

Singular Potentials*

K. M. CASE

Institute for Advanced Study, Princeton, New Jersey

(Received May 15, 1950)

The difficulties arising in quantum mechanics when the potential is highly singular are considered. It is found that the Hamiltonian needs further specification in such cases. This may be done conveniently by requiring a fixed phase for the wave functions at the origin. A proof that all the well-known singular examples are amenable to this treatment is given. For illustration the spectra for spin zero and one-half particles in the fields of highly charged nuclei are found. It is also shown that a complete set of eigenfunctions for a vector particle in a Coulomb field can be found.

I. INTRODUCTION

SINCE the advent of quantum mechanics, a number of problems have been found which seemingly do not fall into the formal structure of the Schrödinger equation and its conventional interpretation. Thus, with sufficiently singular potentials, the customary methods of finding energy eigenvalues and eigenfunctions fail. When these examples have been encountered in the literature, they have been rather summarily dismissed. In this paper an attempt will be made to show how the exceptional cases may be dealt with and what physical interpretations are necessary.

Historically, the first¹ place where these difficulties showed up was probably the strongly attractive $1/r^2$ potential. Other non-relativistic examples are potentials which behave as $1/r^n$ near the origin with $n > 2$ and the tensor force problem with a $1/r^3$ singularity. With relativistic wave equations, even a Coulomb potential is highly singular. Thus, for spin 0 or $\frac{1}{2}$ particles, "singular" cases arise if the nucleus is sufficiently highly charged. For spin 1, difficulties arise in any Coulomb field.² It will be shown that the difficulties in these diverse problems can all be resolved by the same technique.

II. THE $1/r^2$ POTENTIAL

Consider the non-relativistic Schrödinger equation with a potential

$$V(r) = [-V_0 f(r/r_0)/(r/r_0)^n]. \quad (1)$$

On separation of the angular dependence, the radial wave equation is:

$$\frac{d^2 u}{dx^2} + \left[\frac{\lambda f(x)}{x^n} - \frac{l(l+1)}{x^2} - \eta^2 \right] u = 0, \quad 0 \leq x < \infty, \quad (2)$$

where

$$x = r/r_0; \quad \lambda = MV_0 \sigma_0^2 / \hbar^2; \quad \eta = r_0 (-ME/\hbar^2)^{1/2}, \quad \psi = u/r. \quad (3)$$

Hence, $\lambda > 0$ implies an attractive potential. It is

* This work was supported by a grant-in-aid from the Institute for Advanced Study, supported by the AEC.

¹ Mott and Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), p. 30.

² H. C. Corben and J. Schwinger, *Phys. Rev.* **58**, 953 (1940); I. Tamm, *Phys. Rev.* **58**, 952 (1940).

assumed that

$$f(0) = 1. \quad (4)$$

Since for the general arguments that follow, the exact functional form of $f(x)$ and the value of l are unimportant, we shall consider the case $f(x) = 1$ and S states only. Then for the $1/r^2$ potential the radial Schrödinger equation is:

$$\frac{d^2 u}{dx^2} + \left[\frac{\lambda}{x^2} - \eta^2 \right] u = 0. \quad (5)$$

Assuming u to be expressible as a power series in the neighborhood of the origin beginning with x^ρ , the indicial equation for (5) is:

$$\rho(\rho-1) + \lambda = 0, \quad (6)$$

or

$$\rho = \frac{1}{2} \pm (\frac{1}{4} - \lambda)^{1/2}. \quad (7)$$

For $\lambda < \frac{1}{4}$ the treatment is conventional and can be found in reference 1. For $\lambda > \frac{1}{4}$, that is if the potential is sufficiently attractive, (7) shows that both solutions of (5) behave in essentially the same way. An elegant means of deciding between the solutions of (5) has been given by Von Neumann³ using the general principles of quantum mechanics. These tell us that a complete, quadratically integrable, orthonormal set of solutions of (5) is needed. Since

$$\int \psi^* \psi d\tau \sim \int_0^\infty u^2(x) dx, \quad (8)$$

Eq. (7) shows that all solutions are quadratically integrable in the neighborhood of the origin. Usually this integrability condition suffices to distinguish between the two independent solutions (7). Here the orthogonality condition must be used. Take the general solution of (5) to be real. Then for small x

$$u \sim A x^{1/2} \cos(\lambda' \ln x + B), \quad (9)$$

where

$$\lambda' = (\lambda - \frac{1}{4})^{1/2}.$$

Suppose further that the solutions are chosen so as to fall off exponentially with large x . Then for small x

³ Private communication from W. Pauli.

the corresponding solutions will [from Eq. (9)] behave as:

$$\begin{aligned} u_1 &\sim A_1 x^{\frac{1}{2}} \cos(\lambda' \ln x + B_1), \\ u_2 &\sim A_2 x^{\frac{1}{2}} \cos(\lambda' \ln x + B_2), \end{aligned} \quad (9a)$$

and A and B are arbitrary constants.

Consider solutions of (5), u_1 and u_2 , corresponding to two different η_1 and η_2 . These satisfy

$$d^2 u_1 / dx^2 + [(\lambda/x^2) - \eta_1^2] u_1 = 0, \quad (10a)$$

$$d^2 u_2 / dx^2 + [(\lambda/x^2) - \eta_2^2] u_2 = 0. \quad (10b)$$

Multiplying (10a) by u_1 , (10b) by u_2 , subtracting, and integrating yields:

$$(\eta_1^2 - \eta_2^2) \int_0^\infty u_2 u_1 dx = \left[u_2 \frac{du_1}{dx} - u_1 \frac{du_2}{dx} \right]_0^\infty. \quad (11a)$$

Usually the orthogonality relations are deduced from the vanishing of the right-hand side of (11a). However, here one obtains on inserting (9a) and remembering that u_1 and u_2 vanish at infinity:

$$(\eta_1^2 - \eta_2^2) \int_0^\infty u_2 u_1 dx = A_1 A_2 \lambda' \sin(B_2 - B_1). \quad (11b)$$

Hence, in general, solutions corresponding to two different energies are not orthogonal. However, if it is required of the solutions that

$$B_1 = B_2 = B, \quad (12)$$

then orthogonality is achieved. (It is to be noted that choosing

$$B_i = B + n\pi, \quad (13)$$

where n is a positive or negative integer will also insure orthogonality. It is shown below that no greater generality is so obtained.) The significance of B will be discussed later.

The eigenvalue problem for (5) can now be stated. We require those values of η for which u vanishes exponentially for large x and behaves as

$$u \sim x^{\frac{1}{2}} \cos(\lambda' \ln x + B), \quad (9b)$$

for x small.

The eigenvalues and eigenfunctions can now be computed. Two linearly independent solutions of (5) are:

$$u = x^{\frac{1}{2}} I_{\pm i\lambda'}(\eta x), \quad (14)$$

where I is the Bessel function defined by Watson.⁴ Taking as solution the linear combination

$$u = x^{\frac{1}{2}} [e^{i\alpha} I_{i\lambda'}(\eta x) + e^{-i\alpha} I_{-i\lambda'}(\eta x)], \quad (15)$$

one finds for small x that

$$u \approx 2x^{\frac{1}{2}} \cos(\lambda' \ln \eta x + \alpha). \quad (16)$$

Hence, if

$$\alpha = B - \lambda' \ln \eta, \quad (17)$$

then u is of the requisite form (9b). Using the asymptotic forms of the Bessel functions, one finds for large x

$$u \approx \frac{1}{(2\pi\eta)^{\frac{1}{2}}} \{ [e^{i\alpha} + e^{-i\alpha}] e^{\eta x} + (\text{constant}) e^{-\eta x} \}. \quad (18)$$

Hence, if

$$\cos \alpha = 0, \quad (19)$$

or

$$\alpha = (n + \frac{1}{2})\pi, \quad (20)$$

where n is any positive or negative integer, u decays exponentially.

Inserting (17) into (20) and solving for η gives the eigenvalues:

$$\eta_n = \exp[(B - (n + \frac{1}{2})\pi)/\lambda']. \quad (21)$$

From (3) it can be seen that the bound states then form a point spectrum extending from minus infinity to zero. At zero there is a point of accumulation. From (21) it is seen that a displacement of B by a multiple of π has no effect on the spectrum.

III. THE $1/r^n$ POTENTIAL: $n > 2$

The Schrödinger equation is:

$$d^2 u / dx^2 + [(\lambda/x^n) - \eta^2] u = 0. \quad (22)$$

Since the singular behavior is different for each n in this form, it is convenient to introduce the new variable

$$y = x^{1-\frac{1}{n}}, \quad (23)$$

in terms of which (22) becomes:

$$\frac{d^2 u}{dy^2} + \frac{n-1}{n-2} \frac{du}{dy} + \frac{4}{(n-2)^2} \left[\lambda - \frac{\eta^2}{y^{2n/n-2}} \right] u = 0. \quad (24)$$

Here we are interested in the behavior of the solution for large y . It is obvious that a series of descending powers of y will not satisfy (24) since the occurrence of the λ term will always require the vanishing of the highest power in the series, and hence of the entire series. The correct treatment at such essential singularities is well known.⁵ Let

$$u = e^{\alpha y} v. \quad (25)$$

Then:

$$\begin{aligned} v'' + \left[2\alpha + \frac{n}{n-2y} \right] v' \\ + \left[\frac{4\lambda}{(n-2)^2} + \alpha^2 + \frac{\alpha n}{(n-2)y} - \frac{4\eta^2}{(n-2)^2} \cdot \frac{n-2}{2ny} \right] v = 0. \end{aligned} \quad (26)$$

If we choose

$$\alpha^2 = -4\lambda/(n-2)^2, \quad (27)$$

⁴ G. N. Watson, *Theory of Bessel Functions* (The Macmillan Company, New York, 1944), p. 77.

⁵ See E. L. Ince, *Ordinary Differential Equations* (Dover Publications, New York, 1944), p. 425.

it is possible to obtain a descending power series for v . The highest power is y^ρ where

$$\rho = -n/2(n-2). \quad (28)$$

Restricting ourselves to real solutions the behavior of the general solution of (22) for small x is:

$$u \sim Ax^{n/4} \cos \left[\frac{2}{n-2} \left(\frac{\lambda}{x^{n-2}} \right)^{\frac{1}{2}} + B \right]. \quad (29)$$

As in Section II, consider the solutions u_1 and u_2 of

$$d^2u_1/dx^2 + [(\lambda/x^n) - \eta_1^2]u_1 = 0, \quad (30a)$$

$$d^2u_2/dx^2 + [(\lambda/x^n) - \eta_2^2]u_2 = 0, \quad (30b)$$

where η_1 and η_2 are two different values. In particular it is required that u_1 and u_2 vanish at infinity. Then for small x

$$u_1 \sim A_1 x^{n/4} \cos \left[\frac{2}{n-2} \left(\frac{\lambda}{x^{n-2}} \right)^{\frac{1}{2}} + B_1 \right], \quad (31)$$

$$u_2 \sim A_2 x^{n/4} \cos \left[\frac{2}{n-2} \left(\frac{\lambda}{x^{n-2}} \right)^{\frac{1}{2}} + B_2 \right].$$

As usual one finds:

$$(\eta_1^2 - \eta_2^2) \int_0^\infty u_2 u_1 dx = \left[u_2 \frac{du_1}{dx} - u_1 \frac{du_2}{dx} \right]_0^\infty. \quad (32)$$

Insertion of the asymptotic forms for small and large x gives:

$$(\eta_1^2 - \eta_2^2) \int_0^\infty u_2 u_1 dx = A_1 A_2 \lambda^{\frac{1}{2}} \sin(B_1 - B_2). \quad (33)$$

Hence, if all eigenfunctions are required to behave as

$$u \sim x^{n/4} \cos \left[\frac{2}{n-2} \left(\frac{\lambda}{x^{n-2}} \right)^{\frac{1}{2}} + B \right], \quad (34)$$

where now B is a fixed phase factor common to *all* eigenfunctions, we will have orthogonality. Conversely, it can be said that the requirement of vanishing at infinity and having the designated behavior for small x makes the eigenvalue problem uniquely soluble.

IV. DISCUSSION OF THE NON-RELATIVISTIC CASE

The principal difference between "singular" and "non-singular" potentials is seen to be that in the latter case the solutions of the Schrödinger equation subject to the condition of quadratic integrability form a complete orthonormal set. In the singular case the solutions are too numerous and hence, over complete. Some other parameter in addition to the functional form of the potential is needed to specify completely the potential. This is conveniently taken as the phase, B .

This distinction may be expressed in physical terms

somewhat differently. In any physical problem in which we express the interaction between two systems by means of a potential which becomes infinite when the distance between them becomes zero, we are dealing with an idealization. Thus, the Coulomb interaction between an electron and a nucleus is not strictly proportional to $1/r$ down to $r=0$. The finite size of the nucleus sets one limit. Even for a single proton there is the probable finite radius of the proton. The important point is, however, that if the $1/r$ law holds down to sufficiently small distances the eigenvalues and eigenfunctions are essentially independent of exactly when or how the power law breaks down. For potentials as singular as $1/r^2$ or greater, this is no longer true. The eigenvalues and eigenfunctions do depend on the nature of the cut-off. The main conclusion from the above work is, though, that only a single parameter is needed to describe the situation for small distances. Thus it is not necessary to know exactly at what distance the power law breaks down and what functional form replaces it. All one would need to know from experiment is the value of B for the given system.

From this it is seen that B describes the breakdown of the power law at small r . For a simple model one might consider the true potential to be $1/r^n$ down to $r=\epsilon$ and then to be an infinitely high repulsive square well. Then B is directly related to the "cut-off radius," ϵ .

For the non-relativistic cases, this discussion is rather academic, since the spectrum of energy values is a point spectrum extending from minus infinity to zero, plus the usual positive energy continuum. That the negative energies are discrete follows from the quadratic integrability of the wave functions. That the spectrum extends to minus infinity is obvious, since the Hamiltonian operator is not bounded below. Now no physical system has an infinite binding energy. Therefore such singular potentials have no application as an approximation in the calculation of term values of real systems. One possible remaining application is to describe some scattering processes. Resonance, for example, is well exemplified by scattering by such potentials.

If only the non-relativistic Schrödinger equation were to be considered, these highly singular potentials might well be forgotten.

V. RELATIVISTIC WAVE EQUATIONS WITH SINGULAR POTENTIALS—SPIN 1/2

Here the situation is altered considerably. Firstly, much weaker infinities in the potential are "highly singular." Even the Coulomb field gives rise to difficulties of the form considered above. Secondly, the discrete energy levels of a relativistic system are restricted to the region between $\pm mc^2$. Thus, it certainly will not be possible to ignore singular potentials because they lead to infinite binding energies.

The most famous singular example is that of the Dirac equation for an electron in the Coulomb field of a fictitious nucleus of charge such that $\alpha Z > 137$. Sepa-

rating out the angular dependence the equations for the radial wave functions may be written in the form given by Bethe.⁶

$$\begin{aligned} \frac{du}{dr} - \chi \frac{u}{r} &= \left(1 - E - \frac{\alpha Z}{r}\right)w, \\ \frac{dw}{dr} + \chi \frac{w}{r} &= \left(1 + E + \frac{\alpha Z}{r}\right)u. \end{aligned} \tag{35}$$

(Here Bethe's notation has been altered slightly and units such that $\hbar=c=m=1$ have been chosen.) χ is the angular momentum quantum number of Dirac such that

$$\begin{aligned} \chi &= -(j + \frac{1}{2}) \quad \text{for } j = l + \frac{1}{2}, \\ \chi &= +(j + \frac{1}{2}) \quad \text{for } j = l - \frac{1}{2}. \end{aligned} \tag{36}$$

The normalization is such that the scalar product of two different eigenfunctions

$$\begin{pmatrix} u_1 \\ w_1 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} u_2 \\ w_2 \end{pmatrix}$$

is defined by

$$\int_0^\infty (u_1 u_2 + w_1 w_2) dr. \tag{37}$$

Consider solutions of (35), in the neighborhood of the origin, of the form:

$$\begin{aligned} u &= r^\rho [a_0 + a_1 r + \dots], \\ w &= r^\rho [b_0 + b_1 r + \dots]. \end{aligned} \tag{38}$$

Inserting into (35) and equating to zero the coefficient of the lowest power of $r(r^{\rho-1})$ gives as the indicial equations:

$$\begin{aligned} a_0 \rho - \chi a_0 &= -\alpha Z b_0, \\ b_0 \rho - \chi b_0 &= \alpha Z a_0, \end{aligned} \tag{39}$$

or solving for b_0/a_0 and ρ :

$$\begin{aligned} \rho &= \pm [\chi^2 - (\alpha Z)^2]^{\frac{1}{2}}, \\ b_0/a_0 &= \alpha Z / (\rho + \chi). \end{aligned} \tag{40}$$

Since the smallest possible value of j is $\frac{1}{2}$ one sees from (36) that

$$\chi^2 \geq 1. \tag{42}$$

Hence, if $\alpha Z > 1$, at least for $j = \frac{1}{2}$ the two possible solutions (40) are equally good. In fact, from (37) one sees that both solutions of (35) are quadratically integrable in this case.

For convenience, limiting ourselves to real solutions when $(\alpha Z)^2 > \chi^2$ one sees that the general solution of (35) can be written as:

$$\begin{pmatrix} u \\ w \end{pmatrix} \approx C \begin{pmatrix} \cos(\lambda \ln r + B) \\ a \cos(\lambda \ln r + B + \gamma) \end{pmatrix} \quad \text{for } r \text{ small} \tag{43}$$

⁶ H. A. Bethe, *Handbuch der Physik* XXIV, 1, p. 313 (1933).

where

$$\begin{aligned} \lambda &= +[\alpha^2 Z^2 - \chi^2]^{\frac{1}{2}}, \\ (\chi - i\lambda) / \alpha Z &= ae^{i\gamma}, \end{aligned} \tag{44}$$

and C and B are two unknown constants.

Consider Eqs. (35) corresponding to two different energies E_1 and E_2 . These are:

$$\frac{du_1}{dr} - \chi \frac{u_1}{r} = \left(1 - E_1 - \frac{\alpha Z}{r}\right)w_1, \tag{45a}$$

$$\frac{dw_1}{dr} + \chi \frac{w_1}{r} = \left(1 + E_1 + \frac{\alpha Z}{r}\right)u_1, \tag{45b}$$

$$\frac{du_2}{dr} - \chi \frac{u_2}{r} = \left(1 - E_2 - \frac{\alpha Z}{r}\right)w_2, \tag{46a}$$

$$\frac{dw_2}{dr} + \chi \frac{w_2}{r} = \left(1 + E_2 + \frac{\alpha Z}{r}\right)u_2. \tag{46b}$$

Multiplying (45a) by w_2 , (46a) by w_1 , (45b) by $(-u_2)$, (46b) by $(-u_1)$, adding and integrating yields:

$$(E_1 - E_2) \int_0^\infty (u_2 u_1 + w_2 w_1) dr = [u_2 w_1 - u_1 w_2]_0^\infty. \tag{47}$$

Suppose the solutions 1 and 2 are adjusted to vanish exponentially at infinity. Inserting the asymptotic behavior (43) into (47) yields:

$$\begin{aligned} (E_1 - E_2) \int_0^\infty (u_2 u_1 + w_2 w_1) dr \\ = a C_1 C_2 \sin(B_1 - B_2) \sin \gamma, \end{aligned} \tag{48}$$

where the B_i, C_i are the constants describing the respective solutions. From (48) one sees that if all

$$B_i = B, \tag{49}$$

where B is a fixed constant all eigensolutions will be orthogonal. It is also possible to prove completeness in this case.

To solve this eigenvalue problem we make the substitution given by Bethe:⁶

$$\begin{aligned} u &= (1 - E)^{\frac{1}{2}} e^{-\rho/2} (\varphi - \psi), \\ w &= (1 + E)^{\frac{1}{2}} e^{-\rho/2} (\varphi + \psi), \\ \rho &= 2(1 - E^2)^{\frac{1}{2}} r, \end{aligned} \tag{50}$$

one finds:

$$\begin{aligned} d\varphi/d\rho &= [1 - (E\delta/\rho)]\varphi - (\chi + \delta)\psi/\rho, \\ d\psi/d\rho &= (E\delta/\rho)\psi - (\chi - \delta)\varphi/\rho, \end{aligned} \tag{51}$$

where

$$\delta = \alpha Z / (1 - E^2)^{\frac{1}{2}}. \tag{52}$$

Elimination of φ from (51) gives:

$$\frac{d^2\psi}{d\rho^2} + \left(\frac{1}{\rho} - 1\right) \frac{d\psi}{d\rho} + \left(\frac{E\delta}{\rho} + \frac{\alpha^2 Z^2 - \chi^2}{\rho^2}\right) \psi = 0. \tag{53}$$

Let

$$\psi = [e^{\rho/2} \rho^{-\frac{1}{2}}] w. \quad (54)$$

Then:

$$\frac{d^2 w}{d\rho^2} + \left(-\frac{1}{4} + \frac{k}{\rho} + \frac{\frac{1}{4} - m^2}{\rho^2} \right) w = 0, \quad (55)$$

where

$$k = E\delta + \frac{1}{2}; \quad m = +i\lambda. \quad (56)$$

(55) is just the canonical form of the confluent hypergeometric equation.⁷ Two linearly independent solutions are: $M_{k, \pm m}(\rho)$. For small r the corresponding φ and ψ are:

$$\begin{aligned} \psi &\sim \rho^{\pm m}, \\ \varphi &\sim \pm [(m - E\delta)/(\delta - \chi)] \rho^{\pm m}, \end{aligned} \quad (57)$$

which gives

$$u \sim (\text{constant}) \left[\pm \frac{m - E\delta}{\delta - \chi} - 1 \right] \rho^{\pm m}. \quad (58)$$

Let

$$w = e^{i\alpha} M_{k, +m}(\rho) + e^{-i\alpha} M_{k, -m}(\rho). \quad (59)$$

Then if

$$\Pi e^{i\theta} = \frac{i\lambda - E\delta}{\delta - \chi} - 1, \quad (60)$$

one finds for small r :

$$u \approx 2 \cos[\lambda \ln r + \alpha + \theta + \lambda \ln 2(1 - E^2)^{\frac{1}{2}}]. \quad (61)$$

Comparing with (43) we see:

$$\alpha = B - \theta - \lambda \ln 2(1 - E^2)^{\frac{1}{2}}. \quad (62)$$

With this solution:

$$\psi = \rho^{-\frac{1}{2}} e^{\rho/2} [e^{i\alpha} M_{k, m}(\rho) + e^{-i\alpha} M_{k, -m}(\rho)]. \quad (63)$$

The condition of exponential decrease at infinity yields:

$$e^{i\alpha} \frac{\Gamma(2m+1)}{\Gamma(\frac{1}{2} + m - k)} + e^{-i\alpha} \frac{\Gamma(-2m+1)}{\Gamma(\frac{1}{2} - m - k)} = 0. \quad (64)$$

Let

$$\frac{\Gamma(2m+1)}{\Gamma(\frac{1}{2} + m - k)} = b e^{i\sigma}. \quad (65)$$

Then condition (64) is:

$$b \cos(\alpha + \sigma) = 0, \quad (66)$$

or

$$\alpha + \sigma = (n + \frac{1}{2})\pi, \quad (67)$$

where n is a positive or negative integer. Using (62) and (60) one has with

$$B' = B - \lambda \ln 2 - \arg[\Gamma(2i\lambda + 1)] - \pi/2, \quad (68)$$

$$\frac{B' - n\pi}{\lambda} - \frac{1}{\lambda} \tan^{-1} \frac{\lambda}{\chi - \delta(1 + E)}$$

$$- \frac{1}{\lambda} \arg \left[\Gamma \left(\frac{-E\alpha Z}{(1 - E^2)^{\frac{1}{2}}} + i\lambda \right) \right] = \ln(1 - E^2)^{\frac{1}{2}}. \quad (69)$$

Let us consider this equation for small λ . The right-hand side as a function of E goes from $-\infty$ at $E = -1$ to 0 at $E = 0$ to $-\infty$ at $E = +1$.

$$\frac{B' - n\pi}{\lambda} \text{ is constant. } \frac{1}{\lambda} \arg \left[\Gamma \left(\frac{-E\alpha Z}{(1 - E^2)^{\frac{1}{2}}} + i\lambda \right) \right]$$

suffers jumps of $-\pi/\lambda$ at the poles of the Γ function; i.e., at

$$-E\alpha Z / (1 - E^2)^{\frac{1}{2}} = n', \quad (70)$$

where $n' = 0$ or a positive integer. $\tan^{-1}[\lambda/(\chi - \delta(1 + E))]$ is approximately constant if $\chi = -|\chi|$. If $\chi = +|\chi|$ this quantity suffers a jump of $+\pi$ if E passes from -0 to $+0$. Hence, if λ is small the discrete spectrum consists of levels near $-E\alpha Z / (1 - E^2)^{\frac{1}{2}} = n'$ where $n' = 1, 2, 3, \dots$ if $\chi = +|\chi|$ and $n' = 0, 1, 2, 3, \dots$ if $\chi = -|\chi|$. Comparison⁶ with the conventional results for $\alpha Z < 1$ but αZ near 1 shows that the levels found for $\alpha Z < 1$ go over into ones close by.

Of particular interest is the behavior of the lowest energy level. As $\alpha Z \rightarrow 1$ from below the lowest Dirac level tends to $E = 0$. What happens for αZ slightly larger? For the case λ is small it is possible to solve (69) for the energy level near zero. One finds:

$$E_0 = \lambda / \tan B'. \quad (71)$$

Thus, if B' is chosen between zero and $\pi/2$ the energy level is positive, while it is negative if $\frac{1}{2}\pi < B' < \pi$. The difficulties of interpretation would be so great if the lowest level passed from positive to negative values as αZ passes through 1 that one is inclined to require that B' lie in the first-named range. Then we have the following picture of the behavior of the levels as Z increases. Approaching 137 all the ordinary levels go to well-defined limiting values, the lowest going to zero. Increasing Z further, all except the lowest of these levels move to nearby positions. The lowest level starts up again from zero. One interesting point to be gleaned from (69) is that the famous degeneracy of the Dirac equation is removed for $Z > 137$. Here the energies of levels for $\chi = |\chi|$ and $\chi = -|\chi|$ are slightly different.

VI. SPIN ZERO AND ONE

For integral spin particles a certain amount of care must be used in formulating the problems. An appropriate "particle form" of the equations must be used. The following equations for integral spin particles given by several authors⁸ are most convenient for our purposes (again units of $\hbar = c = m = 1$ are chosen):

$$i(\partial\psi/\partial t) = \mathcal{H}\psi, \quad (72a)$$

$$\begin{aligned} \mathcal{H} &= eV + \tau_3 [1 + \frac{1}{2}P^2 - \frac{1}{2}e\mathbf{S} \cdot \mathbf{H}] \\ &\quad - i\tau_2 [\frac{1}{2}P^2 - (\mathbf{S} \cdot \mathbf{P})^2 - \frac{1}{2}e\mathbf{S} \cdot \mathbf{H}]. \end{aligned} \quad (72b)$$

⁷ E. T. Whittaker and G. N. Watson, *Modern Analysis* (MacMillan Company, 1943), American Edition, p. 337.

⁸ Sakata and Taketani, Proc. Math. Phys. Soc. Japan 22, 757 (1940); I. Tamm, Comptes Rendus U.S.S.R. 29, 551 (1940); W. Heitler, Proc. Roy. Irish Academy 49, 1 (1943).

(72) is the "Schrödinger equation" for integral spin. Here V is the external electrostatic potential; H is any external magnetic field; τ_1, τ_2, τ_3 are three Pauli spin matrices; and S_1, S_2, S_3 are the matrices describing the infinitesimal rotations in an irreducible representation of the rotation group. Thus, for spin zero the S_i are zero and ψ has two components. For spin one the S_i are 3×3 matrices and ψ has six components. The energy of a state described by a given ψ is:

$$W = \int \psi^* \tau_3 \mathcal{H} \psi d\tau, \quad (73)$$

and the charge is:

$$Q = e \int \psi^* \tau_3 \psi d\tau. \quad (74)$$

One notes that \mathcal{H} is not hermitean and hence the eigenvalues of (73) are not necessarily real. Of course $\tau_3 \mathcal{H}$ is hermitean, and so the energy is real. Mathematically speaking, the eigenvalue problem is defined by the non-hermitean operator \mathcal{H} and an indefinite metric suggested by (74). This defines the scalar product between two states ψ_1 and ψ_2 as:

$$(\psi_2, \psi_1) = \int \psi_2^* \tau_3 \psi_1 dV. \quad (75)$$

Specializing to the Coulomb field of a nucleus of charge Z and no magnetic field gives for the "Hamiltonian"

$$\mathcal{H} = -(\alpha Z/r) + \tau_3(1 + \frac{1}{2}P^2) - i\tau_2[\frac{1}{2}P^2 - \frac{1}{2}(\mathbf{S} \cdot \mathbf{P})^2]. \quad (76)$$

Consider the scalar theory. Let

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} e^{-iEt}. \quad (77)$$

Inserting into (72) gives:

$$\begin{aligned} (E + \alpha Z/r)\psi_1 &= \psi_1 - \frac{1}{2}\Delta\psi_1 + \frac{1}{2}\Delta\psi_2, \\ (E + \alpha Z/r)\psi_2 &= -\psi_2 + \frac{1}{2}\Delta\psi_2 - \frac{1}{2}\Delta\psi_1. \end{aligned} \quad (78)$$

Let

$$\varphi = (i/\sqrt{2})(\psi_1 - \psi_2). \quad (79)$$

Then

$$\Delta\varphi - \varphi + (E + \alpha Z/r)^2\varphi = 0. \quad (80)$$

This is just the Klein-Gordon equation, as was to be expected.

Separating out the angular dependence and setting

$$\varphi = u/r, \quad (81)$$

gives the radial wave equation:

$$\frac{d^2u}{dr^2} + \left[-(1-E^2) + \frac{2E\alpha Z}{r} + \frac{\alpha^2 Z^2 - l(l+1)}{r^2} \right] u = 0. \quad (82)$$

Before solving (82) let us consider the behavior of u for small r and the orthogonality relations. Setting

$$u \approx r^\gamma [1 + a_1 r + \dots], \quad (83)$$

gives for the indicial equation of (82)

$$\gamma(\gamma-1) + \frac{1}{4} - m^2 = 0, \quad (84)$$

or

$$\gamma = \frac{1}{2} \pm m, \quad (85)$$

where

$$m = [(l + \frac{1}{2})^2 - \alpha^2 Z^2]^{\frac{1}{2}}. \quad (86)$$

If $\alpha^2 Z^2 > (l + \frac{1}{2})^2$ both solutions of (85) have essentially the same behavior near the origin. In case $\alpha Z > \frac{1}{2}$ this certainly occurs at least for S states. Let us then assume

$$m = i\lambda, \quad (87)$$

where λ is real. Then the most general u for small r is:

$$u \sim Cr^{\frac{1}{2}} \cos(\lambda \ln r + B). \quad (88)$$

Let

$$r\psi_1 = v, \quad r\psi_2 = w. \quad (89)$$

Consider (78) for two different energies E_1 and E_2 . The equations for v and w are:

$$\begin{aligned} E_1 v_1 &= -\frac{\alpha Z}{r} v_1 - \frac{1}{2} v_1'' + \frac{l(l+1)}{2r^2} v_1 \\ &\quad + v_1 + \frac{1}{2} w_1'' - \frac{l(l+1)}{2r^2} w_1, \end{aligned} \quad (90a)$$

$$\begin{aligned} E_1 w_1 &= -\frac{\alpha Z}{r} w_1 + \frac{1}{2} w_1'' - \frac{l(l+1)}{2r^2} w_1 \\ &\quad - w_1 - \frac{1}{2} v_1'' + \frac{l(l+1)}{2r^2} v_1, \end{aligned} \quad (90b)$$

$$\begin{aligned} E_2 v_2 &= -\frac{\alpha Z}{r} v_2 - \frac{1}{2} v_2'' + \frac{l(l+1)}{2r^2} v_2 \\ &\quad + v_2 + \frac{1}{2} w_2'' - \frac{l(l+1)}{2r^2} w_2, \end{aligned} \quad (90c)$$

$$\begin{aligned} E_2 w_2 &= -\frac{\alpha Z}{r} w_2 + \frac{1}{2} w_2'' - \frac{l(l+1)}{2r^2} w_2 \\ &\quad - w_2 - \frac{1}{2} v_2'' + \frac{l(l+1)}{2r^2} v_2. \end{aligned} \quad (90d)$$

Multiplying (90a) by v_2 , (90b) by w_2 , (90c) by $(-v_1)$, (90d) by $(-w_1)$, adding and integrating yields:

$$\begin{aligned} (E_1 - E_2) \int_0^\infty (v_2 v_1 - w_2 w_1) dr \\ = \frac{1}{2} [(w_2' - v_2')(w_1 - v_1) - (w_2 - v_2)(w_1' - v_1')]_0^\infty. \end{aligned} \quad (91)$$

The integral on the left-hand side is just the scalar product (75) after integration over angular coordinates. Noting that

$$w - v = \sqrt{2}iu, \quad (92)$$

and requiring u_1 and u_2 to vanish exponentially sim-

plifies (91) to:

$$(E_1 - E_2) \int_0^\infty (v_2 v_1 - w_2 w_1) dr = (w_2' u_1 - u_1' w_2)_0. \quad (93)$$

From (88) one sees that:

$$\begin{aligned} u_1 &\sim C_1 r^{\frac{1}{2}} \cos(\lambda \ln r + B_1), \\ u_2 &\sim C_2 r^{\frac{1}{2}} \cos(\lambda \ln r + B_2). \end{aligned} \quad (94)$$

Inserting into (93):

$$(E_1 - E_2) \int_0^\infty (v_2 v_1 - w_2 w_1) dr = \lambda C_1 C_2 \sin(B_1 - B_2). \quad (95)$$

Hence, again we see that orthogonality is obtained if all eigenfunctions are required to be of the form (88) for small r . Now B is to be considered as a fixed constant, the same for all solutions, describing the Coulomb potential.

With this condition (82) can be solved. Let

$$\rho = 2(1 - E^2)^{\frac{1}{2}} r. \quad (96)$$

Then:

$$\frac{d^2 u}{d\rho^2} + \left[-\frac{1}{4} + \frac{k}{\rho} + \frac{\frac{1}{4} - m^2}{\rho^2} \right] u = 0, \quad (97)$$

where

$$k = E\alpha Z / (1 - E^2)^{\frac{1}{2}}. \quad (98)$$

Two linearly independent solutions are again $M_{k, \pm m}(\rho)$. Let

$$u = e^{i\alpha} M_{km}(\rho) + e^{-i\alpha} M_{k, -m}(\rho). \quad (99)$$

The condition for small r gives:

$$\alpha = B - \lambda \ln 2(1 - E^2)^{\frac{1}{2}}. \quad (100)$$

Let

$$\sigma = \text{arg}[\Gamma(2m+1)/\Gamma(\frac{1}{2} + m - k)]. \quad (101)$$

The condition of exponential decrease at infinity yields:

$$\cos(\alpha + \sigma) = 0, \quad (102a)$$

or

$$\alpha + \sigma = (n + \frac{1}{2})\pi. \quad (102b)$$

If

$$B' = B - \lambda \ln 2 + \text{arg}[\Gamma(1 + 2i\lambda)] - \frac{1}{2}\pi, \quad (103)$$

the eigenvalues of the energy are given by the equation

$$\frac{B' - n\pi}{\lambda} - \frac{1}{\lambda} \text{arg} \left[\Gamma \left(\frac{1}{2} - \frac{E\alpha Z}{(1 - E^2)^{\frac{1}{2}}} + i(\alpha^2 Z^2 - (l + \frac{1}{2})^2)^{\frac{1}{2}} \right) \right] = \ln(1 - E^2)^{\frac{1}{2}}. \quad (104)$$

This is seen to be quite similar to Eq. (69) for the eigenvalues of the Dirac equation. The same arguments apply. Hence, for small λ (i.e., $\alpha Z \sim l + \frac{1}{2}$) the spectrum consists of a set which occurs approximately at the poles of the Γ -function. For $\alpha Z < l + \frac{1}{2}$ these poles are just the energy eigenvalues. Thus, considering S states only, as αZ passes through $\frac{1}{2}$ the spectrum changes continuously. The situation is slightly different from that

of the Dirac equation for low-lying states. The lowest Klein-Gordon level tends to $mc^2/\sqrt{2}$ as $\alpha Z \rightarrow \frac{1}{2}$ from below. Therefore, no such paradoxical result as having an energy level change sign can occur.

These considerations are slightly less academic for spin zero than for spin $\frac{1}{2}$, since nuclei with charge greater than $137/2$ do exist. Moreover, spin zero particles (π mesons?) may even be bound to such nuclei. However, since π mesons are quite heavy the corresponding orbits will be within or very close to the nucleus. The approximation of regarding all protons as lumped at the origin is then so crude as to make the above considerations more than questionable.

For a unit spin particle in a central Coulomb field we follow the treatment of Gunn⁹ in separating out the radial and angular portions of (72). For $l=j$ and $j=0$, one obtains the radial Klein-Gordon equation appropriate to the given angular momentum. Here nothing new arises and so we skip these cases. For $l \neq j \neq 0$ the radial equations arising from (72) can be expressed in terms of four functions (F_1, F_2, G_1, G_2). Then with

$$v = (E + \alpha Z/r) / [j(j+1)]^{\frac{1}{2}}, \quad (105)$$

the radial wave equations given by Gunn⁹ are (with a few minor changes in notation and units):

$$vF_1 - \frac{F_2}{j(j+1)} = \frac{1}{r} \left[\frac{dG_2}{dr} + \frac{F_2}{r} \right], \quad (106a)$$

$$vG_1 - G_2 = -\frac{d^2 G_2}{dr^2} - \frac{1}{r} \left[\frac{d}{dr} + \frac{1}{r} \right] F_2, \quad (106b)$$

$$vG_2 - \frac{G_1}{j(j+1)} = \frac{G_1}{r^2} + \frac{1}{r} \left[\frac{d}{dr} + \frac{1}{r} \right] F_1, \quad (106c)$$

$$vF_2 - F_1 = -\left(\frac{d^2}{dr^2} - \frac{2}{r^2} \right) F_1 - \frac{1}{r} \left(\frac{d}{dr} - \frac{2}{r} \right) G_1. \quad (106d)$$

Solving for F_2 and G_1 one finds:

$$F_2 = (r^2 v F_1 - r G_2') / [1 + r^2 / j(j+1)], \quad (107a)$$

$$G_1 = (r^2 v G_2 - (r F_1' + F_1)) / [1 + r^2 / j(j+1)]. \quad (107b)$$

Let

$$G = (G_2 + F_1) / \sqrt{2}; \quad F = (G_2 - F_1) / \sqrt{2}. \quad (108)$$

Then the resulting equations for F and G can be written as:

$$\begin{aligned} \frac{d^2 G}{dr^2} + \frac{2}{r} \frac{j(j+1)}{j(j+1) + r^2} \frac{dG}{dr} \\ + \left[j(j+1) \left(v^2 - \frac{1}{r^2} \right) - 1 - \frac{1}{j(j+1) + r^2} \right. \\ \left. + \frac{j(j+1)v'}{r} - \frac{2vj(j+1)}{j(j+1) + r^2} \right] G + \frac{F}{j(j+1) + r^2} = 0, \end{aligned} \quad (109)$$

⁹ J. C. Gunn, Proc. Roy. Soc. 193, 559 (1946).

$$\frac{d^2F}{dr^2} + \frac{2}{r} \frac{j(j+1)}{j(j+1)+r^2} \frac{dG}{dr} + \left[j(j+1) \left(v^2 - \frac{1}{r^2} \right) - 1 - \frac{1}{j(j+1)+r^2} - \frac{j(j+1)v'}{r} + \frac{2vj(j+1)}{j(j+1)+r^2} \right] F + \frac{G}{j(j+1)+r^2} = 0. \quad (110)$$

The forms (109) and (110) are particularly useful for examining the behavior near the origin, since there the two equations are effectively decoupled, the coupling term being regular. The behavior of the four linearly independent solutions of (109) and (110) can then be determined by first setting $F=0$ in (109) and finding the two solutions of (110). Then treat (110) with $G=0$ similarly. As noted by earlier authors, these equations have an essential singularity at the origin. This, of course, prohibits a power series development. However, it is possible, as in (25), to split off an exponential factor¹⁰ and then to find a power series development. Doing this the four linearly independent solutions are, in the vicinity of the origin:

$$G = r^{-1} \exp(\pm i\lambda/r^{\frac{1}{2}}); \quad F = (\text{const.}) r^{-1} r^3 \exp(\pm \lambda/r^{\frac{1}{2}}), \quad (111a, b)$$

$$F = r^{-1} \exp(\pm i\lambda/r^{\frac{1}{2}}); \quad G = (\text{const.}) r^{-1} r^3 \exp(\pm i\lambda/r^{\frac{1}{2}}), \quad (112a, b)$$

where now

$$\lambda = 2(\alpha Z)^{\frac{1}{2}} [j(j+1)]^{\frac{1}{2}}. \quad (113)$$

Of these solutions (111a) is obviously unacceptable, since it has a horrible infinity at the origin. (111b) vanishes very strongly, and so is completely satisfactory. For (112) further investigation is necessary. Again, taking real solutions the general linear combination of (112) may be written

$$F \sim (\text{const.}) r^{-1} \cos(\lambda r^{-\frac{1}{2}} + B); \quad G = 0, \quad (114)$$

and then:

$$F_1 \cong -r^{-1} \cos(\lambda r^{-\frac{1}{2}} + B); \quad G_2 \sim r^{-1} \cos(\lambda r^{-\frac{1}{2}} + B),$$

$$F_2 \sim -r^{-1} \left\{ \left[-\frac{1}{4} + \frac{\alpha Z}{j(j+1)} r \right] \cos(\lambda r^{-\frac{1}{2}} + B) + \frac{\lambda}{2r^{\frac{1}{2}}} \sin(\lambda r^{-\frac{1}{2}} + B) \right\},$$

$$G_1 \approx r^{-1} \left\{ \left[\frac{3}{4} + \frac{\alpha Z}{(j(j+1))^{\frac{1}{2}}} r \right] \cos(\lambda r^{-\frac{1}{2}} + B) + \frac{\lambda}{2r^{\frac{1}{2}}} \sin(\lambda r^{-\frac{1}{2}} + B) \right\}. \quad (115)$$

Now:

$$\int \psi^* \tau_3 \psi dV \sim \int_0^\infty [F_1^* F_2 + F_2^* F_1 + G_1^* G_2 + G_2^* G_1] dr. \quad (116)$$

Inserting (115) into (116) one finds for the contribution near the origin:

$$\int \psi^* \tau_3 \psi dV \sim \int r^{-1} \cos^2(\lambda r^{-\frac{1}{2}} + B) dr. \quad (117)$$

This integral certainly exists and so the charge density is integrable for these solutions. Contrary to previous statements, this means that there are too *many* rather than too few solutions of (72) which are quadratically integrable near the origin. Instead of one, there are three physically acceptable solutions of (109) and (110). The resulting set of eigenfunctions is then *over* complete. The two solutions described by (114) are, of course, to be narrowed to one by requiring orthogonality. Consider equations (106) for two different energies E_a and E_b . Multiplying these equations by various functions, adding and integrating following the previous methods and using (106), one finds on integrating out angular coordinates:

$$(E_a - E_b) \int \psi_a^* \tau_3 \psi_b dV \sim \{ r(F_1^b G_1^a - F_1^a G_1^b) + r(G_2^b F_2^a - G_2^a F_2^b) \}_0^\infty. \quad (118)$$

Requiring an exponential decrease at infinity and assuming

$$F^a \sim r^{-1} \cos(\lambda r^{-\frac{1}{2}} + B_a), \quad F^b \sim r^{-1} \cos(\lambda r^{-\frac{1}{2}} + B_b), \quad (119)$$

gives:

$$(E_a - E_b) \int \psi_a^* \tau_3 \psi_b dV \sim -\lambda \sin(B_a - B_b). \quad (120)$$

Once again one sees that requiring all solutions to behave like (114) with a *fixed* B gives orthogonality. With this condition the eigenfunctions of the vector meson in a Coulomb field do form a complete set, in contradiction to previous communications on the subject. Of course, the actual computation of these functions, except possibly by machine, gives rise, as pointed out by Bartlett,¹⁰ to great difficulties.

There is, however, one possible experimental verification which would not rest on tedious calculations. The π meson may have unit spin. Then even for hydrogen the introduction of a phase constant would be necessary. It can be shown then that resonances should occur in scattering. Thus, if a beam of low energy mesons were incident on a hydrogen target one would expect maxima

¹⁰ J. H. Bartlett, Phys. Rev. **72**, 219 (1947).

and minima in the cross section as the energy of the beam varies.

With the information now at hand, it is possible to say something concerning the common conjecture that as Z increases over 137 for the Dirac particles (or over 137/2 for Klein-Gordon particles) pairs will be produced. This is, properly speaking, a many-particle process and so certainly not to be encompassed by the present single particle theory results. However, since it is found that nothing spectacular happens to the energy levels at these transition points, it is difficult to see why pairs should suddenly occur. Consider a state with certain levels filled, others empty. As Z is adiabatically increased, one would expect the particles in a given state to continue in this state as the state is slowly altered. If this happens, one sees that nothing of importance occurs at the transition points.

VII. MATHEMATICAL BASIS

In the preceding work a number of examples of singular potentials have been considered. The structures of the various problems have been rather different, and yet the same method has always worked. At each step the success seemed to be a minor miracle. Here the underlying reason that the method works and a general proof of its applicability will be given.

Two characteristics have been true of all the above problems. (1) The linearly independent solutions of the differential equations are distinguishable by a phase constant B . (2) By requiring all eigenfunctions to approach the origin with the same B , orthogonality is achieved.

In words, the general proof runs as follows: Let the potential go to infinity sufficiently rapidly (defined more precisely below) so that V is uniformly large for small r . Then the behavior of the solutions of the differential equations near the origin are determined by the potential alone; i.e., for r small all the equations approach some standard equation, say that corresponding to $E=0$. Under these conditions, Sturm's oscillation theorem shows the behavior of solutions of the standard equation to be oscillatory and hence describable by a phase constant. Requiring all eigenfunctions to have this same phase constant means that these functions are *all* to approach the same solution of the standard equation. Two solutions of the standard equation have constant Wronskian. In particular, for linearly dependent solutions, this constant is zero. Since two different eigenfunctions approach the same solution, the Wronskian of these eigenfunctions tends to zero for small r . This last is just the orthogonality condition.

For purposes of simplicity we restrict ourselves to the non-relativistic case in carrying out the proof. The generalization will then be evident and so merely sketched.

Consider the Schrödinger equation (2) in the slightly altered form:

$$d^2u/dx^2 + [f(x) - \eta^2]u = 0. \quad (121)$$

Let $f(x)$ go to $+\infty$ uniformly for x sufficiently small. Then for x small (121) approaches the equation:

$$d^2u_0/dx^2 + [f(x)]u_0 = 0. \quad (122)$$

The asymptotic integration for x small is obtained by what is essentially the WKB method.

Let

$$u_0 = e^{iS}. \quad (123)$$

Then

$$(S')^2 - iS'' = f(x). \quad (124)$$

If

$$|S''| \ll S'^2, \quad (125)$$

one has approximately:

$$(S')^2 = f(x), \quad (126)$$

or

$$S = \pm \int_x^{x_0} (f(x))^{1/2} dx, \quad (127)$$

where x_0 is some constant. The condition of validity (125) gives:

$$f(x) \gg |\frac{1}{2}f^{-1/2}f'|, \quad (128)$$

or since f' is negative, $f(x)$ positive,

$$f(x) \gg -f'/2f^{1/2}. \quad (129)$$

On integration

$$f(x) \gg 1/x^2, \quad x \text{ small.} \quad (130)$$

Equation (130) is our definition of "sufficiently singular." As a second approximation under the conditions (130) one finds:

$$S = \pm \int_x^{x_0} (f(x))^{1/2} dx + \frac{1}{4}i \ln f(x). \quad (131)$$

Combining the two solutions for u_0 into real solutions one finds:

$$u_0 \cong f(x)^{-1/4} \cos \left[\int_x^{x_0} (f(x))^{1/2} dx + B \right] \quad (132)$$

where B is an arbitrary constant. Consider two solutions of (122), u_0^a and u_0^b , with constants B_a and B_b . Then:

$$W(u_0^a, u_0^b) = u_0^a u_0^{b'} - u_0^b u_0^{a'} = \sin(B_b - B_a). \quad (133)$$

Let us integrate (121) by assuming:

$$u = \varphi(x)u_0, \quad (134)$$

where u_0 is a solution of (122). Then (121) becomes:

$$\varphi' = \frac{1}{2}(\eta^2 \varphi - \varphi'')u_0/u_0'. \quad (135)$$

But

$$|u_0/u_0'| \sim 1/(f(x))^{1/4} \ll 1 \text{ by (127).}$$

Hence,

$$\varphi' \approx 0. \quad (136)$$

Improving the approximation by taking into account the first term on the right-hand side of (135) we find:

$$\varphi \approx \exp\left[\frac{\eta^2}{2} \int_0^x \frac{u_0}{u_0'} dx\right]. \quad (137)$$

Consider solutions of (121) corresponding to two different energies η^a, η^b . Then:

$$\begin{aligned} u^a &\sim \left[\exp\left(\frac{\eta_a^2}{2} \int_0^x \frac{u_0^a}{u_0^{a'}} dx\right) \right] u_0^a, \\ u^b &\sim \left[\exp\left(\frac{\eta_b^2}{2} \int_0^x \frac{u_0^b}{u_0^{b'}} dx\right) \right] u_0^b. \end{aligned} \quad (138)$$

Familiar operations on the Eqs. (121) give:

$$[(\eta^b)^2 - (\eta^a)^2] \int_0^\infty u_b u_a dx = W(u_a, u_b)|_0. \quad (139)$$

But from (138):

$$\begin{aligned} W(u_a, u_b) &\sim \exp\left[\frac{\eta_a^2}{2} \int_0^x \frac{u_0^a}{(u_0^a)'} dx + \frac{\eta_b^2}{2} \int_0^x \frac{u_0^b}{(u_0^b)'} dx\right] \\ &\times \left\{ W(u_0^a, u_0^b) + u_0^a u_0^b \left[\frac{u_0^b}{u_0^{b'}} - \frac{u_0^a}{u_0^{a'}} \right] \right\} \end{aligned} \quad (140)$$

$$\rightarrow W(u_0^a, u_0^b) = \sin(B_b - B_a). \quad (141)$$

Hence, if u_a and u_b are required to approach the same solution of (122), orthogonality results.

The generalization to the more complicated relativistic equations is evident. For small r , solutions will tend to those of a standard equation whose behavior is completely determined by the singularity. In all such equations an identity exists between two solutions for different energies of the form:

$$(E_1 - E_2)(\psi_1, \psi_2) = dW_G(\psi_1, \psi_2)/dr, \quad (142)$$

where (ψ_1, ψ_2) is an appropriately defined scalar product

density, and W_G is a function generalizing the ordinary Wronskian which vanishes for $\psi_1 = \psi_2$. Now $E_1 = E_2$ for two solutions of the standard equation. Hence, $W_G = \text{constant}$ for this case. Integrating (142) shows the integrated scalar product is proportional to $W_G|_0$. Since W_G , for small r , tends to that for solutions of the standard equation, it is constant sufficiently near the origin. In particular, if all eigenfunctions are required to tend to a *unique* solution of the standard equation, this constant is zero. Hence, the eigenfunctions will form an orthonormal set.

VIII. CONCLUSIONS

The above discussion gives a method for solving eigenvalue problems with a potential which tends to infinity very strongly at one end of an interval. It can be shown that the method is applicable to the $1/r^3$ tensor force problem, but with the attendant non-relativistic difficulties. However, one can prove that the relativistic equation from which the $1/r^3$ arises as an approximation gives no difficulties no matter how large the coupling constants are.

On the mathematical side the following can be said. In quantum mechanics we are interested in operators having complete orthonormal sets of eigenfunctions. Usually this requirement is taken to be hermiticity. Von Neumann¹¹ has shown that the condition is really that it be possible to construct a unitary operator generated by the hermitian operator. Here we have found that by formally supplementing the definition of an operator it is possible to obtain an hermitian operator with a complete set of eigenfunctions. It would be useful to have simple criteria for when this is necessary and when it is possible.

In conclusion I should like to thank Professor W. Pauli for several very instructive discussions, Professor J. Von Neumann for permission to use his unpublished results, and Professor J. R. Oppenheimer for suggestions and the kind hospitality of the Institute.

¹¹ W. Pauli, *Handbuch der Physik* XXIV, 1, p. 142 (1933).