4$ it is 0·044; for $l=6$ it is 0·030, and for $l=7$ it is 0·026.

There are two sources of error in both (14) and (15). There is an error in the integral due to the neglect of F'' in the equation (8), and there is also an error in the constant term $\pi/4$ which takes account of the tail of the wave in the totally reflecting region $r<r_0$. The $\pi/4$ term is obtained by replacing the expression (6) by a linear function of r with the same zero r_0. The P-equation (3) can then be solved in terms of Bessel functions of order $\pm\frac{1}{3}$, and the relation between their asymptotic behaviour for $r-r_0$ positive and for $r-r_0$ negative then gives the term $\pi/4$. This procedure clearly depends upon the Bessel functions closely approaching their asymptotic behaviour before the representation of (6) by a linear function becomes inadequate.

It is of interest to see which of these two sources of error mainly accounts for the difference between Jeffreys's value and the exact value of the phases. An estimate of the error due to the neglect of F'' in (8) can be found as follows. If we do not neglect F'' we can write in place of (10)

$$F = k^{\frac{1}{2}}\left[k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2} + \frac{F''}{F}\right]^{-\frac{1}{4}},$$

$$\phi = \int \frac{k}{F^2}\,dr = \int\left[k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2} + \frac{F''}{F}\right]^{\frac{1}{2}} dr,$$

and therefore

$$\phi = \int\left[k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right]^{\frac{1}{2}}\left[1 + \frac{F''}{F\left(k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right)}\right]^{\frac{1}{2}} dr.$$

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

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Jeffreys's approximation (10) is good provided that the F'' term in the second square bracket is numerically very small compared with unity. This is the condition given by (9). If this term, although not very small compared with unity, is yet less than unity we obtain

$$\phi = \int \left[k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right]^{\frac{1}{2}} dr + \frac{1}{2}\int \frac{F''}{F\left[k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right]^{\frac{1}{2}}} dr.$$

Making use of the approximate expression (10) in the correction term we have

$$\phi = \int \left[k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right]^{\frac{1}{2}} dr + \frac{1}{2k}\int FF''\, dr.$$

Thus in place of the first approximations given by (14) and (15) we have to a higher approximation

$$\tfrac{1}{4}\pi + \int_{r_0}^{\infty} \left[k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right]^{\frac{1}{2}} dr + \frac{1}{2k}\int_{r_0}^{\infty} FF''\, dr, \tag{16}$$

$$\tfrac{1}{4}\pi + \int_{r_0'}^{\infty} \left[k^2 - \frac{l(l+1)}{r^2}\right]^{\frac{1}{2}} dr + \frac{1}{2k}\int_{r_0'}^{\infty} ff''\, dr, \tag{17}$$

where f and f'' are the corresponding expressions for F and F'' when $V(r)$ is zero. δ_l is the phase difference between (16) and (17).

To obtain F and f in the correction terms, and also their second derivatives, we use the first approximation in which F'' and f'' are neglected. Thus

$$F = k^{\frac{1}{2}}\left[k^2 + \frac{2Z_p}{r} - \frac{l(l+1)}{r^2}\right]^{-\frac{1}{4}} \tag{18}$$

and

$$f = k^{\frac{1}{2}}\left[k^2 - \frac{l(l+1)}{r^2}\right]^{-\frac{1}{4}}. \tag{19}$$

The correction term* in (16) and (17) corrects the first approximations (14) and (15) for the neglect of F'' and f'' only. There still remains the error in the constants $\pi/4$ occurring in (16) and (17).

Now since F and f are always positive over the range of integration, the sign of the correction will be given by the sign of F'' and f''. By differentiation of (19) it is found that f'' is positive for all values of k and l over the range of r from r_0' to ∞, i.e. over the limits of the integral in (17). Therefore we see that the effect of correcting (15) for the neglect of f'' is to *increase* its value. But it has been shown (p. 166) that (15) is *greater* than the exact value, i.e. the error in (15) is already positive. Therefore the main error in (15) is not due to the neglect of f'', and can only be due to an error in the $\pi/4$ term which takes account of the tail of the wave in the totally reflecting region, this factor $\pi/4$ being too large.

* In the following discussion it should be remembered that the correction term in (16) and (17) is only a first approximation correction for the neglect of F'' and f'' owing to the approximations made in determining it.

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We shall now investigate the effect of correcting (14) for the neglect of F''. Differentiation of (18) shows that the sign of F'' over the range of integration in (16), unlike that of f'', depends upon the values of k and l. Consequently F'' has been obtained by numerical differentiation of F for several values of k and l. In Figs. 2*a* and 3 the ratio

$$\frac{F''}{F\left[k^2+\frac{2Z_p}{r}-\frac{l(l+1)}{r^2}\right]} \tag{20}$$

has been plotted against r over the effective range of integration in (14), i.e. from the zero r_0 to $r=7{\cdot}0$ atomic units at which Z_p is effectively zero. We see from (9) that the neglect of F'' will not be serious if the above ratio is very small compared with unity.

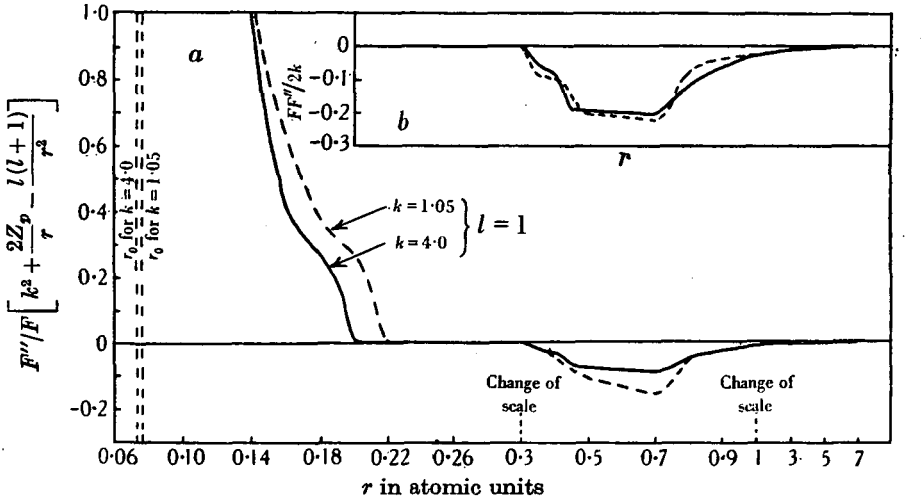


Fig. 2. (*a*) Expression (20) as a function of r for $l=1$ and for $k=1{\cdot}05$ and $4{\cdot}0$. (*b*) The correction factor $FF''/2k$ as a function of r for the curves in (*a*).

It would appear from Figs. 2*a* and 3 that the neglect of F'' is very serious near the zero r_0. However, this rise of the curves near r_0 is largely spurious, and is due to errors in the determination of F'' from the approximate values for F given by (18), which is not valid when the function (20) approaches or exceeds unity. The value of F given by (18) tends to infinity at the zero r_0. But F is the amplitude of the P-wave which is certainly not infinite at r_0, and probably is not very different from its value at a point at quite a considerable distance from r_0. Thus the curves in Figs. 2*a* and 3 represent to a close approximation the true value of the function (20) only where their ordinates are considerably less than unity.

We see from Fig. 2*a* that an error will be produced in δ_1 for $k=1{\cdot}05$ and for $k=4{\cdot}0$ because F'' has an appreciable negative value when r is greater than 0·3.

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Fig. 2*b* shows the correction factor $FF''/2k$ as a function of r, the r-scale being that of Fig. 2*a*. Integration of these curves over the range $r = 0{\cdot}22$ to $r = 7{\cdot}0$ gives for the correction to δ_1 the value $-0{\cdot}093$ for $k = 1{\cdot}05$, and $-0{\cdot}097$ for $k = 4{\cdot}0$. These corrections reduce the error in δ_1 to practically zero for both values of k.

Referring now to Fig. 3*a* we see that the function (20) for δ_2 for $k = 1{\cdot}05$ is numerically considerably greater than unity over the range $r = 1{\cdot}5$ to $r = 2{\cdot}5$, F being negative. This indicates that a large positive error is to be expected in δ_2, as in fact does occur. However, as has been pointed out above, the curve is not

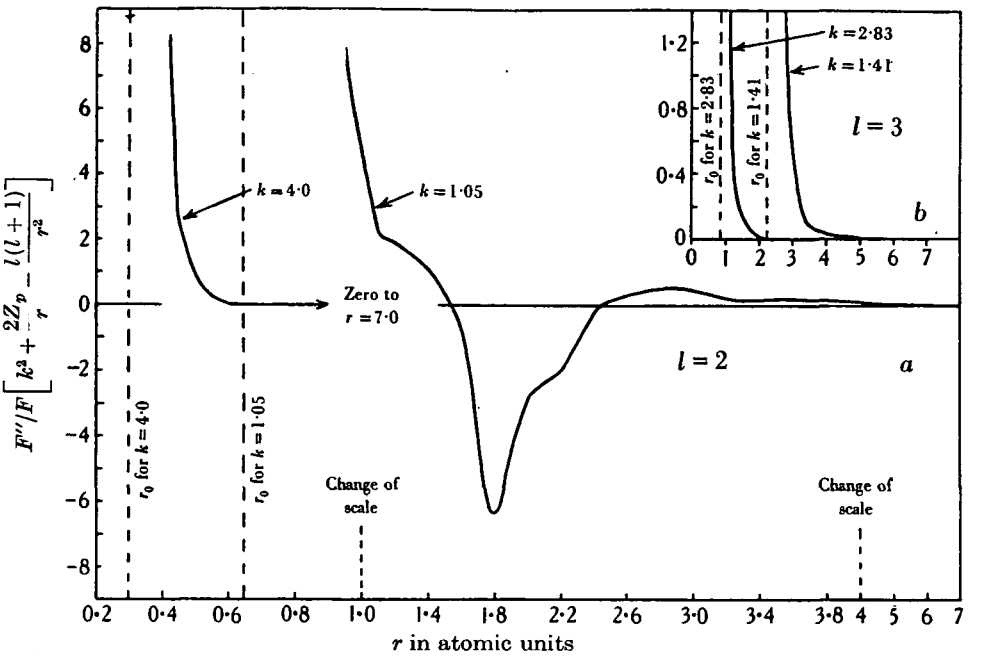


Fig. 3. Expression (20) as a function of r, (*a*) for $l = 2$, $k = 1{\cdot}05$ and $4{\cdot}0$; (*b*) for $l = 3$, $k = 1{\cdot}41$ and $2{\cdot}83$.

even an approximate representation of the function (20) over this range where its ordinates are greater than unity. For this reason we cannot validly apply the correction term of (16).

Fig. 3*a* also contains the curve for δ_2 for $k = 4{\cdot}0$. Here we see that the function (20) is, after the initial steep drop, practically zero over the whole remaining range of r, thus showing that the error due to neglect of F'' is practically zero. By plotting $FF''/2k$, and integrating this over r, omitting as before the initial steep drop near r_0, the correction is found to be $-0{\cdot}006$. Since the actual error is more than ten times as great as this we must conclude that practically all the error in δ_2 for $k = 4{\cdot}0$ arises from errors in the $\pi/4$ terms in (14) and (15).

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Considering now errors in δ_3, we determined the function (20) for two values of k. These curves as a function of r are shown in Fig. 3*b*. Since F'' is positive over the whole range of r the correction will be positive, and therefore in the right sense to reduce the negative error in δ_3 for $k = 1{\cdot}41$. However, when the curve drops almost monotonically to zero, as do those of Fig. 3*b*, it is not possible to decide over what range of r to integrate $FF''/2k$ to obtain the correction. This correction must be at least $+0{\cdot}013$, which would be obtained by integrating $FF''/2k$ from about $r = 5{\cdot}0$ outwards. If we suppose the correction to be just this amount then no error will be introduced by the $\pi/4$ terms.

Since the curve in Fig. 3*b* for δ_3 for $k = 2{\cdot}83$ is positive over the whole range of r any correction for the neglect of F'' will increase the total error in the phase which is positive, and consequently the error in δ_3 for this value of k must be mainly due to errors arising from the $\pi/4$ terms in (14) and (15). Since the curve in Fig. 3*b* for this value of k drops very sharply to zero it is probable that the error due to neglect of F'' is almost zero.

For higher values of l the function (20) is likewise positive over the whole range of r, and drops sharply to zero, so that the errors in these phases must be mainly due to errors in the $\pi/4$ terms.

The results discussed above are illustrated in Table II, where the total error in the phase is given in the third column, and the correction for the neglect of F'', calculated by integration of $FF''/2k$, in the fourth column. The error remaining after this correction is made may be due either to neglect of f'' in (15) or to errors in the $\pi/4$ terms in (14) and (15), or to both of these. It has been shown (p. 167) that f'' is always positive, and hence the error due to its neglect is negative, but the total error in (15) is always positive (see p. 166), so that the main error in (15) must be due to the $\pi/4$ terms. Integration of $ff''/2k$ shows that the error due to neglect of f'' is small compared with that which must arise from the $\pi/4$ term, so that we may take the total error in (15) to be due to the $\pi/4$ term being too great to account for the tail of the P-wave in the totally reflecting region. The correction arising from the $\pi/4$ terms, which is then deduced from the fact that this correction must be just sufficient to reduce the remaining error to zero, is given in the fifth column. In the final column are given the correct values for the "tail-correcting" terms which should replace the $\pi/4$ terms in (14) and (15). The correct value for the tail-correcting term in (15) is determined by correcting it for the error given on p. 166.

The following conclusions can be drawn from Table II: the errors in δ_0 will be discussed later. The error* in Jeffreys's phases due to the neglect of F'' is positive for small values of l (0, 1, 2) and decreases numerically as l increases. This is not true for δ_2 at small values of k, but this exception is due to a special

* The error has a sign opposite to that of the correction. A positive error means that Jeffreys's phase is too large.

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peculiarity in the function (21) for δ_2 (see p. 173). After passing through the value zero this error becomes negative and increases numerically to a maximum as l increases, after which it decreases to zero without becoming positive again.

The error in the $\pi/4$ term in (15) decreases as l increases, and is independent of k, as was shown on p. 166. The error in the $\pi/4$ term in (14) decreases also as l increases, but increases as k increases, i.e. it varies directly with the degree of penetration of the P-wave into the atom, this penetration being greater the smaller l and the greater k.

Table II. *Corrections for the two sources of error*

Phase	k	Total error	Correction for neglect of F''	Correction for tails of P-waves	Tail-correcting terms replacing $\frac{\pi}{4}-\frac{\pi}{4}$
δ_0	0·01	1·039	$>-$ 0·684	—	—
	1·05	0·704	− 0·684	—	—
δ_1	1·05	0·093	− 0·093	0·000	$\frac{\pi}{4\cdot83}-\frac{\pi}{4\cdot83}$
	4·00	0·105	− 0·097	−0·008	$\frac{\pi}{4\cdot88}-\frac{\pi}{4\cdot83}$
δ_2	1·05	0·556	—	—	—
	4·00	0·064	− 0·006	−0·058	$\frac{\pi}{4\cdot84}-\frac{\pi}{4\cdot44}$
δ_3	1·41	−0·013	+ 0·013	0·000	$\frac{\pi}{4\cdot34}-\frac{\pi}{4\cdot34}$
	2·83	0·041	+(0·000)	−0·041	$\frac{\pi}{4\cdot61}-\frac{\pi}{4\cdot34}$
δ_4	2·00	0·001	+(0·000)	−0·001	$\frac{\pi}{4\cdot25}-\frac{\pi}{4\cdot24}$
	4·00	0·003	+(0·000)	−0·003	$\frac{\pi}{4\cdot26}-\frac{\pi}{4\cdot24}$
δ_6	4·00	0·004	+(0·000)	−0·004	$\frac{\pi}{4\cdot18}-\frac{\pi}{4\cdot16}$
δ_7	4·00	0·000	+(0·000)	0·000	$\frac{\pi}{4\cdot15}-\frac{\pi}{4\cdot15}$

The sign of the error in the $\pi/4$ term in both (14) and (15) is positive in each case; and since the error in the $\pi/4$ term in (14) is greater than that in the $\pi/4$ term in (15), the resultant error, which is due to the difference of these two terms, is positive.

Thus the resultant error in the phases arising from the $\pi/4$ terms in (14) and (15) is always positive, i.e. it makes Jeffreys's phases too large, and it increases with k.

Considering now the total error in Jeffreys's phases, we see that the error due to the neglect of F'' and the error arising from the $\pi/4$ terms are both positive

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for low values of l (1, 2), and so add up numerically to give the total error*. For $l = 1$ the error is almost entirely due to the neglect of F''.

As l increases, the error due to neglect of F'' decreases to zero, so that for intermediate values of l the main contribution to the total error may come from the $\pi/4$ terms, as occurs in the above table for δ_2 for $k = 4{\cdot}0$.

As l becomes still larger (equal to 3 and higher values) the error due to neglect of F'' becomes negative, while that arising from the $\pi/4$ terms is still positive; and, since in general the total error is positive, the main contribution to the total error must come from the $\pi/4$ terms.

For high values of l (4, 6, 7) the total error is not only mainly, but probably entirely, due to errors in the $\pi/4$ terms. At high values of l the total error in the phase is extremely small. This is readily explained if, as it appears, the total error is all due to the $\pi/4$ terms; for when l is large the two zeros r_0 and r_0' in (14) and (15) are very close together, and consequently the errors in the two $\pi/4$ terms are practically the same, and so cancel each other. The two zeros r_0 and r_0', and the difference between them are given in Table III for δ_4 at several values of k.

Table III

k	Total error in δ_4	r_0	r_0'	$r_0' - r_0$
2·00	0·001	2·10	2·24	0·140
2·45	0·001	1·65	1·825	0·175
2·83	0·003	1·39	1·58	0·190
4·00	0·003	0·94	1·12	0·180

Jeffreys's phases are sometimes calculated by using the exact value of P when $V(r)$ is zero given by (4) in place of the approximate value given by (12). When this is done there is, of course, no error to cancel the error in the $\pi/4$ term of (14), which for δ_4 amounts to about 0·044; and consequently an error of this amount would be obtained in δ_4 so calculated, when the error was zero when calculated by the method used in this paper.

This explains why Hartree, Kronig and Petersen obtained errors of 0·034 and 0·026 in δ_6 and δ_7 for $k = 4{\cdot}0$. When these phases are calculated by the method of this paper these errors will be reduced by the errors in the second $\pi/4$ term which are respectively 0·030 and 0·026 (see p. 166). The view of Hartree and his collaborators that the main error in δ_6 and δ_7 as calculated by them arises from errors in the $\pi/4$ term in their formula is therefore undoubtedly correct. Their values for δ_6 and δ_7 given in Table I have been corrected in the above manner.

The exceptionally large error in δ_2 for low values of k is due to the unusual

* For $l = 0$ there are no $\pi/4$ terms in the expressions (14) and (15), and hence the error is entirely due to neglect of F''. See also p. 174.

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behaviour of the function (6) which occurs in the first integral of the equation (13) for the phases. This is shown in Fig. 4, where the function

$$\frac{2Z_p}{r} - \frac{l(l+1)}{r^2} \tag{21}$$

has been plotted against r for $l=1$, 2 and 3. It will be seen that the curve for $l=2$, instead of rising smoothly to zero at larger r, as do the curves for higher values of l, reaches a maximum at $r=0{\cdot}9$, and a minimum at $r=1{\cdot}8$. The presence of this maximum and minimum causes the function (20) to be very much greater than unity over this range of r, as is shown in Fig. 3, and is consequently the cause

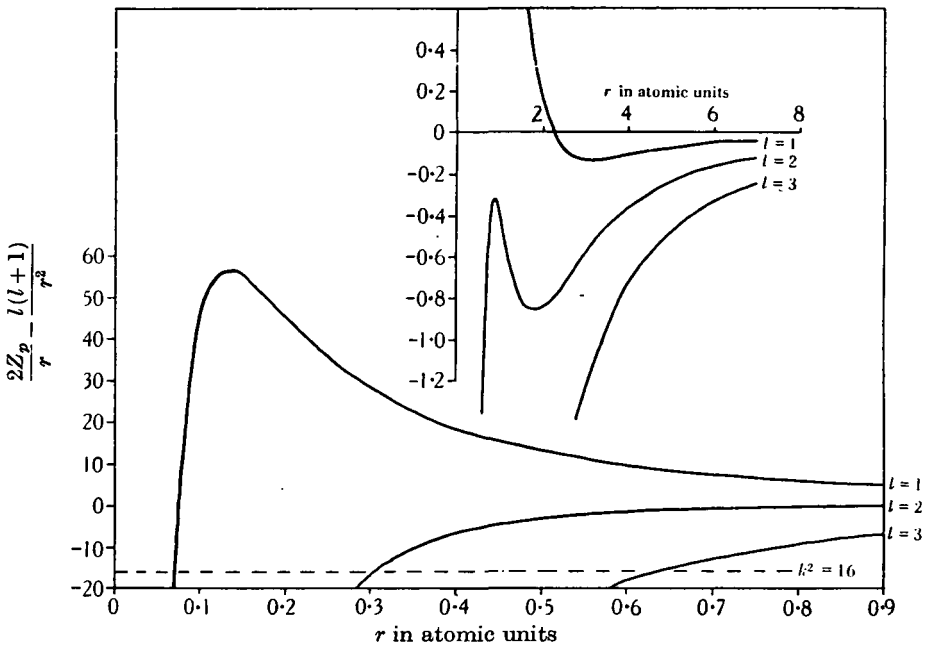


Fig. 4. Expression (21) as a function of r for $l=1$, 2, and 3.

of the large error in δ_2. The effect of this maximum and minimum on the value of the phase will clearly be greater the smaller the value of k.

When k^2 lies between 0·32 and 0·84 the first integrand in the phase equation (13) has three zeros close together, and consequently Jeffreys's approximation is hopelessly wrong; for not only is F'' then large, but also Jeffreys's method of obtaining the $\pi/4$ correction for the exponential tail of the P-wave is not applicable.

I am indebted to Prof. Hartree for pointing out that this maximum at $r=0{\cdot}9$ is related to the incipient formation of the 3d group of electrons, which begins to form a few places on in the Periodic Table. This maximum grows with increasing

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atomic number until, when scandium is reached, it is finally high enough and wide enough to contain a whole wave function with negative energy; and this, roughly speaking, is the beginning of the iron group of elements.

It is of practical importance to point out that the presence of a maximum and minimum of this nature can immediately be detected when working out Jeffreys's phases, for in the evaluation of the phases the function (21) with the addition of the constant k^2 is tabulated against r. When this behaviour of the curve is found to occur we must expect Jeffreys's phase to contain a large error.

(2) *The error in phases of zero order*

For the zero order phases Jeffreys's expression (13) reduces to

$$\delta_0 = \int_0^\infty \left[k^2 + \frac{2Z_p}{r}\right]^{\frac{1}{2}} dr - \int_0^\infty k\,dr. \tag{22}$$

There is no implicit factor of $\pi/4$ in each term, as there is in (13) when $l > 0$, for there is now no totally reflecting region for the P-waves which penetrate right into $r = 0$. No error is introduced by the second integral which represents the exact phase of the P-wave when $V(r)$ is zero*. Consequently there is only one source of error in Jeffreys's expression for δ_0, and that is neglect of F'' in (8).

Fig. 5*a* represents the function (20) plotted against r for two values of k. The continuous curve is for $k = 1{\cdot}0$ and the broken curve, which coincides with the continuous curve for values of r less than 0·7, is for $k = 0{\cdot}01$.

Let us first consider the continuous curve for $k = 1{\cdot}0$. We see that the function (20) is quite appreciable over the whole range of r, and therefore a large error is to be expected due to neglect of F''. Integration of $FF''/2k$ from $r = 0{\cdot}02$ to $r = 7{\cdot}0$ gives for the correction for this error the value $-0{\cdot}684$, shown in Table II, which reduces the error to practically zero. Following the practice adopted in Figs. 2 and 3 the integration of $FF''/2k$ has not been carried out over the range of r from 0 to 0·02, where the curve in Fig. 5*a* assumes large values greater than unity, and consequently is not a true representation of the function (20).

Since k^2 is very small compared with $2Z_p/r$ for all values of k used in Table I, except at large values of r, the curve shown in Fig. 5*a* will represent the function (20) for all values of k used except at large values of r. Now the function (20) is almost zero at large r for all values of k greater than unity. Consequently the error produced in δ_0 from neglect of F'' will be practically constant for all our values of k greater than unity. This is borne out by the results given in Table I and Fig. 1.

At very small values of k, however, the function (20) at large r goes first to a very large positive value and then to a very much larger negative value, as shown by the broken curve in Fig. 5*a* for $k = 0{\cdot}01$. The positive maximum of 1820 occurs

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

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at $r = 6{\cdot}5$, and the negative maximum of $-12{,}000$ occurs at $r = 6{\cdot}8$, after which the curve goes to zero at $r = 7{\cdot}0$. The reason for this marked change at large r is shown by Fig. 5*b* which represents the curves for F for $k = 0{\cdot}01$ and $k = 1{\cdot}0$. It will be seen that for $k = 1{\cdot}0$ the curvature of F is concave towards the r-axis over the whole range of r, and so F'' is negative. But for $k = 0{\cdot}01$ F is concave up to $r = 1{\cdot}0$; convex from $r = 1{\cdot}0$ to $r = 6{\cdot}65$, and concave from $r = 6{\cdot}65$ to $r = 7{\cdot}0$.

Since the curve of Fig. 5*a* for $k = 0{\cdot}01$ is very much larger than unity beyond $r = 1{\cdot}0$, it will not represent the true value of the function (20), and consequently

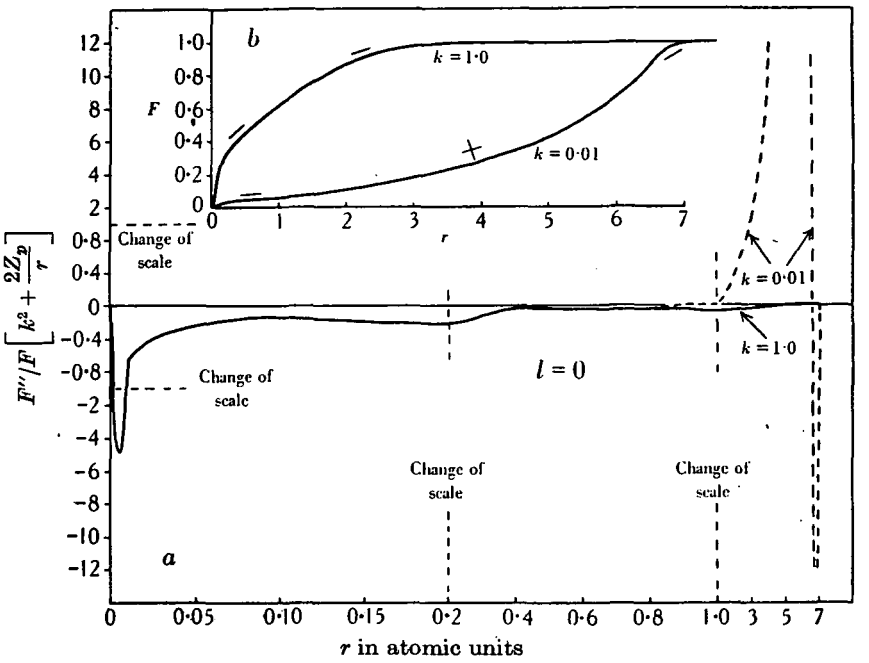


Fig. 5. (*a*) Expression (20) as a function of r for $l = 0$ and for $k = 0{\cdot}01$ and $1{\cdot}0$. (*b*) F as a function of r for these values of l and k.

the correction for neglect of F'' cannot be applied to this portion of the curve. However, since the negative maximum at $r = 6{\cdot}8$ is more than six times as large as the positive maximum at $r = 6{\cdot}5$, the sign of the correction for the neglect of F'' beyond $r = 1{\cdot}0$ is probably negative. Thus the total correction for $k = 0{\cdot}01$ is greater than the correction for $k = 1{\cdot}0$ by this indeterminate amount. This explains the sharp increase in the error curve for δ_0 at small values of k shown in Fig. 1 of this paper, and in Fig. 1 of the paper by Arnot and Baines (*loc. cit.*).

We thus see that the almost constant error in δ_0 over the range of k from $0{\cdot}5$ to $4{\cdot}0$ is due to neglect of F'' in (8) at values of r less than about $3{\cdot}0$, no appreciable error being caused by neglect of F'' at greater values of r. The rapid increase in

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error for values of k less than 0·5 results from an error now coming in due to neglect of F'' at large values of r, greater than about 2·0 or 3·0 atomic units.

THE PRACTICAL APPLICATION OF CORRECTIONS TO JEFFREYS'S PHASE

Since it would be of considerable practical importance to have a correction curve from which the correction to Jeffreys's value of δ_0 could be read off for any atom an attempt has been made to construct such a graph from the data given in this paper and that by Arnot and Baines. In Fig. 6 the correction in radians to Jeffreys's value of δ_0 for $k = 0$ has been plotted as a function of the atomic number of the atom. The data from which this graph has been drawn are taken from Table II

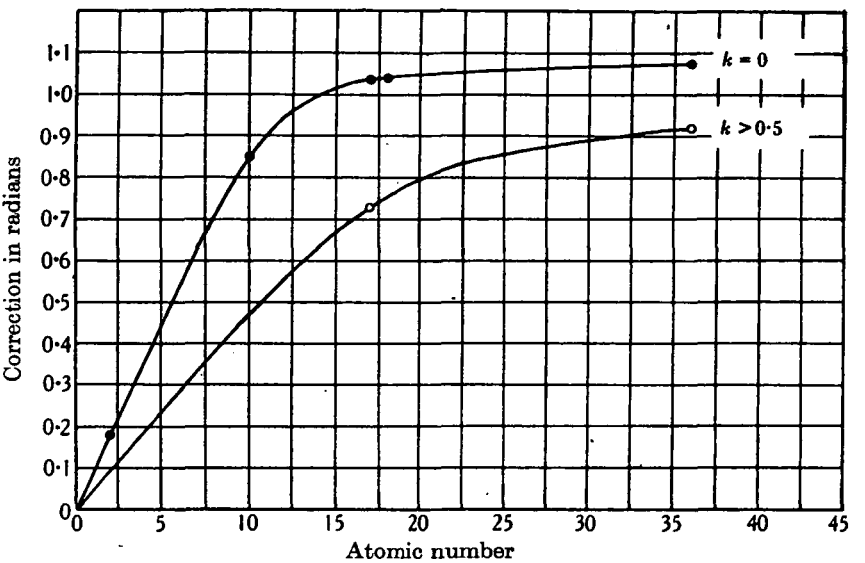


Fig. 6. Correction curve for δ_0 for atoms of atomic number up to 36. The correction is to be subtracted from Jeffreys's value.

of the paper by Arnot and Baines, where the correction to δ_0 for helium, neon, argon and krypton* is given, together with the correction to δ_0 for chlorine given in Table I of this paper. All the points fall on a smooth curve as shown in Fig. 6. This curve becomes almost flat at high atomic number, and thus an extrapolation

* The error of 2·740 given by Arnot and Baines for krypton was determined using the Hartree field with Holtsmark's polarization correction. This polarization correction causes the error in δ_0 for $k = 0$ to be much larger than when the Hartree field alone is used. Consequently δ_0 for $k = 0$ has been recalculated using the Hartree field without any polarization correction. The error is then found to be 1·075. This value has been used in Fig. 6. The errors for the other rare gases given by Arnot and Baines were calculated using the Hartree field without any polarization correction.

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to higher atomic number should not involve much error. Such an extrapolation is valid since most of the correction to δ_0 is due to neglect of F'' at small values of r, and the fields at small values of r for atoms of higher atomic number should be similar.

From the point of view of practical importance, however, we require to know, not the error at $k=0$, but the almost constant error for values of k above about 0·5. Unfortunately we have only three points, one for chlorine, one for krypton and the origin to fix this curve. However, the curve through these three points is of the same shape as the curve for $k=0$, and therefore the curve as drawn in Fig. 6 for $k>0{\cdot}5$ will be a good approximation to the true error curve. There is no doubt that Jeffreys's value for δ_0 corrected by this curve will be very much closer to the exact value than if no correction were made. The correction given by this curve is to be *subtracted* from Jeffreys's value for δ_0.

As regards the correction of phases of higher order, the determination of the correction to be applied by integrating $FF''/2k$ over r, omitting that portion of the range of r near the zero r_0 where the function (20) goes to spuriously high values, has been shown in this paper to be of definite value when the correction has a negative sign. The calculation of this correction can be made quite rapidly, since

$$F=\left[\frac{k}{\left(k^2+\frac{2Z_p}{r}-\frac{l(l+1)}{r^2}\right)^{\frac{1}{2}}}\right]^{\frac{1}{2}},$$

and the function

$$\left(k^2+\frac{2Z_p}{r}-\frac{l(l+1)}{r^2}\right)^{\frac{1}{2}}$$

has been already tabulated against r in the determination of the phase. The intervals of r are close enough together to allow F'' to be found by difference columns.

For still higher values of l the correction for the neglect of F'' in (8) becomes positive and of small value. For these high values of l the error is due mainly to errors in the $\pi/4$ terms which practically cancel one another, resulting in only a very small error in the third place of decimals, and consequently no correction is necessary.

It may be asked why I have not used the exact values of F and F'' in the correction term $FF''/2k$ instead of the approximate values given by (18). The object of this work was to find the source of the errors in Jeffreys's approximation, and then to obtain a simple and essentially practical method of correcting for these errors. The latter can only be accomplished by using the approximate values of F and F''; for if one is prepared to go to the trouble of finding the exact values of F and F'' by numerical integration of (8), then Jeffreys's approximation is of no use, since these give the exact phases.

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The numerical work involved in the calculation of the phases given in Table I was carried out by Mr J. C. McLauchlan, to whom I am greatly indebted for this assistance.

SUMMARY

The errors occurring in a large number of Jeffreys's phases for neutral chlorine have been determined. A discussion of the source of these errors is given, from which it appears that errors in the phases of zero order and of order unity are due to a cumulative error over the range of integration. A method of correcting for this error is obtained. This method is of easy practical application, and it reduces the error almost to zero for phases of these orders.

The error occurring in higher order phases is found to be mainly due to errors in the two $\pi/4$ terms, which take into account the exponential tails of the waves in the totally reflecting region. For phases of high order these errors in the two $\pi/4$ terms cancel each other, and consequently the total error in phases of high order is practically zero.

A correction graph for the zero-order phase is given from which the error in this phase for atoms of atomic number up to 36 can be read off. The graph is such that an extrapolation to higher atomic number would not involve much error.

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