Scattering of Ions by Polarization Forces

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The interaction potential of a charge carrier and a gaseous atom is attractive at large distances, varying as r^{-4}. This potential has simple classical properties since it has a cross section which varies inversely as the speed. For most ions the mechanism which removes the singularity of the potential is irrelevant classically —we find that this is also the case in quantum theory: the well-known indeterminacy of the wave function for singular potentials can be removed in an obvious way and a cross section of the capture type can be computed. This cross section oscillates sinusoidally about its classical value but has apparently no average deviation over one cycle, even when the de Broglie wavelength is long. In the limit of low velocities, the quantum-mechanical cross section has twice the classical value. These two facts combine to make the classical law of variation of the cross section approximately valid even in the quantum range.

I. INTRODUCTION

WHEN gaseous ions or electrons move through a gas whose molecules are not too large, then the two interact according to the law

$$V=-\tfrac{1}{2}e^2\alpha/r^4, \tag{1}$$

where e is the ionic charge, α the molecular polarizability, and r the distance between the ion and the molecule. The classical theory of the motion under this force is simple because the cross sections derived from this force are proportional to $1/v$, where v is the relative velocity. This feature of the classical theory can be derived from a dimensional argument. The cross sections must be constructed from the quantities $e^2\alpha$, v, and m, where m is the reduced mass. This construction can be made only in a single way, namely,

$$\sigma=\text{const}(e^2\alpha/mv^2)^{\frac{1}{2}}, \tag{2}$$

where the constant is a pure number. However, this simple result of classical mechanics will be modified if the relative velocity is so small that the square of the de Broglie wavelength,

$$\lambda^2=h^2/m^2v^2, \tag{3}$$

becomes comparable with the cross section (2). This can easily occur in practical situations. The question of interest is: what modifications does quantum theory introduce into the classical description of the motion of ions in gases?

It is a common experience in modern physics to find an analogy between classical and quantum results which goes beyond the limiting law of quantum mechanics. This is particularly true for simple classical results such as Rutherford's law or the resonance frequency of a harmonic oscillator. Since we are dealing here with another simple classical answer, it is of interest to see how this becomes modified in quantum theory. This is a second point of interest in the problem.

A third point of interest is provided by the fact that we have here a simple case of a singular potential, that is, a case in which the negative energy states cannot be quantized. Such states have been considered in the study of Case.[1] Case points out that the attractive potential is always terminated in reality by a repulsive wall and that this wall will determine the choice of the phase of the rapidly oscillating wave function. While this observation is undoubtedly true, in a great number of physical situations the choice of phase at the repulsive wall is very complicated. Further, this manner of pointing out that the singular potentials are "really" not singular is actually side-stepping the issue; there are many classical situations, generally in the positive energy spectrum, where the presence of a repulsive term in addition to (1) has no importance; furthermore, when it is important the simple classical properties just described are destroyed. Extremely complicated treatments are then required as, for instance, those of Langevin,[2] Hassé and Cook,[3] and others. Hence, to follow up the suggestion of Case of introducing the repulsive wall explicitly into the theory would simply mean making a difficult problem needlessly more complicated. Analogy with classical physics suggests that there must be a way of removing the ambiguity of the wave function by physical reasoning, without appeal to an irrelevant repulsive force. Indeed, the ambiguity is present in classical physics also: there exist separate ingoing and outgoing spiralling orbits rather than a single hyperbolic type orbit which combines the ingoing and the outgoing features in a fixed way. Hence, whatever argument is used to remove the ambiguity in the latter case should also be applicable in some form to the former.

II. CLASSICAL AND ELEMENTARY QUANTUM DESCRIPTION OF THE $-1/r^4$ POTENTIAL

The wave equation for a particle moving in the potential (1) is

$$\nabla^2\psi+\frac{A^2}{r^4}\psi+\frac{q^2}{A^2}\psi=0, \tag{4a}$$

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[1] K. M. Case, Phys. Rev. **80**, 797 (1950).
[2] P. Langevin, Ann. chim. et phys. **5**, 245 (1905).
[3] H. R. Hassé and W. R. Cook, Phil. Mag. **12**, 554 (1931).

where

$$A=(e^2\alpha m/\hbar^2)^{\frac{1}{2}}, \tag{5}$$

$$q=A(mv/\hbar)=(2e^2\alpha m^2E/\hbar^4)^{\frac{1}{2}}. \tag{6}$$

A has the dimensions of a length; q is a dimensionless quantity giving the De Broglie wave vector in terms of this length. The Hamilton-Jacobi equation for the particle moving in the potential (1) is

$$(\nabla S)^2=\frac{A^2}{r^4}+\frac{q^2}{A^2}. \tag{4b}$$

For zero q we may apply to (4a) and (4b) the substitution

$$u=1/r, \tag{7}$$

yielding, respectively,

$$\nabla_u^2\left(\frac{1}{u}\psi\right)+A^2\left(\frac{1}{u}\psi\right)=0, \tag{8a}$$

$$(\nabla_u S)^2=A^2, \tag{8b}$$

while for finite q the substitution

$$\rho=A^2/qr \tag{9}$$

yields

$$\nabla_\rho^2\left(\frac{1}{\rho}\psi\right)+\frac{A^2}{\rho^4}\left(\frac{1}{\rho}\psi\right)+\frac{q^2}{A^2}\left(\frac{1}{\rho}\psi\right)=0, \tag{10a}$$

$$(\nabla_\rho S)^2=\frac{A^2}{\rho^4}+\frac{q^2}{A^2}. \tag{10b}$$

Equations (8a) and (8b) show that, in both classical and quantum theory, the zero-energy case is equivalent to the free particle problem for finite energy. The case of finite energy, on the other hand, is mapped upon itself by inversion since the Eqs. (10) are identical in form to (4). The radius r_0 of the circle of symmetry is obtained from (9) as

$$r_0=A/q^{\frac{1}{2}}. \tag{11}$$

It follows from the above that the classical orbits at zero energy are straight lines through the origin if the angular momentum is zero and circles through the origin if it is finite. In the former case the sense of motion can be either away from or toward the scattering center; in the latter case the two types are linked in a fixed way because the orbit is bound. In the same way Eq. (15) has two solutions of zero angular momentum,

$$\psi_{0,+}=e^{iA/r}, \tag{12}$$

$$\psi_{0,-}=e^{-iA/r}, \tag{13}$$

which are distinguished by their sense of motion. For finite angular momentum, on the other hand, only the function

$$\psi_l=\frac{1}{r^{\frac{1}{2}}}J_{l+\frac{1}{2}}\left(\frac{A}{r}\right)Y_{l,m}(\theta,\varphi) \tag{14}$$

is possible. In analogy to the classical case this wave function links ingoing and outgoing waves in a fixed way and vanishes at large distance.

When we now pass from zero to positive energy the classical picture changes as follows. For small angular momentum the orbits are similar to the straight lines discussed previously: they are spirals passing through the center of force and reaching to infinity. For large angular momentum there is no qualitative change; the bound orbits remain bound; however, because of the internal symmetry just discussed there is a second orbit which results from a bound one by inversion at the circle of symmetry. This second orbit is a dibrachoid similar to the hyperbola familiar from the case of $1/r^2$ forces. The two types of orbits are separated from each other by limiting orbits such as

$$r=\frac{A}{q^{\frac{1}{2}}}\coth\frac{\varphi}{\sqrt{2}}, \tag{15}$$

in which the particle cannot make up its mind where to go and thus ends up, asymptotically, on the circle of symmetry. The impact parameter b_0 for this orbit is

$$b_0=\sqrt{2}A/q^{\frac{1}{2}}=\sqrt{2}r_0. \tag{16}$$

It defines a simple intrinsic cross section for this potential, that is, the cross section for spiralling orbits or capture cross section σ_0,

$$\sigma_0=\pi b_0^2=2\pi A^2/q=2\pi(e^2\alpha/mv)^{\frac{1}{2}}. \tag{17}$$

The form of it is, of course, in agreement with (2). Figure 1 shows the classical pattern of orbits resulting from a uniform ion stream. The critical impact parameter b_0 is clearly discernible.

It has been pointed out elsewhere[4] that the capture

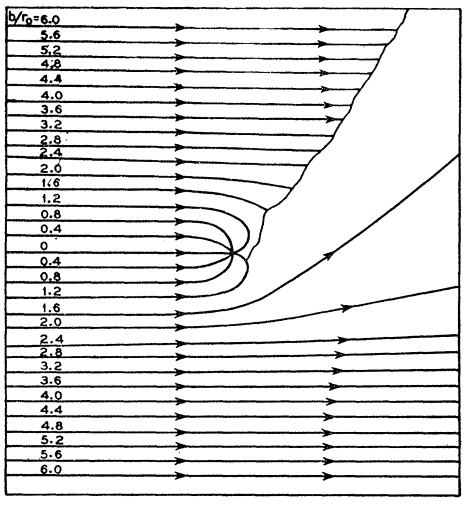

FIG. 1. The pattern of classical orbits for the $-1/r^4$ potential. The same pattern applies in quantum theory for large energy except for local corrections behind the scattering center.

[4] G. H. Wannier, Bell System Tech. J. 32, 70 (1953), Sec. IIIB.

cross section σ_0, defined by (17), is a good approximation to the usual kinetic type of cross section,

$$\sigma_k=\int(1-\cos\theta)d\sigma. \tag{18}$$

The reason for this fact is that the final directions of the spiralling orbits are very nearly random—$\langle\cos\theta\rangle=0$—, whereas the deflections in the dibrachoids are so small that the latter type of scattering events make a small contribution to an integral of the above type. Because of this the capture cross section is a generally useful expression. The development which follows will discuss principally the quantum-mechanical analog of this classical capture cross section.

Without calculation the behavior of the wave functions, for finite energy, can be understood in analogy to the classical picture. There will now be two wave functions for finite as well as zero angular momentum, in analogy to the independent existence of ingoing and outgoing spirals. Furthermore, in contradistinction to the classical case, there will be no finite angular momentum where this behavior ceases, since the classical decomposition of the orbit into two independent pieces arises because there is a belt in which the potential of the centrifugal force is stronger than the total kinetic energy available. This type of separation is not complete in quantum mechanics because of the tunnel effect. Hence, there will be two permissible radial wave functions at all angular momenta. These two wave functions can be distinguished either by their behavior near the origin, where they can behave like (12) or (13), or else by their behavior at large distances, where they behave as $(1/r)e^{iqr/A}$ or $(1/r)e^{-iqr/A}$. Connection formulas will link any three of these asymptotic forms. An extra boundary condition must be imposed to make the problem definite in the usual sense. This boundary condition must describe the fate of the particle as it approaches the center of force.

Two examples will illustrate the general nature of this boundary condition. (a) For helium ions moving in the helium gas the constant A has a value in the neighborhood of 2×10^{-7} cm, while for (b) electrons moving in the helium gas $A\approx6\times10^{-9}$ cm. In the former case the wave functions (12) and (13), near the center of force, oscillate very rapidly: when r is in the neighborhood of the diameter of a helium atom, a number of complete oscillations occur in a distance which is small compared to this diameter. In case (b), however, the oscillation is very much slower. Therefore, in case (a), the phase change effected by the mechanism which removes the singularity of the polarization potential varies extremely rapidly with the energy of the incoming wave. A small spread in the energy of the incoming wave will make the outgoing wave incoherent. Thus, the proper boundary condition is obtained by treating the origin of co-ordinates as a sink. In case (b) the total change of phase is always comparatively small. Only the s-wave phase shift η_0 is large[5] and it is never larger than 3π. The detailed properties of the "repulsion" mechanism are therefore important here—the coherently scattered waves yield the familiar Ramsauer-Townsend effect.

For most ions other than electrons the physical situation is similar to the example (a), above. The detailed properties of the "repulsion" mechanism are irrelevant just as in the classical description of this motion. On the other hand, when the properties of the "repulsion" mechanism are important, as in case (b) above, then the classical description becomes very complicated and in quantum theory the involved prescription of Case[1] is necessary. Our discussion will be limited to those cases in which the origin of coordinates may be considered as a sink.

With the definition of the origin as a sink the wave function near the origin consists entirely of ingoing waves and hence behaves as

$$[\psi]_{r\to0}\sim e^{iA/r}g(\theta). \tag{19}$$

This, together with the usual specification that the wave function at large distance behave as

$$[\psi]_{r\to\infty}\sim e^{iqz/A}+f(\theta)(1/r)e^{iqr/A}, \tag{20}$$

completely determines the wave function. The capture cross section σ_c is then obtained by computing the flux entering the sink at the origin divided by the flux density in the plane wave, that is

$$\sigma_c=\frac{A^2}{q}\int|g(\theta)|^2d\Omega. \tag{21}$$

For small energy the program just outlined can be implemented immediately. If the energy is so small that $e^{iA/r}$ has reached unity before $e^{iqz/A}$ differs materially from this value, that is, if $q\ll1$, then the two limiting functions may simply be patched together by multiplication, yielding the wave function

$$\psi\approx e^{i(A/r+qz/A)}. \tag{22}$$

Figure 2 shows the streamlines resulting from this procedure. The resemblance of these streamlines to the classical orbits of Fig. 1 is marked. There exists even in this extreme quantum limit an impact parameter b_{lim} separating capture and escape; its shift in location from Fig. 1 is small. From (21) and (22) the cross section is found to be[6]

$$\sigma_c=4\pi A^2/q=4\pi(e^2\alpha/mv^2)^{\frac{1}{2}}. \tag{23}$$

This is exactly twice the classical capture cross section

[5] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (The Clarendon Press, Oxford, 1952), p. 118.

[6] There are rigorous methods of deriving (23) which will not be discussed here. We hope to extend them so as to gain a procedure valid at small as well as zero velocity.

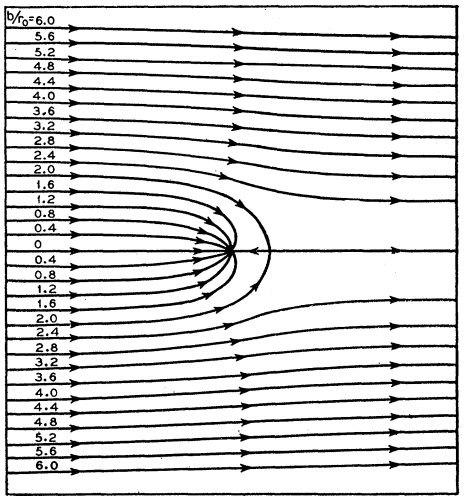

FIG. 2. Streamlines for the extreme quantum case (small energy). Comparison with Fig. 1 shows a strong resemblance of these two extreme situations.

(17). It appears surprising at first sight that this extreme quantum case does not contain h at all. Upon reflection, we can understand the answer on dimensional grounds, as follows. If the energy is made small enough the capture process becomes independent of energy because the wave function (22) becomes identical to (12). Anything derived from this wave function must then be proportional to the particle density D outside the scattering center; hence the inward flux I must also be proportional to this density:

$$I=\text{const}D.$$

Now the cross section is defined as

$$\sigma=I/Dv.$$

Combining the two predictions, we find that σ must vary as $1/v$. Now there is only one way in which an area can be made up out of (2) and (3) in such a way that it varies as $1/v$, namely by using only (2). Hence the result (23) follows.

For finite energies the wave function is not as easily written down. To obtain it requires a study of the Mathieu differential equation of imaginary argument.

III. THE QUANTUM-MECHANICAL CAPTURE CROSS SECTION

The radial equation obtained from the Schrödinger Eq. (4) is

$$\frac{\partial^2\psi}{\partial r^2}+\frac{2}{r}\frac{\partial\psi}{\partial r}-\frac{l(l+1)}{r^2}\psi+\frac{A^2}{r^4}\psi+\frac{\alpha^2}{A^2}\psi=0. \tag{24}$$

If we substitute

$$\psi=\varphi/r^{\frac{1}{2}}, \tag{25a}$$

$$r=r_0e^z, \tag{25b}$$

where r_0 is given by (11), then the radial equation becomes

$$\frac{d^2\varphi}{dz^2}-[(l+\tfrac{1}{2})^2-2q\cosh 2z]\varphi=0, \tag{26}$$

which is Mathieu's equation of imaginary argument.[7] The transformation (25) has mapped the radius of symmetry r_0 on the origin; small values of $r(1/r\gg 1/r_0)$ have become large negative values of z and large values of r ($r\ll r_0$) have become large positive values of z.

The asymptotic behavior of the solutions of (24) at large distance is

$$\varphi(r)\sim\frac{1}{r^{\frac{1}{2}}}e^{\pm iqr/A}. \tag{27}$$

They are the Mathieu analogs of the Hankel functions, that is, the functions $he^{(1)}$ and $he^{(2)}$, defined in (29) and (30) of reference 7. Near the sink at the origin we find the behavior

$$\varphi(r)\sim(r)^{\frac{1}{2}}e^{\pm iA/r}. \tag{28}$$

The solutions with this behavior are the two remaining Hankel-type functions $he^{(3)}$ and $he^{(4)}$. More exactly, we have, for large r,

$$\frac{1}{r^{\frac{1}{2}}}he_l^{(1)}\left(i\ln\frac{r}{r_0}\right)\sim e^{-i\pi/4}\left(\frac{A}{q}\right)^{\frac{1}{2}}\frac{1}{r}e^{-iqr/A}, \tag{29}$$

$$\frac{1}{r^{\frac{1}{2}}}he_l^{(2)}\left(i\ln\frac{r}{r_0}\right)\sim e^{i\pi/4}\left(\frac{A}{q}\right)^{\frac{1}{2}}\frac{1}{r}e^{iqr/A}, \tag{30}$$

and for small r,

$$\frac{1}{r^{\frac{1}{2}}}he_l^{(3)}\left(i\ln\frac{r}{r_0}\right)\sim e^{-i\pi/4}\frac{1}{A^{\frac{1}{2}}}e^{-iA/r}, \tag{31}$$

$$\frac{1}{r^{\frac{1}{2}}}he_l^{(4)}\left(i\ln\frac{r}{r_0}\right)\sim e^{i\pi/4}\frac{1}{A^{\frac{1}{2}}}e^{iA/r}. \tag{32}$$

$he_l^{(1)}$ and $he_l^{(2)}$ together form a complete solution of (26) and so do $he_l^{(3)}$ and $he_l^{(4)}$. The boundary condition (19) demands that the solutions used be $he_l^{(4)}$, and the condition (20) that the various angular momentum solutions be superimposed with such multipliers as to make the incoming spherical waves at large distance [that is the types $he_l^{(1)}$] agree with the contribution of a plane wave. To carry this out we need the decomposition of a plane wave into spherical harmonics, which is well known,[8] and the behavior of $he_l^{(4)}$ at large distance; this is given in the connection formula (64)

[7] G. H. Wannier, Quart. Appl. Math. **11**, 33 (1952). Our equation is equivalent to Eq. (3) of this reference. Most of the properties of the Mathieu equation required for our development are to be found there.

[8] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), Sec. II, p. 1.

of reference 7.

$$he_l^{(4)} = -ie^{\Phi} he_l^{(2)} + (ie^{\Phi}\cos\pi\beta - \cos\pi\gamma) he_l^{(1)}. \quad (33)$$

Here Φ is a real function of the equation parameters which is discussed in Sec. (2) of reference 7; β and γ are also functions of the equation parameters, the only property of which this discussion requires is that

$$i\sin\pi\gamma/\sin\pi\beta = e^{\Phi}, \quad (34)$$

and that $\cos\pi\beta$ and $\cos\pi\gamma$ are always real. Carrying out these operations, we find for the wave function

$$\psi = \tfrac{1}{2}\left(\frac{A}{rq}\right)^{\frac{1}{2}} e^{3i\pi/4} \times \sum_{l=0}^{\infty} \frac{(-)^l(2l+1)P_l(\cos\theta) he_l^{(4)}(i\ln r/r_0)}{ie^{\Phi}\cos\pi\beta - \cos\pi\gamma}. \quad (35)$$

The radial current flowing toward the origin can be found anywhere in principle. We shall do it here by the method indicated in (19) and (21). We find

$$g(\theta) = -\frac{1}{2q^{\frac{1}{2}}} \sum_{l=0}^{\infty} \frac{(-)^l(2l+1)P_l(\cos\theta)}{ie^{\Phi}\cos\pi\beta - \cos\pi\gamma}, \quad (36)$$

and hence, with the help of (34),

$$\sigma_c = \pi\frac{A^2}{q^2} \sum_{l=0}^{\infty} \frac{2l+1}{1+e^{2\Phi}}. \quad (37)$$

Comparison with Eq. (17) yields

$$\sigma_c/\sigma_0 = \frac{1}{2q} \sum_{l=0}^{\infty} \frac{2l+1}{1+e^{2\Phi(l+\frac{1}{2},q)}}, \quad (38)$$

as the ratio of the quantum-mechanical capture cross section to its classical analog.

The result of the above development, although exact, imparts only an imperfect knowledge of the capture cross section σ_c. The reason for this is the appearance of the function $\Phi(l+\frac{1}{2}, q)$ which is exactly defined, but only approximately known. In reference 7, Sec. 2, a lower limit Φ_0 and two upper limits Φ_1 and Φ_2 are derived [Eqs. (16), (24), and (27)], which bracket it quite closely for large l and q. Asymptotic expansions of the cross section σ_c for large velocity are derived in the Appendix. If $\frac{1}{2}(\Phi_0+\Phi_1)$ is used for Φ, the result is formula (y) for σ_c, or (z) for the ratio σ_c/σ_0. The curve in Fig. 3 illustrates the result (z). This curve must be qualified by a statement about the accuracy of the asymptotic expansion (z) and about the intrinsic error caused by the lack of knowledge of Φ.

Calculations of individual points on the plot of Fig. 3 can be made without reliance on an asymptotic expansion, namely, by summing (38) directly by numerical methods. Such calculations are indicated by rings in Fig. 3. [Near $2q=100$ the numerical points are actually more dense than shown; they prove that the asymptotic expansion is accurate to less than 0.02 percent, in this neighborhood; this justifies its use also for values of q, which are larger.]

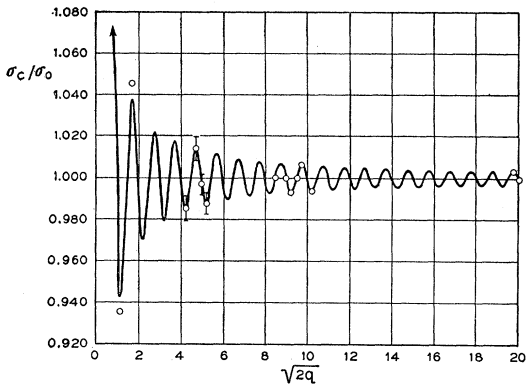

FIG. 3. Capture cross section σ_c *versus* speed for the polarization force. The ordinate is the ratio of σ_c to its classical counterpart σ_0. The abscissa is a dimensionless parameter proportional to the spuare root of the speed.

The error caused by the lack of knowledge of Φ is indicated by the vertical bars attached to some of the rings in Fig. 3. This error becomes larger as the energy becomes smaller; this, in fact, makes it very hard to connect the curve to the point $\sigma_c/\sigma_0=2$, for $q=0$, which we can substantiate by other means. We believe that the arithmetic mean of the two limits, $\frac{1}{2}(\Phi_0+\Phi_1)$, which was used to obtain the curve in Fig. 3, is very close to the correct value of Φ over most of the range shown, because it results from a first-order perturbation applied to Φ_0.

The most striking feature in Fig. 3 is the oscillation which the cross section exhibits when plotted against velocity. This can be understood qualitatively from the Bohr theory. If we treat the problem classically but postulate that the impact parameters assume only the discrete values allowed by the quantum condition for the angular momentum, then the capture cross section jumps suddenly each time that b_0 has increased sufficiently to include one more such impact parameter. The result would be a sawtooth oscillation of the cross section about the classical value. In the wave mechanical result the term $1/(1+e^{2\Phi})$ is a smoothed out step function reminiscent of the simple picture. As expected, the sawtooth oscillations of the Bohr theory capture cross section have an amplitude ($\sim 0.5/q^{\frac{1}{2}}$) which is an order of magnitude larger than the amplitude of the sinusoidal oscillation of the quantum-mechanical cross section, but the oscillation period deduced from this picture, coincides exactly with the one exhibited in Fig. 3.

A surprising feature of Fig. 3 is the fact that there is no indication of a steady deviation of the capture cross section from its classical value. This was first noticed in the numerical evaluation of the cross section. This same feature reappears in the asymptotic expan-

sion, where it shows up as an "accidental" cancellation of terms representing steady deviations; thus the final expression (y) does not contain such terms although they are present in earlier partial results such as (u). It appears plausible to us that this maintenance of the classical cross section in the mean is an exact feature of the quantum mechanics of the $-1/r^4$ potential. However, the method employed here, with its dependence on an imperfectly known Φ, could not yield a proof of this fact, if true.

IV. CONCLUSION

It has been shown that the quantum-mechanical description of the polarization force is in many respects similar to the classical description of this force. The development of the preceding sections have brought out this analogy in a twofold manner. First of all, it was shown that when the method of removing the singularity of such a potential is irrelevant in classical theory then it is also irrelevant in quantum theory. Within this range of validity the reasoning employed is clearly applicable to all singular potentials, thus offering a simple alternative to the procedure of Case .[1] Secondly, a detailed comparison of the quantum-mechanical capture cross section to its classical analog has been made. The result is summed up in Fig. 3 and Eq. (23). It means that the $1/v$ law for the cross section is correct, within certain limits of error and with specifically known deviations, for all values of the velocity.

The theory of the capture cross section developed above, is valid when the "repulsion mechanism" is unimportant. Expressions for other types of cross sections are obtainable from the wave function (35), but their evaluation is encumbered by the lack of knowledge of the parameter β which occurs in the wave function. A numerical calculation of these cross sections at a few values of q indicated that in quantum theory also the capture cross section makes much the largest contribution to the kinetic cross sections.

APPENDIX

Asymptotic Evaluation of the Capture Cross Section

In evaluating the sum entering into the capture cross section (38), namely

$$S=\sum_{l=0}^{\infty}\frac{2l+1}{1+e^{2\Phi(l+\frac{1}{2},q)}}, \tag{a}$$

we may observe first that it converges rapidly for small values of q. The case of q large is, however, more important. For this case we shall follow the basic procedure of Mulholland[9] of comparing S with the corresponding integral by means of contour integration. The

[9] H. P. Mulholland, Proc. Cambridge Phil. Soc. (London) **24**, 280 (1928).

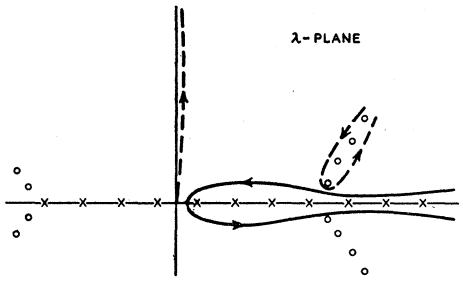

FIG. 4. Path of the contour integrals arising in the evaluation of S. ×—poles of $\tan\pi\lambda$; ○—poles of $1/(1+e^{2\Phi})$; —— Path of integration, Eq. (b); ---- Path of integration, Eq. (e).

function

$$-\pi\tan\pi\lambda$$

has poles of unit strength at the positions $\lambda=\frac{1}{2}, \frac{3}{2}, 5/2, 7/2, \cdots$. Hence, S may be written in the form

$$S=-\frac{1}{i}\int\frac{\lambda\tan\pi\lambda}{1+e^{2\Phi(\lambda,q)}}d\lambda. \tag{b}$$

Here, the contour proceeds in the complex λ plane as shown by the solid curve of Fig. 4, *including* all positive poles of $\tan\pi\lambda$, and *excluding* all negative poles of $\tan\pi\lambda$ and all poles of $1/(1+e^{2\Phi})$. We observe that the two parts of the path of integration on either side of the real axis give conjugate complex contributions. Hence, we may drop one of these parts and write S in the form

$$S=\Re\left[\frac{2}{i}\int_0^{\infty+\epsilon i}\frac{\lambda\tan\pi\lambda}{1+e^{2\Phi}}d\lambda\right],$$

where $\Re[\ ]$ denotes the real part of the bracketed quantity. The path of integration goes through the first quadrant, leaving all poles of $\tan\pi\lambda$ on the right and all poles of $1/(1+e^{2\Phi})$ on the left. Now follows the transformation which Mulholland ascribes to Lindelöf:

$$\tan\pi\lambda=i-\frac{2i}{e^{-2\pi i\lambda}+1},$$

which yields

$$S=\int_0^{\infty}\frac{2\lambda d\lambda}{1+e^{2\Phi}}-\Re\left[\int_0^{\infty+\epsilon i}\frac{4\lambda d\lambda}{(1+e^{2\Phi})(e^{-2\pi i\lambda}+1)}\right].$$

The next step is made possible by the fact that, for large λ, the limits bracketing Φ approach each other. Using the analytic expressions for any of these limits one obtains, for large λ,

$$\Phi\sim 2\lambda\ln(2\lambda/ek), \tag{c}$$

where we have set

$$q=k^2, \tag{d}$$

in accordance with the usual nomenclature for the Mathieu equation. Formula (c) shows that $1/(1+e^{2\Phi})$ decreases exponentially when λ gets large along the

positive real axis, approaches 1 when λ gets large along the positive imaginary axis. On a line asymptotically parallel to the imaginary axis there are the poles $\Phi=\frac{1}{2}(2m+1)\pi i$. Inbetween these poles there are saddle points where $\Phi=m\pi i$ and $1/(1+e^{2\Phi})=\frac{1}{2}$. Therefore, as the path of integration is extended out to large imaginary values, that part of the path which in the limit is infinitely far from the real axis makes a vanishingly small contribution because the second factor in the denominator of the integral produces convergence. It follows that the path of integration in the first quadrant can be broken as shown by the dashed curve of Fig. 4. One integral runs from 0 to $i\infty$, the other is shrunk onto the poles of $1/(1+e^{2\Phi})$. This converts part of the integral back into a sum but of a different type, namely

$$S=\int_0^\infty \frac{2\lambda d\lambda}{1+e^{2\Phi}}-\Re\left[\int_0^{i\infty}\frac{4\lambda d\lambda}{(e^{2\Phi}+1)(e^{-2\pi i\lambda}+1)}\right]$$
$$-\Re\left[\sum_m \oint_{\lambda+m}\frac{4\lambda d\lambda}{(e^{2\Phi}+1)(e^{-2\pi i\lambda}+1)}\right]. \quad \text{(e)}$$

Here, λ_1, λ_2, $\cdots$ are the poles of $1/(1+e^{2\Phi})$ in the first quadrant and the integrals under the summation sign are residue integrals proceeding in the positive sense around these poles.

It is remarkable that we have in (e) a rigorously correct decomposition of the sum S into

1. the corresponding integral;
2. a smoothly varying deviation term;
3. a sum of residues oscillating rapidly with q.

In order to evaluate the quantities in (e) explicitly, Φ should be known as a function of λ. Since only upper and lower limits on Φ are known we shall determine S first using the lower limit Φ_0, and then using the next order approximation, $\frac{1}{2}(\Phi_0+\Phi_1)$. The evaluation will be carried out assuming that q is moderately large. (See Fig. 3.)

Utilizing Φ_0, we consider, first of all, the second term. For k large and λ zero, $2\Phi_0$ equals $-3.4k$, and hence the exponential will be small. This is true, *a fortiori*, along the imaginary axis. Hence we may write

$$\text{second term}=-\int_0^{i\infty}\frac{4\lambda d\lambda}{e^{-2\pi i\lambda}+1}+O(e^{-3.4k}),$$

or

$$\text{second term}=(1/12)+O(e^{-3.4k}). \quad \text{(f)}$$

The procedure for evaluating the two other terms in (e) is based on the fact that they both depend critically only on the variations of Φ near the crossing of the two sets of poles (Fig. 4). Hence an expansion about this crossing point can be substituted for the analytic expressions for Φ which involve elliptic integrals. As a first approximation we set

$$2\Phi=\sigma\lambda^2-\tau, \quad \text{(g)}$$

in which σ and τ are constants. This yields

$$(\text{first term})_1=\frac{1}{\sigma}\ln(e^\tau+1)=\frac{\tau}{\sigma}+O(e^{-\pi k}). \quad \text{(h)}$$

In the case $\Phi=\Phi_0$, we have $\sigma=\pi/2k$, $\tau=\pi k$, and hence

$$(\text{first term})_1=2k^2+O(e^{-\pi k}). \quad \text{(i)}$$

Obviously, this approximation must be improved. We do this by observing that Φ_0 is of the form

$$\Phi_0(\lambda,k)=k\varphi(\lambda/k), \quad \text{(j)}$$

and hence, for $\Phi=\Phi_0$,

$$(\text{first term})=k^2\int_0^\infty\frac{2\xi d\xi}{e^{2k\varphi(\xi)}+1}.$$

Differentiation will remove the leading term just found:

$$\frac{d}{dk}\left(\frac{\text{first term}}{k^2}\right)=-\frac{1}{k^3}\int_0^\infty\frac{\lambda\Phi_0(\lambda,k)d\lambda}{\cosh^2\Phi_0(\lambda,k)}$$
$$=-\frac{1}{k^3}\int_{-\infty}^\infty\frac{\lambda(d\lambda/d\Phi_0)\Phi_0 d\Phi_0}{\cosh^2\Phi_0}+O(e^{-3.4k}). \quad \text{(k)}$$

The error arises here from extending the lower limit of integration beyond $\lambda=0$. The term $\lambda(d\lambda/d\Phi)$ must now be expanded in powers of Φ_0. From the structural relation (j),

$$\lambda\frac{d\lambda}{d\Phi_0}=k\cdot(\text{a function of }\Phi_0/k),$$

or in detail, from reference 7, Eq. (16),

$$\lambda\frac{d\lambda}{d\Phi_0}=\frac{2k}{\pi}+\frac{1}{2\pi^2}\Phi_0+O\left(\frac{\Phi_0^2}{k}\right)+O\left(\frac{\Phi_0^3}{k^2}\right). \quad \text{(l)}$$

Substitution into (k) and subsequent integration yields

$$(\text{first term})_{\Phi=\Phi_0}=2k^2+\frac{1}{25}+O\left(\frac{1}{k^2}\right)+O(e^{-3.4k}). \quad \text{(m)}$$

For the third term in (e) we also start out with a first approximation based on (g), then follow up with a better technique, applicable to Φ_0 only, using (j). In first approximation the poles λ_m are given by

$$\sigma\lambda_m^2-\tau=(2m+1)\pi i, \quad m=0, 1, 2, 3, \cdots. \quad \text{(n)}$$

The third term then takes on the form

$$(\text{third term})_1=-\frac{2\pi}{\sigma}\sum_{m=0}^\infty\frac{\sin 2\pi u_m}{\cosh 2\pi v_m+\cos 2\pi u_m}, \quad \text{(o)}$$

where

$$\lambda_m=u_m+iv_m, \quad \text{(p)}$$

and u_m and v_m are positive. For large k, they are ap-

proximately given by

$$u_m \approx \sqrt{2}k, \quad v_m \approx \sqrt{2}(m+\tfrac{1}{2}).$$

Upon substitution of these quantities into (o), the oscillatory character of the third term becomes evident. Another feature also comes out, namely that all terms in the sum are negligible compared to the first because they are of the order $e^{-3\pi\sqrt{2}} \sim 10^{-5}$. Thus dropping all but the first term in (o), and using (n) and (p), we get

$$\begin{aligned}(\text{third term})_1 &= -\frac{4\pi}{\sigma}\left\{\exp\left(-\frac{\pi^2}{(\sigma\tau)^{\frac{1}{2}}}\right)\sin\left[2\pi\left(\frac{\tau}{\sigma}\right)^{\frac{1}{2}}+O\left(\frac{1}{k}\right)\right]\right. \\ &\quad \left.-\exp\left(-\frac{2\pi^2}{(\sigma\tau)^{\frac{1}{2}}}\right)\sin\left[4\pi\left(\frac{\tau}{\sigma}\right)^{\frac{1}{2}}\right]\right\}+O(ke^{-3\pi\sqrt{2}}) \\ &\quad +O\left(\frac{1}{k}e^{-\sqrt{2}\pi}\right)\sin\left[2\pi\left(\frac{\tau}{\sigma}\right)^{\frac{1}{2}}\right]+O\left(\frac{1}{k^2}e^{-\sqrt{2}\pi}\right). \quad \text{(q)}\end{aligned}$$

To improve this approximation for $\Phi=\Phi_0$ we still need only the residue at the first pole. Let λ_0 be the value attained by λ when Φ_0 equals $\frac{1}{2}\pi i$. Then we may write

$$\begin{aligned}(\text{third term}) &= -\Re\left[\frac{4\lambda_0\left(\frac{d\lambda}{d\Phi_0}\right)_{\lambda=\lambda_0}}{e^{-2\pi i\lambda_0}+1}\right. \\ &\quad \left.\times\oint^{(\frac{1}{2}\pi i)}\frac{d\Phi_0}{e^{2\Phi_0}+1}\right]+O(ke^{-3\sqrt{2}\pi}) \\ &= \Re\left[\frac{4\pi i\lambda_0\left(\frac{d\lambda}{d\Phi_0}\right)_{\lambda=\lambda_0}}{e^{-2\pi i\lambda_0}+1}\right]+O(ke^{-3\sqrt{2}\pi});\end{aligned}$$

or, substituting (p) and dropping superfluous indices,

$$\begin{aligned}(\text{third term}) &= -\frac{4\pi\Re\left[\lambda\frac{d\lambda}{d\Phi_0}\right]_{\lambda=\lambda_0}\sin 2\pi u}{e^{2\pi v}+2\cos 2\pi u} \\ &\quad -\frac{4\pi\Im\left[\lambda\frac{d\lambda}{d\Phi_0}\right]_{\lambda=\lambda_0}(\cos 2\pi u+e^{-2\pi v})}{e^{2\pi v}+2\cos 2\pi u}. \quad \text{(r)}\end{aligned}$$

u and v can be found from the power series (l), with $\Phi_0=\pi i/2$. This yields

$$u=\sqrt{2}k\left[1+\frac{3}{32k^2}+O\left(\frac{1}{k^4}\right)\right], \quad (s_1)$$

$$v=\frac{1}{\sqrt{2}}+O\left(\frac{1}{k^2}\right). \quad (s_2)$$

We can now write the third term in its final form, adding cosine terms as phase shifts to the sine terms.

$$\begin{aligned}(\text{third term})_{\Phi=\Phi_0} &= -8ke^{-\sqrt{2}\pi}\sin\left(2\pi\sqrt{2}k+\frac{3\pi\sqrt{2}}{16k}+\frac{1}{8k}\right) \\ &\quad +8ke^{-2\pi\sqrt{2}}\sin\left(4\pi\sqrt{2}k+\frac{3\pi\sqrt{2}}{8k}+\frac{1}{8k}\right) \\ &\quad +O\left(\frac{1}{k}e^{-\sqrt{2}\pi}\right)\sin(2\pi\sqrt{2}k) \\ &\quad +O\left(\frac{1}{k^2}e^{-\sqrt{2}\pi}\right)+O(ke^{-3\pi\sqrt{2}}). \quad \text{(t)}\end{aligned}$$

We now combine (f), (m), and (t) to yield (e) for the case $\Phi=\Phi_0$. Calling this result S_0, we get

$$\begin{aligned}S_0 &= 2k^2+\tfrac{1}{8}+O(1/k^2)+O(e^{-3.4k}) \\ &\quad -8ke^{-\sqrt{2}\pi}\sin\left(2\pi\sqrt{2}k+\frac{3\pi\sqrt{2}}{16k}+\frac{1}{8k}\right) \\ &\quad +8ke^{-2\pi\sqrt{2}}\sin\left(4\pi\sqrt{2}k+\frac{3\pi\sqrt{2}}{8k}+\frac{1}{8k}\right) \\ &\quad +O\left(\frac{1}{k}e^{-\sqrt{2}\pi}\right)\sin(2\pi\sqrt{2}k)+O(ke^{-3\pi\sqrt{2}}). \quad \text{(u)}\end{aligned}$$

We must now consider the modifications imposed upon S if Φ_0 is replaced by $\frac{1}{2}(\Phi_0+\Phi_1)$. Obviously the second term is not modified since Φ terms enter only in the estimation of the error. For the other two terms the change is also a small correction of higher order; it is therefore sufficient to look at the modification in the first order results (i) and (g) when the more accurate values for σ and τ in (g) are employed. The new values are

$$\sigma=\frac{\pi}{2k}-\frac{5\pi}{256k^3}+O\left(\frac{1}{k^5}\right), \quad (v_1)$$

$$\tau=\pi k-\frac{13\pi}{128k}+O\left(\frac{1}{k^3}\right). \quad (v_2)$$

They yield

correction to the first term

$$\begin{aligned}&= (\tau/\sigma)_{\Phi=\frac{1}{2}(\Phi_0+\Phi_1)}-(\tau/\sigma)_{\Phi=\Phi_0} \\ &= -\tfrac{1}{8}+O(1/k^2). \quad \text{(w)}\end{aligned}$$

In the third term most of the modifications produced are comparable with terms already neglected. The most important exception is a phase shift in the first sine

term which is

phase correction

$$=2\pi\{[(\tau/\sigma)_{\Phi=\frac{1}{2}(\Phi_0+\Phi_1)}]^{\frac{1}{2}}-[(\tau/\sigma)_{\Phi=\Phi_0}]^{\frac{1}{2}}\}$$
$$=-\pi\sqrt{2}/16k. \quad \text{(x)}$$

A similar phase correction in the second sine term will be neglected. Combination of (u), (w), and (x) yields then, for $\Phi=\frac{1}{2}(\Phi_0+\Phi_1)$ and $k^2=q$,

$$S=2k^2-8ke^{-\sqrt{2}\pi}\sin[2\pi\sqrt{2}k+(\sqrt{2}\pi+1)/8k]$$
$$+8ke^{-2\pi\sqrt{2}}\sin[4\pi\sqrt{2}k+O(1/k)]$$
$$+O(1/k^2)+O(e^{-\sqrt{2}\pi}/k)\sin(2\pi\sqrt{2}k)$$
$$+O(ke^{-3\pi\sqrt{2}})+O(e^{-3.4k}). \quad \text{(y)}$$

Inserting this value into Eq. (38) of Sec. III, we end up with the following value for the ratio of the quantum to the classical capture cross section:

$$\frac{\sigma_c}{\sigma_0}=1-\frac{4}{k}e^{-\sqrt{2}\pi}\sin[2\pi\sqrt{2}k+(\sqrt{2}\pi+1)/8k]$$
$$+\frac{4}{k}e^{-2\pi\sqrt{2}}\sin[4\pi\sqrt{2}k+O(1/k)]$$
$$+O\left(\frac{1}{k^4}\right)+O\left(\frac{1}{k^3}e^{-\pi\sqrt{2}}\right)\sin(2\pi\sqrt{2}k)$$
$$+O\left(\frac{1}{k}e^{-3\pi\sqrt{2}}\right)+O\left(\frac{1}{k^2}e^{-3.4k}\right). \quad \text{(z)}$$

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Ionizing Collisions of Very Fast Particles and the Dipole Strength of Optical Transitions

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This note discusses how the Bethe theory of ionizing collisions should be adapted to gases other than atomic hydrogen. Experimental data on primary ionization, analyzed by the method of McClure, yield the value of the total dipole strength for ionization, $\int_I^\infty |x_W|^2 dW$, an atomic property which is otherwise poorly known and whose relationship to the diamagnetic susceptibility should be of interest.

THE primary specific ionization of fast charged particles in gases has been calculated long ago by Bethe.[1,2] His calculation applies specifically to atomic hydrogen, and its application to other gases does not seem to have been developed adequately.[3,4] McClure[4] utilized the general structure of the Bethe theory to express his experimental results—specific ionization *vs* energy of incident electrons—in terms of two empirical constants for each gas. It is proposed, in the present note, to review briefly the pertinent elements of the Bethe theory, to specify the theoretical definition of McClure's constants, and to point out that one of these constants represents an atomic property of considerable interest and is a worthwhile target for systematic experimental study.

The majority of the ionizing collisions of fast particles are of the "glancing" (or "optical") type, with large impact parameters. These collisions affect gas molecules through a short electromagnetic pulse whose spectrum has a practically uniform intensity over the frequency range of interest. The portion of this spectrum most effective in producing ionizations lies in the very far ultraviolet, where the optical properties of different substances have not yet been studied systematically. Therefore, data on ionizing collisions may complement conventional optical studies.

This connection with optical properties takes a precise form through an analysis of the *dependence of ionizing collisions on the energy* of the incident particles. When the collisions are classified according to impact parameter—more precisely, according to momentum transfer—the majority of them have a probability inversely proportional to the particle velocity squared. In addition, the maximum impact parameter depends on the velocity. This particular dependence affects only "optical" collisions and thus provides an opportunity to disentangle optical properties of gas molecules from other properties which influence the occurrence of close collisions.

A particle of charge ze and velocity $v=\beta c$ produces per cm path in a gas an average number of ionizations ("primary specific ionization") represented by the formula

$$S=(2\pi z^2e^4N/mc^2)\beta^{-2}\int_I^\infty dW\int_{Q_{\min}}^{Q_{\max}} dQ\,Q^{-2}|\eta_W(Q)|^2, \quad (1)$$

which is an integral of (B50.8).[2,5] Here e and m are the

[1] H. A. Bethe, Ann. Physik **5**, 325 (1930).
[2] Geiger-Scheel, *Handbuch der Physik* (J. Springer, Berlin, 1933), Vol. 24/1, p. 491 ff., which will be referred to as "B".
[3] See, e.g., B. Rossi, *High Energy Particles* (Prentice Hall, Inc., New York, 1952), p. 45.
[4] G. W. McClure, Phys. Rev. **90**, 796 (1953).
[5] A factor $E'/E=1-W/E$ has been dropped from (B50.8) because it practically equals 1 in most collisions as pointed out in reference 2.