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The Effect of Exchange on the Scattering of Slow Electrons from Atoms

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Reasons are given why the Born approximation is incapable of dealing with the scattering of slow electrons. Since this approximation assumes that the sine of the phase angle δ equals δ, the results computed by the Born method become completely unreliable when δ is greater than $\pi/2$. Exact solutions then must be obtained. Equations are set up, including exchange effects, for the best possible wave function for an electron scattered from hydrogen or helium when the complete wave function is of the separable type usually used in atomic theory. These equations are solved on the differential analyzer to find the best possible curves for the δ's, for the angle distribution of scattering and for the total cross section, for this type of wave function. The check with experiment for helium is good, the maximum discrepancy in any of the δ's being only ten degrees. No data for atomic hydrogen are available. The small error introduced by the use of separable wave functions (neglect of polarization) is discussed. The conclusions are that exchange effects are not important for electron energies greater than 30 volts, and below this energy have an appreciable effect only on the angle distribution curves, and not on the cross section curves. An analytic solution of the equations, valid for any atom having closed electronic shells, is obtained for a simplified form of atomic wave function and potential. The results confirm the above conclusions, and also show that exchange is less important in scattering from heavy atoms than from light ones.

INTRODUCTION

IN the past several years a number of fairly satisfactory methods have been devised for the treatment of the bound states of atomic electrons; but, although numerous attempts have been made, no correspondingly satisfactory methods have been found for the treatment of states involving one or more unbound electrons being scattered by an atom. This is essentially due to the fact that the interesting property of a bound state is its energy, and the energy matrix for bound states is pleasantly insensitive to changes in the shape of the wave functions. On the other hand, the interesting property of an unbound wave function is its distribution-in-angle, and the integral of this distribution, the cross section. This property is quite sensitive to changes in the wave function; a choice of function which is a little in error may give a completely erroneous scattering curve.

It is not difficult to see the reason for this sensitiveness if we expand the wave function in a series of spherical harmonics times radial functions $R(r)/r$. If there is no atom at the origin, then the R corresponding to the λ'th spherical harmonic will have an asymptotic form $\sin(kr-\lambda\pi/2)$, where k^2 is the electron's initial kinetic energy (atomic units are used throughout this paper). When the atom is present the radial function becomes more complicated, but its asymptotic value becomes $\sin(kr-\lambda\pi/2+\delta_\lambda)$, differing from the R when no atom is present only by a shift in phase, δ_λ.

These shifts in phase for the different values of λ completely determine the distribution in angle and cross section for scattering of the electron. The current scattered[1] per unit solid angle at an angle θ from the initial direction, per unit primary current density is

$$f^2(\theta)=\sum_{\lambda,\lambda'}(2\lambda+1)(2\lambda'+1)(\sin\delta_\lambda/k)(\sin\delta_{\lambda'}/k)\cos(\delta_\lambda-\delta_{\lambda'})P_\lambda P_{\lambda}' \qquad (1)$$

and the cross section for scattering is

$$q=4\pi\sum_{\lambda}(2\lambda+1)(\sin\delta_\lambda/k)^2. \qquad (2)$$

Now when the λ'th radial function has several oscillations inside the atom, a slight error in its

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[1] See Morse, Rev. Mod. Phys. **4**, 577 (1932) for a general discussion. This paper will be called (I) hereafter.

form can easily produce an error in δ_λ of more than $(\pi/2)$, and the resulting values of f^2 and q will therefore be considerably in error.

A more detailed discussion of the behavior of δ_0 for an electron in a spherically symmetric field $V(r)$ will illustrate some of these facts. If we express the coefficient of P_0/r by means of the functions $\mu(r)$ and $A(r)$ such that $R_0 = A(r)\sin(kr+\mu(r))$, and arrange the relation between A and μ so that (dR/dr) will equal $kA(r)\cos(kr+\mu)$, then the equation which μ must satisfy is

$$-k(d\mu/dr) = V(r)\sin^2(kr+\mu). \qquad (3)$$

The value of μ for r very large is equal to the phase shift δ_0 which we need to compute f^2 and q. We also must have μ approach zero as r approaches zero.

Now Eq. (3) is a particularly intractable one, and one usually tries to solve it by approximate methods. The obvious method is to set μ equal to zero on the right-hand side of the equation, when

$$-\mu(r) = \int_0^r V(r)\sin^2(kr)dr/k. \qquad (4)$$

If we now set $\sin\delta_0/k$, which is needed for Eqs. (1) and (2), equal to $\mu(\infty)/k$, we have the Born approximation.[2] There are thus two approximations made in obtaining the Born formula, and both of them are *only valid when* $\mu(r)$ *is always small compared to* $\pi/2$. When k is large enough this is true, and the approximation is not a bad one, but when k is small the neglect of μ on the right side of (3) may cause the $\sin^2$ term in (4) to be unity at a place where it should be zero and *vice versa;* and the assumption that $\sin\delta_0$ is nearly equal to $\mu(\infty)$ is also a bad one.

The discrepancy becomes quite marked when k is quite small. The approximate Eq. (4) indicates that μ should increase fairly uniformly with r, reaching some constant value when r becomes great enough so that $V(r)$ is practically zero (the outside of the atom). But the correct solution of (3) for small k is very different. It is a sort of "step function," remaining nearly zero as r increases from zero, then suddenly jumping to a value π, remaining at that value for a while, then jumping to a value 2π, and so on, until the outside of the atom is reached, after which it is practically independent of r. The number of "steps" depends on the size and depth of the atomic potential hole, and as one increases this size and depth, keeping k constant, more steps appear, each one showing itself by a sudden increase in δ_0 by π. A curve showing the behavior of $\mu(r)$ for a simple form of potential field[3] is shown by the solid line in Fig. 1. The dotted line gives the behavior of the approximate function given in (4). The same sort of a discussion can be made for λ other than zero. The larger λ is, the larger V must be before a step appears in the δ_λ.

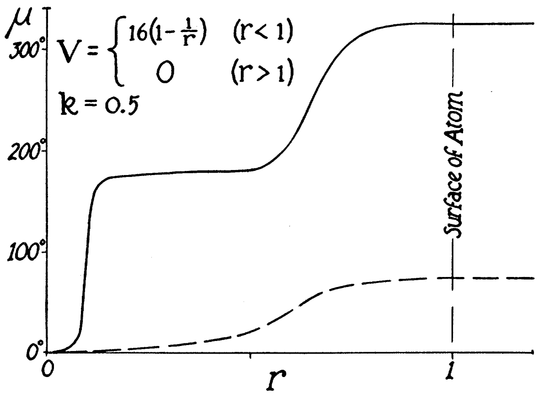

FIG. 1. Phase function $\mu(r)$ for a simple form of potential field. Solid line gives exact solution, dotted line gives corresponding Born approximation.

So we are forced to view with considerable skepticism the use of any scattering formula obtained by the Born method for small values of k, and to use the formula (if we must) with considerable trepidation. Unfortunately it does not seem possible to get along entirely without the Born approximation in the treatment of the collision of an electron and an atom. If the atom were just a potential field as far as the incoming electron is concerned, an exact solution could be obtained for the δ_λ's by a not impossibly great expenditure of energy. But the atom is not just a potential field, its electrons can be excited or can change places with the incoming electron.

In the treatment of inelastic collisions there seems at present no feasible method better than the Born method, bad as it is; but in the treat-

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[2] See (I), page 589.

[3] See (I), page 581, and also Allis and Morse, Zeits. f. Physik **70**, 567 (1931).

ment of the exchange effects in elastic collisions, it is possible to obtain a better solution.

HYDROGEN AND HELIUM

The elastic collision of an electron and a hydrogen atom can be represented by a stationary state function where one electron is bound and the other is not. An exact solution would give a wave function which could not be separated into factors involving the coordinates of just one of the electrons, as the atomic electron's function would depend on the position of the unbound electron, and *vice versa*. However, separable wave functions work very well for bound states, so that it is interesting to find out if, in at least one case, they give fairly good approximations for the δ_λ's of an unbound state. If agreement is satisfactory in that case, it will be worth investigating others; if not, methods must be devised for the solution of nonseparable equations before further advance can be made.

By a method entirely analogous to that used by Fock[4] in atomic problems one can show that the best possible solution for the hydrogen atom plus electron problem having the separable form

$$\psi=\varphi(1)\chi(2)\pm\varphi(2)\chi(1) \tag{5}$$

will be when the atomic wave function φ is a solution of

$$(\nabla^2+2/r-E_a)\varphi=0, \tag{6}$$

and where the wave function χ of the scattered electron is a solution of

$$(\nabla^2+k^2-V(r_1))\chi(1)=\pm\varphi(1)\left[2\int\varphi(2)\chi(2)\frac{dv_2}{r_{12}}\right.$$
$$\left.+(k^2-E_a)\int\varphi(2)\chi(2)dv_2\right]. \tag{7}$$

The function V is the combined potential of the nucleus and of the atomic electron. Since we shall deal with the scattering from normal hydrogen we have

$$V(r)=-2e^{-2r}(1+r)/r.$$

The plus sign in (5) and (7) corresponds to the symmetric function and therefore to the singlet state, while the minus sign corresponds to the antisymmetric function and to the three triplet states. The total cross section will equal ($\frac{1}{4}$) times the singlet cross section plus ($\frac{3}{4}$) times the triplet one.

In the antisymmetric case $\chi=\varphi$ makes ψ zero and hence satisfies (7) identically. $\chi+a\varphi$ is therefore as good a solution[5] as χ and we can make use of this to orthogonalize φ and χ and thus eliminate the second integral on the right of (7).

If we now set

$$\chi=\sum_\lambda P_\lambda(\cos\theta)R_\lambda(r)/r,$$

the R's must satisfy the equations,

$$\left(\frac{d^2}{dr^2}-\frac{\lambda(\lambda+1)}{r^2}-V+k^2\right)R_{\lambda s}=\frac{4\pi}{2\lambda+1}\varphi\left[2r^{\lambda+1}\int_r^\infty r^{-\lambda}\varphi R_{\lambda s}dr-2r^{-\lambda}\int_r^\infty r^{\lambda+1}\varphi R_{\lambda s}dr\right.$$
$$\left.+\left(r^{-\lambda}-\frac{k^2-1}{2}\delta_{0\lambda}\right)2\int_0^\infty r^{\lambda+1}\varphi R_{\lambda s}dr\right] \tag{8}$$

for the symmetric case, and

$$\left(\frac{d^2}{dr^2}-\frac{\lambda(\lambda+1)}{r^2}-V+k^2\right)R_{\lambda a}=-\frac{4\pi}{2\lambda+1}\varphi\left[2r^{\lambda+1}\int_r^\infty r^{-\lambda}\varphi R_{\lambda a}dr\right.$$
$$\left.-2r^{-\lambda}\int_r^\infty r^{\lambda+1}\varphi R_{\lambda a}dr+(1-\delta_{\lambda 0})2r^{-\lambda}\int_0^\infty r^{\lambda+1}\varphi R_{\lambda a}dr\right] \tag{9}$$

for the antisymmetric case.

The best separable wave function for scattering from helium corresponds to the antisymmetric case only, and must satisfy an equation of the form of (9), where φ is the Hartree wave

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[4] Fock, Zeits. f. Physik **61**, 126 (1930).

[5] Feenberg, Phys. Rev. **42**, 17 (1932).

function for helium and V is the corresponding potential.

An analytic solution of (8) and (9) for any but the most rudimentary forms of φ and V seems quite impossible. Several approximate solutions[5, 6] have been carried through, but these all have the same inherent defects which were brought out in the discussion of the Born approximation. It is possible, however, to solve these equations mechanically. We have obtained exact solutions of (8) and (9), and of these equations without the right-hand sides, on the differential analyzer.[7] From them were computed the δ_a's for the antisymmetric, the δ_s's for the symmetric, and the δ_n's for the no-exchange case. Fig. 2 gives curves of these quantities as functions of k for hydrogen, and Fig. 3 gives them for helium[8] (the δ_s's were not computed for helium, since they are not needed). It is to be noticed that the effect of exchange in the case of hydrogen introduced an extra step in the $\mu(r)$ function, making δ_{0a} approach 180° instead of 0° as k goes to zero. It is obvious that the usual approximate methods of computing exchange cannot cope with so drastic an alteration of the δ curve.

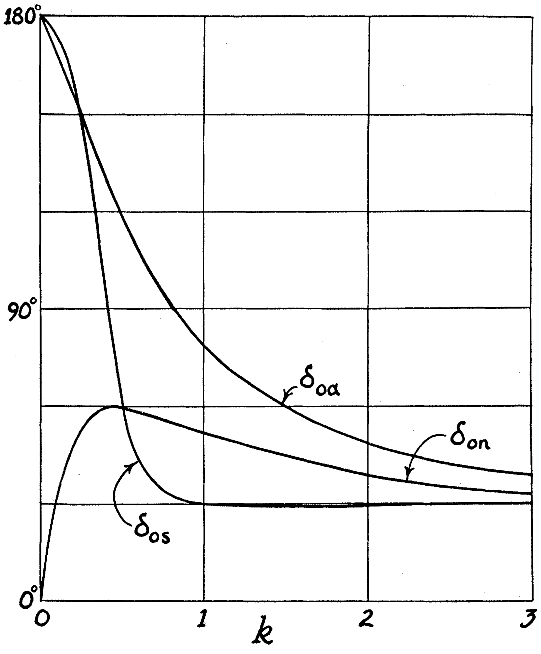

FIG. 2. Phase shifts for hydrogen.

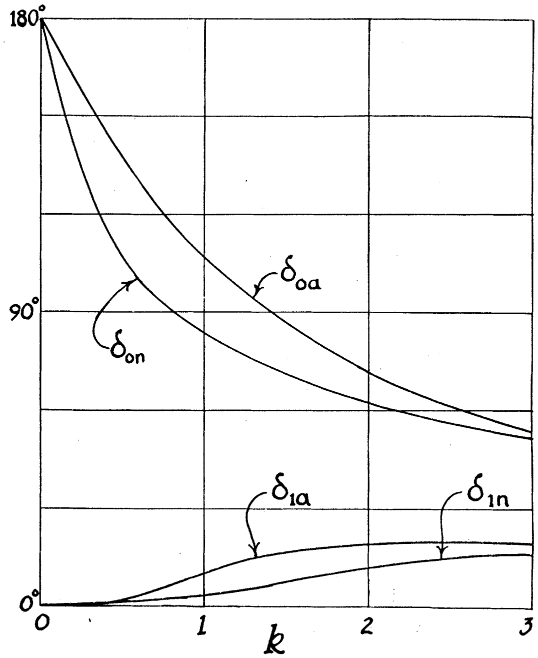

FIG. 3. Phase shifts for helium.

The only experimental data available are for helium.[9] Since both sets of data on angle scattering check with each other, it seems reasonable to consider them as fairly correct, although probably the amount measured for small angles is larger than the true atomic scattering curve, due to multiple scattering, and to possible spreading of the primary beam. The data on cross section are for total cross section, and therefore larger than the elastic cross section for large values of k.

Fig. 4 gives curves of the angle distribution for several different accelerating potentials. The solid lines are the values computed when exchange is included, the dotted lines the values when exchange is neglected, and the circles are the experimental points. Fig. 5 gives the corresponding curves for cross section as a function of

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[6] Oppenheimer, Phys. Rev. **32**, 361 (1928); Massey and Mohr, Proc. Roy. Soc. **A132**, 605 (1931).

[7] V. Bush, J. Frank. Inst. **212**, 447 (1931).

[8] The Hartree atomic functions for helium were computed on the differential analyzer by S. H. Caldwell (paper to appear shortly). The writers are indebted to Mr. Caldwell for his kindness in supplying these data.

[9] For angle scattering, see Bullard and Massey, Proc. Roy. Soc. **A133**, 637 (1931); Ramsauer and Kollath, Ann. d. Physik **12**, 529 (1932); and Hughes, McMillen and Webb, Phys. Rev. **41**, 154 (1932). For cross section, see Normand, Phys. Rev. **35**, 1217 (1930).

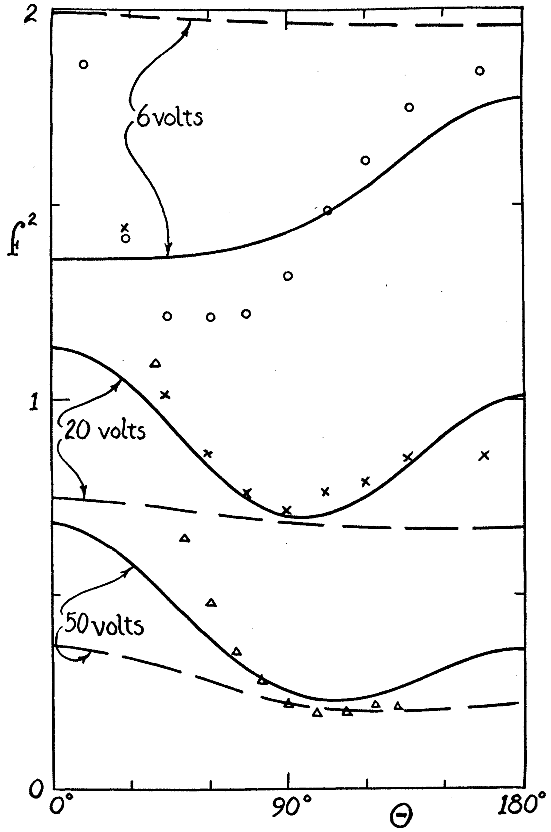

FIG. 4. Angle distribution of scattered electrons, f^2, for helium. Solid line, computed with exchange. Dotted line, computed without exchange. Circles and crosses, experimental data by Ramsauer and Kollath. Triangles, experimental data by Bullard and Massey (multiplied by a single arbitrary constant, since Bullard and Massey do not give absolute magnitudes).

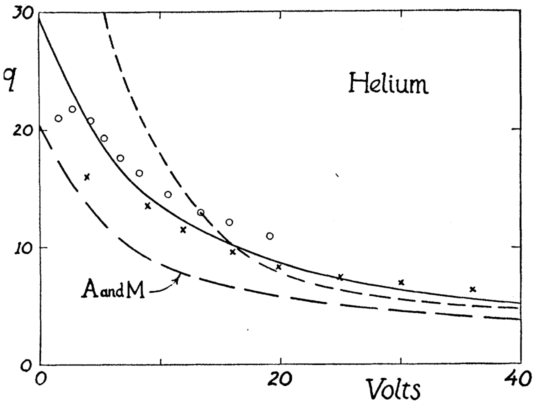

FIG. 5. Elastic cross section of helium. Circles, experimental data by Ramsauer and Kollath; crosses, data by Normand.

electron velocity in square root volts. The curve marked A and M is that computed[4] for a considerably cruder form of potential field, without exchange.

It is seen that the check with experiment is better for the curves computed including exchange than for the curves neglecting exchange. For instance, the exchange angle scattering curves for small velocities exhibit the curious phenomenon that more electrons are scattered backward than forward, a phenomenon found experimentally. It is also seen that curves for the cross section check better than the curves for angle distribution; and that the effect of exchange is much more important in the angle distribution curves than in the cross section curves. This is due to the fact that the angle distribution curves are sensitive to the magnitude of the terms involving products of two different spherical harmonics (especially the term in P_0P_1), and these terms integrate out to zero when the cross section is computed. One might say that exchange distorts the distribution of the electrons which are scattered without causing any great change in their total number.[10]

The check for the angle distribution is not particularly good, but this only shows the extreme sensitivity of the angle distribution to the form of the wave functions. If the values of δ_{1a} be increased only slightly, with a maximum change of less than 10°, *the check with experiment is well-nigh perfect.* This corresponds to a 1 percent change in the abscissa of the wave function where the phase shift was measured. As this difference is much larger than the error within which the machine will repeat itself, it is not unreasonable to assume that it is due to the fact that separable wave functions were used instead of the correct nonseparable ones.

As a matter of fact, it seems surprising that the discrepancy is so small. If we attempt to estimate the effect of the "nonseparableness" by an equivalent polarization field, we find that this field is of the same order of magnitude as the atomic field V, and is many times larger than V at large distances. The addition of a field of any such size would change the δ's, not by the needed 10°, but by 180° or twice 180°, and the curves

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[10] See (I), page 615.

for f^2 and q would be of a completely different character from the experimentally determined ones, as Holtzmark has already noticed.[11]

It is not hard to see that a "polarization field" is a very poor way of including the effect of nonseparability. To obtain such a field we assume that φ, and therefore E_a depend parametrically on the position of the unbound electron, but that χ is independent of the position of the atomic electron. The polarization field is obtained by computing the change of φ and of E_a produced by a stationary electron at a certain distance away and then computing the effect of this distortion on the field in which the unbound electron travels. An argument analogous to that used by Born and Oppenheimer[12] in discussing the motions of electrons and nuclei in diatomic molecules can be used to show that such an approximation is quite bad when the incoming particle is an electron. Thus, it is not likely that the method suggested by Feenberg[5] to include "polarization" will be successful.

However, it does not seem possible at present to go beyond these rather negative remarks in discussing the error due to the use of separable wave functions.

To conclude, Figs. 2 and 3 show that exchange effects become unimportant for electronic energies larger than 30 volts ($k>2$) for helium and hydrogen. This is about the limiting value of k at which the Born approximation has any validity at all. Consequently, the correction for exchange is always smaller than the errors inherent in the Born method and it is senseless to add the exchange terms when using it. This conclusion applies, of course, only to elastic scattering.

MANY ELECTRON PROBLEMS

The extension of Eq. (9), for the case of any atom consisting of closed shells, is not difficult.[13, 5] If the atomic wave function is a determinant involving N pairs of electrons, each pair having a wave function

$$\varphi_\nu(r)=A_{m,\,l,\,n}e^{im\varphi}\sin^m\theta P_l{}^m(\cos\theta)R_\nu(r)/r$$

and opposing spins, then each of these N functions is orthogonal to the others, and is a solution of the equation

$$\left[\nabla_1{}^2+E_\nu+\frac{4N}{r_1}-V(r_1)\right]\varphi_\nu(r_1)=-\sum_{\mu=1}^{N}2\varphi_\mu(r_1)\int\varphi_\mu(r_2)\varphi_\nu(r_2)\frac{dv_2}{r_{12}}$$

$$=-2\sum{}' A^2{}_{0,\,l,\,n}\frac{R_\mu}{r_1}\int P_l(\cos\theta_{12})\frac{R_\mu(r_2)\varphi_\nu(r_2)}{r_2r_{12}}dv_2,\qquad(10)$$

where $\sum'$ is a sum over all the different values of l and n in the atom. The potential

$$V(r_1)=4\sum_{\mu=1}^{N}\int\varphi_\mu{}^2(r_2)\frac{dv_2}{r_{12}}.$$

Therefore, each atomic electronic wave function is an eigenfunction of the same equation. The wave function χ is also a solution of (10), and is therefore orthogonal to all of the atomic functions φ. The kinetic energy k^2 must of course be substituted for the negative atomic energy E_ν when (10) is used to find χ.

As the sum $\sum'$ indicates, the incident electron can exchange only with electrons of same spin and m-value, and since there is only one such in each shell, the effect of exchange increases not as

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[11] Holtzmark, Zeits. f. Physik **48**, 239 (1928).

[12] Born and Oppenheimer, Ann. d. Physik **84**, 457 (1927).

[13] See Fock, Zeits. f. Physik **81**, 195 (1933); Lennard-Jones, Proc. Camb. Phil. Soc. **27**, 469 (1931).

the number of electrons but as the number of shells. We shall show that the effect of the inner shells is negligible so that only one or two terms on the right of (10) are worth keeping. (10) then reduces practically to the form of (9) but with a very much larger field V.

In order to study how the effect of exchange varies with the field V, we have studied a very simple form of (9) which has analytic solutions. Although the simplifications are extreme, previous calculations neglecting exchange have shown that the scattering is not at all sensitive to the shape of the potential field, provided the "atomic size factor" is not changed. Therefore, one can expect that the behavior of this solution will correspond in its general aspects to the actual case. If we set

$$V=\begin{cases} -V_0 & (r<r_0) \\ 0 & (r>r_0) \end{cases} \qquad \varphi=\begin{cases} (3/4\pi r_0^3)^{\frac{1}{2}} & (r<r_0) \\ 0 & (r>r_1) \end{cases}$$

it is found that

$$\frac{R_\lambda}{r^{\frac{1}{2}}}=\begin{cases} [s_\lambda J_{\lambda+\frac{1}{2}}(s_\lambda r)/J_{\lambda-\frac{1}{2}}(s_\lambda r_0)]-[t_\lambda J_{\lambda+\frac{1}{2}}(t_\lambda r)/J_{\lambda-\frac{1}{2}}(t_\lambda r_0)] & (r<r_0) \\ C_\lambda J_{\lambda+\frac{1}{2}}(kr)+D_\lambda J_{-\lambda-\frac{1}{2}}(kr) & (r>r_0) \end{cases}$$

is a solution of (9) provided that s_λ and t_λ are roots of the equation

$$y^4-(V_0+k^2)y^2-6/r_0^3=0.$$

C_λ and D_λ are determined by the requirement of continuity of value and slope of R_λ at $r=r_0$, and

$$\delta_\lambda=(-)^\lambda \tan^{-1}(D_\lambda/C_\lambda).$$

There is an error, of course, in that φ is not a solution of the "nuclear field" corresponding to V and hence is not orthogonal to R_0 but it is believed that this does not vitiate the results.

It is found that δ_λ is a function of an electron velocity parameter $x=kr_0$, an atomic size factor $\beta=r_0(V_0)^{\frac{1}{2}}/2$, and an exchange parameter r_0 (which is the size of the atomic wave function). Except in the exchange effect, the radius of the atom only enters in terms of the parameters x and β. In other words, except for the exchange, potential fields having quite different values of r_0 but having the same value of β would give scattering curves of exactly the same form when plotted as functions of x. The parameter r_0 is therefore a sort of exchange parameter, and when it becomes zero the right-hand side of (9) becomes zero, reducing to the form obtained for any value of r_0 when exchange is neglected.

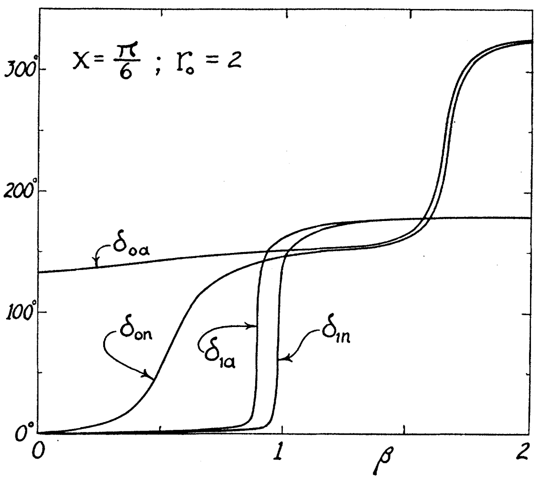

FIG. 6. Phase shifts with and without exchange for a simple atomic model, as functions of the atomic size factor β.

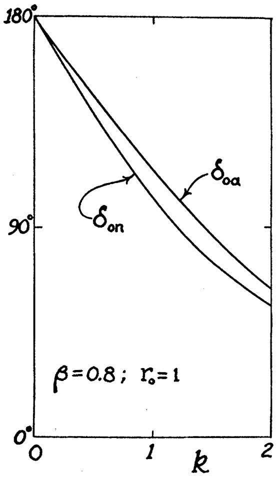

FIG. 7. Phase shifts with and without exchange for the simple model appropriate to helium.

We thus see immediately that the effect of exchange depends on the spread of the atomic wave function, becoming negligible for electrons concentrated in a small space. Nor is it difficult to show that this is true for any form of potential field and atomic wave function. Exchange with atomic electrons in inner shells is therefore extremely unlikely.

Fig. 6 gives plots of δ as a function of the atomic size factor β for $\chi=\pi/6$. It can be seen that the difference between the δ's with and without exchange decreases as β increases, showing that exchange with each electron is less effective in larger atoms than in smaller ones. This, combined with the fact that the electrons in inner shells play practically no rôle in exchange, makes it quite likely that the total exchange effect is smaller for heavy atoms than for light ones.

To show that this crude model of the atom is yet capable of correct results, we give in Fig. 7 phase-defect curves for the parameters appropriate to helium $\beta=0.80$, $r_0=1$. These are to be compared with the correct curves from the machine solution, given in Fig. 3.

In conclusion, we wish to thank Mr. S. H. Caldwell and the staff of the differential analyzer for their care in solving this problem.