The Helium Wave Equation

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This paper is a sequel to the preceding one by Gronwall. In Part I it is shown that the ground state eigenfunction, if it exists, cannot have the form $\psi = \sum_{p,\,k=0}^{\infty} s^{p+\gamma} a^{p,\,k}(\beta) \cos k\varphi$, where $s = r^{\frac{1}{2}} = (r_1^2 + r_2^2)^{\frac{1}{2}}$, and γ is some constant. In Part II, it is assumed that the solution of Gronwall's infinite system of ordinary differential equations (see preceding abstract) is to be found by extrapolation from a finite system. Arguments are given to show that if the wave function is finite everywhere except at the origin, then the expansion about the origin is of the form $\psi = \sum_{k=0}^{\infty} c^{(k)}(s, \beta, \varphi)(\log s)^k$, where the $c^{(k)}$'s are ascending power series in s.

RESEARCHES on hyperfine structure and on isotope shift by the writer[1] and his co-workers have demonstrated that extremely good wave functions are required for significant quantitative results. The chief bar to the finding of accurate solutions of the wave equation is its nonseparability. This has not prevented, however, the construction of a serviceable atomic model, and this is due to the predominant influence of the nucleus. In particular, isotope shifts are very small. Inside the nucleus the situation is quite different, according to our present ideas, for the elementary particles all have approximately equal masses, and the nonseparable terms responsible for "isotope shift" are not at all negligible. It is, therefore, of considerable importance for the development of a satisfactory theory of the nucleus that one study these nonseparable wave equations.

The equation which has received most attention so far has been the helium wave equation, since there are but three particles involved. The mathematical theory of partial differential equations with singularities, of which this is one, is as yet undeveloped, so that we cannot even say whether or not quadratically integrable solutions exist. (The present paper is devoted to this question, and we shall give arguments to show why a large class of quadratically integrable functions cannot be solutions of the helium wave equation.) So far, physicists have assumed that the Schrödinger wave equation is soluble in general. The procedure has then been to guess at the form of an approximating function, and to apply the modified Ritz variational method. This furnishes us with an upper bound to the lowest eigenvalue. Hylleraas[2] has made extensive calculations to determine this upper bound for the ground state of helium, and has shown that the least upper bound attainable with his form of function agrees very closely with the experimentally determined eigenvalue. Nevertheless, this is not completely conclusive by itself. One must be able to find lower bounds, and to show that the approximating functions converge to a solution of the wave equation.

Suppose that φ is an approximating function, and denote $(H\varphi)/\varphi$ by ϵ. If we take the weighted average over configuration space, we have

$$\epsilon_a = \int \varphi^2 (H\varphi/\varphi) d\tau = \int \varphi H \varphi d\tau.$$

The mean square deviation is

$$[(\epsilon - (\epsilon)_a)^2]_a = (\epsilon^2)_a - (\epsilon^2)_a, \quad \text{where} \quad (\epsilon^2)_a = \int \varphi^2 (H\varphi/\varphi)^2 d\tau = \int (H\varphi)^2 d\tau.$$

[1] See, for example, Bartlett and Gibbons, Phys. Rev. **44**, 538 (1933), and Bartlett, Gibbons and Watson, Phys. Rev. **50**, 315 (1936).
[2] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929); **65**, 209 (1930).

We have calculated[5] the root-mean-square deviation of ϵ for the six-term wave function of Hylleraas and found it to be 3.5 electron volts. It is our opinion that this is a large deviation, although it might be argued[3] that the difference between the approximating function and the exact wave function might be small but yet have large second derivatives, so that this difference would be oscillatory over a considerable portion of space.

Weinstein[4] has suggested a method[5] for obtaining lower bounds. According to this, the lower bound is $\epsilon_a - \{[(\epsilon-\epsilon_a)^2]_a\}^{\frac{1}{2}}$, so that the spread between upper and lower bounds for the helium ground state is 3.5 ev. Romberg[6] has developed an empirical method, which gives $-(\epsilon^2)_a^{\frac{1}{2}}$ as the "lower bound." The "lower bound" is then -1.45310, as compared with an upper bound of -1.45162, giving a spread of only 0.08 volt. Now we must have $(\epsilon^2)_a \geq \epsilon_a^2$, and hence if the "lower bounds" keep increasing steadily with improving wave functions, they will converge to the eigenvalue. So far, these "lower bounds" have increased for the helium ground state, but, in the absence of a convergence proof, there is no guarantee that they would continue to do so.

Even granting that a function φ had been found which made $[(\epsilon-\epsilon_a)^2]_a$ very small, which would mean that ϵ were close to a true eigenvalue over most of space, we still would not know how closely the function φ approximated the exact eigenfunction, and it is this information which we should like to have.

In this paper, we attempt to construct functions which will be valid solutions of the wave equation everywhere. As will be shown, great difficulties are encountered, one result being that the continuity assumptions usually made in perturbation theory cannot be true if the helium wave equation is to have a solution.

Since the work of Gronwall[7] is our starting-point, we shall assume that this paper is read in conjunction with his, and shall accordingly refer the reader to that paper for the definition of the symbols used.

The wave equation is

$$\psi_{ss}+(5/s)\psi_s+(4/s^2\sin^2\beta)\psi_{\varphi\varphi}+(4/s^2)(\psi_{\beta\beta}+2\cot 2\beta\psi_\beta)+[E+(4f/s)]\psi=0. \tag{1}$$

(One might suppose that it would be of advantage to convert this into an homogeneous integral equation by means of a Green's function. The problem is then to solve this integral equation, and this is the sticking point. The Fredholm method is impractical, but one might attempt the method of successive approximations. In order to use a Green's function such as $1/R$, one is (practically) forced to expand it in a Laplace series. The function ψ will then be in an expanded form, which we might just as well have assumed at the start. Again, the second approximation will usually be of the wrong functional type, especially if the first approximation is taken as a Hylleraas function. We have, therefore, avoided the integral equation method.)

Part I

Let us now try to find a solution of (1) of the form

$$\psi=\sum_{p=0}^{\infty}a^{(p)}s^{p+\gamma}, \quad a^{(p)}=a^p(\varphi,\beta). \tag{2}$$

[3] This possibility was pointed out to me by Professor Birkhoff, whom I wish to thank for friendly discussions of the equation.

[4] D. H. Weinstein, Phys. Rev. **40**, 737 (1932); **41**, 839 (1932); Proc. Nat. Acad. Sci. **20**, 529 (1934).

[5] Bartlett, Gibbons and Dunn, Phys. Rev. **47**, 679 (1935). In this paper, we said that the methods of Weinstein (reference 4) and MacDonald seemed "difficult to justify rigorously." Since then we have had a lengthy correspondence with Dr. Weinstein, from which it developed that the argument depends essentially on the validity of the inequality $\int[(H-V)\xi]^2d\tau \geq (W_i-V)^2$, (see Nat. Acad. paper, p. 530, Eq. (4)). This we have not been able to deduce without assuming expansibility in terms of orthogonal functions.

[6] W. Romberg, Physik. Zeits. Sowjetunion **8**, 516 (1935); **9**, 546 (1936).

[7] T. H. Gronwall, Phys. Rev. **51**, 655 (1937). We shall refer to this as "G."

Formal solutions of this type would be expected to exist, because the above equation involves s in the manner of the ordinary confluent hypergeometric equation. If then, we substitute the series in the equation and compare coefficients of like powers of s, we find for the recursion formula

$$(p+\gamma+2)(p+\gamma+6)a^{p+2}+(4/\sin^2\beta)a^{p+2}{}_{\varphi\varphi}+4(a^{p+2}{}_{\beta\beta}+2\cot 2\beta a^{p+2}{}_{\beta})+Ea^p+4fa^{p+1}=0. \quad (3)$$

For $p=-2$,
$$\gamma(\gamma+4)a^0+(4/\sin^2\beta)a^0{}_{\varphi\varphi}+4(a^0{}_{\beta\beta}+2\cot 2\beta a^0{}_{\beta})=0.$$

Expand $a^0=\sum_{k=0}^{\infty}a^{0k}\cos k\varphi$, and write $a^{0k}=t^{k/2}v$. Then

$$t(1-t)v_{tt}+[k+1-(k+2)t]v_t+\left[\frac{\gamma(\gamma+4)}{16}-\frac{k}{2}-\frac{k^2}{4}\right]v=0. \quad (4)$$

This equation is similar to Eq. G(4). Exact correspondence may be achieved by making $\gamma=4m-2k$. The solution of the above equation is

$$F\left(\frac{k}{2}-\frac{\gamma}{4},\ \frac{k}{2}+\frac{\gamma}{4}+1,\ k+1,\ t\right).$$

This is of the form $F(a, b, c, t)$ with $c-a-b=0$, and we wish to know its behavior as $t\rightarrow 1$. Lindelof,[8] among others, has shown that in this case

$$F(a, b, c, t)=P(t)-[\Gamma(c)/\Gamma(a)\Gamma(b)]\log(1-t)$$

where P(1) is finite. A glance at G(9) shows that the variational integral will not exist unless the coefficient of $\log(1-t)$ is zero. This will only be so if either a or b is a negative integer or zero. We thus have two possibilities: (1), $(k/2)+(\gamma/4)+1=-n$, $(n=0, 1, 2\cdots)$, implying $\gamma=-4n-4-2k$; and (2), $(k/2)-(\gamma/4)=-n$, or $\gamma=2k+4n$. Now the exponent γ must be the same no matter what the magnitude of the term representing the electronic interaction. If this term were not present, the solution of the wave equation would be

$$\psi=e^{-(1/2)(r_1+r_2)}=e^{-\frac{1}{2}\{[2(r-y)]^{\frac{1}{2}}+[2(r+y)]^{\frac{1}{2}}\}}.$$

For this solution $\gamma=0$, so that $k=0$ and $n=0$. A second exponent $\gamma=-4$ is also possible for these values of n and k. The exponent difference is integral, so that the second solution would involve logarithms. It may be ruled out according to our general boundary condition (existence of the variational integral).

For $\gamma=0$, the solution is $a^0=a^{00}=F(0, 1, 1, t)=$const. We may therefore put $a^0=1$. Now set $p=-1$ in the recursion formula.

$$5a^1+(4/\sin^2\beta)a^1{}_{\varphi\varphi}+4(a^1{}_{\beta\beta}+2\cot 2\beta a^1{}_{\beta})+4fa^0=0. \quad (5)$$

This is an inhomogeneous equation for a^1. The homogeneous equation would correspond to (4) with $\gamma=1$, which is not an eigenvalue of (4). Consequently, any solution of (5) which satisfies the boundary condition will be unique.[9] Such a solution is

$$a^1=-(1/2)^{\frac{1}{2}}\{(1-\sin\varphi\sin\beta)^{\frac{1}{2}}+(1+\sin\varphi\sin\beta)^{\frac{1}{2}}\}+(1/2Z)(1-\cos\varphi\sin\beta)^{\frac{1}{2}}. \quad (6)$$

This reduces, when $Z\rightarrow\infty$, to the solution above for the separable case. If (6) be substituted in (5), then (5) is seen to be linear in $1/2Z$, so that one need only verify that the coefficient of $1/2Z$ vanishes. This is done in the Appendix.

[8] E. Lindelof, Acta. Soc. Scient. Fennicae **19**, 22 (1893).
[9] See Courant, *Methoden der Math. Physik*, edition I, p. 277.

The recursion formula with $p=0$ is

$$12a^2+(4/\sin^2\beta)a^2{}_{\varphi\varphi}+4(a^2{}_{\beta\beta}+2\cot 2\beta a^2{}_\beta)+E+4fa^1=0. \tag{7}$$

The homogeneous part of this equation corresponds to (4) with $\gamma=2$, and this is an eigenvalue. In order, therefore, that a solution satisfying the boundary conditions exist, it is necessary[9] that the inhomogeneity corresponding to the self-adjoint form of (4) be orthogonal to the eigenfunction of (4). Expand (7) in Fourier series, obtaining

$$12a^{2k}-(4k^2/\sin^2\beta)a^{2k}+4(a^{2k}{}_{\beta\beta}+2\cot 2\beta a^{2k}{}_\beta)=-\frac{1}{\epsilon_k\pi}\int\cos k\varphi(E+4fa^1)d\varphi. \tag{8}$$

Now, if $\gamma=2$, then $k=1$ and $n=0$, so that the solution of (4) is $F(0,2,2,t)=\text{const}$. The self-adjoint form of (4) is

$$[t^2(1-t)v']'+\left[\frac{\gamma(\gamma+1)}{16}-\frac{3}{4}\right]tv=0.$$

Substitute $a^{2,1}=t^{\frac{1}{2}}w$, find the equation for w and multiply this by t, and the result is

$$[t^2(1-t)w']'+\left[\frac{\gamma(\gamma+1)}{16}-\frac{3}{4}\right]tw=-(t^{\frac{1}{2}}/16\pi)\int 4fa^1\cos\varphi\, d\varphi. \tag{9}$$

We have already noted that $w=\text{const}$, so that if (9) has a "proper" solution, the equation

$$\int_0^1 t^{\frac{1}{2}}dt\int_0^{2\pi}\cos\varphi fa^1 d\varphi=0$$

must be true. We show in the Appendix that this is not so, so that *the ground state solution of (1), if it exists, is not of the form (2)*. Indeed, it would be an accident if there were a solution of (9) of the required type, for everything which enters is predetermined.

Part II

Since the above assumption as to the radial behavior of the wave function has been shown not to yield a proper solution, one must relax the restrictions. As a preliminary, it is convenient to consider a new system of polar coordinates, which we shall call the H system, while the system of Gronwall will be termed the G system. The H system will be defined by the transformation

$$\begin{aligned} x&=r\cos\theta, & 0&\le\theta\le\pi,\\ y&=r\sin\theta\cos\varphi, & 0&\le\varphi\le\pi,\\ z&=r\sin\theta\sin\varphi, \end{aligned}$$

so that the x axis is the polar axis. In this system, the wave equation is

$$\psi_{ss}+(5/s)\psi_s+(4/s^2\sin^2\theta)(\psi_{\varphi\varphi}+\cot\varphi\psi_\varphi)+(4/s^2)(\psi_{\theta\theta}+2\cot\theta\varphi_\theta)$$
$$+\left\{E+\frac{4}{s[2(1+\sin\theta\cos\varphi)]^{\frac{1}{2}}}+\frac{4}{s[2(1-\sin\theta\cos\varphi)]^{\frac{1}{2}}}-\frac{2}{Zs(1-\cos\theta)^{\frac{1}{2}}}\right\}\psi=0.$$

The corresponding variational problem is

$$\delta\int[\tfrac{1}{4}\psi_s{}^2+(1/s^2\sin^2\theta)\psi_\varphi{}^2+(1/s^2)\psi_\theta{}^2-\tfrac{1}{4}(E-V)\psi^2]s^5\,ds\sin^2\theta\, d\theta\sin\varphi\, d\varphi=0.$$

We are particularly interested in the behavior of ψ near the singularity $\theta=0$, which corresponds to coincidence of the two electrons. Suppose ψ is expansible as an ascending power series in θ at this point, i.e.,

$$\psi=\sum a^{(m)}(s\varphi)\theta^{m+\gamma}.$$

Substituting in the wave equation, we have

$$a^m{}_{ss}+(5/s)a^m{}_s+(4/s^2)(a^{m+2}{}_{\varphi\varphi}+\cot\varphi a^{m+2}{}_\varphi)+(4/s^2)(m+\gamma+2)(m+\gamma+3)a^{m+2}$$
$$+\left(E+\frac{8}{s\sqrt{2}}\right)a^m-\frac{4}{Zs\sqrt{2}}a^{m+1}+\cdots=0.$$

For $m=-2$, $a^0{}_{\varphi\varphi}+\cot\varphi a^0{}_\varphi+\gamma(\gamma+1)a^0=0$.

If $\psi\theta^{-\gamma}$ has a definite value at $\theta=0$, no matter from what direction the axis is approached, then a^0 is independent of φ, and $\gamma=0,\ -1$. This means that ψ is finite[10] at $\theta=0$ (except perhaps for $s=0$).

Along the y axis, one should expect the solution for small electronic interaction to be not very different from that for no interaction, or in other words to be finite. The magnitude of the interaction is determined by the value of the atomic number Z, which may be varied continuously in the above equation, so that we should expect the wave function along the y axis to be finite in general.

If the wave function is finite and sufficiently continuous except at $s=0$, then a development of the type G(10) is probably valid, since this is analogous to a Laplace series, for which corresponding theorems are true. Let us therefore assume such a development and rewrite G(11) as follows:

$$\psi_n''+(5/s)\psi_n'-(4/s^2)(2m-k)(2m+2-k)\psi_n+E\psi_n+\sum_{n'}\frac{2A(nn')}{\pi s(-E)^{\frac{1}{2}}}\psi_{n'}=0. \tag{10}$$

Make the substitution $\psi_n=(F^n/s^{5/2})$ and abbreviations $B(nn')=(2/\pi)[A(nn')/(-E)^{\frac{1}{2}}]$; $\alpha_n=(2m-k)\times(2m+2-k)$, obtaining

$$F^n{}_{ss}-(4\alpha_n/s^2)F^n+[E-(15/4s^2)]F^n+\sum_{n'}[B(nn')/s]F^{n'}=0. \tag{11}$$

This system may be reduced to one of the first order by the usual device of taking $F^n{}_s$ as a new dependent variable, which we denote as p^n.

Then

$$(dF^n/ds)=p^n,\quad (dp^n/ds)=[(4\alpha^n+(15/4))/s^2]F^n-EF^n-\sum[B(nn')/s]F^{n'}. \tag{12}$$

Infinite systems such as this do not seem to have been studied to any great extent. One would expect that solutions could be found by regarding (12) as the limit of a finite system. That one would obtain in this way all analytic solutions is, however, open to question, in view of the work of Ritt.[11, 12] We shall limit ourselves here to the extrapolation from the finite system (thus making the argument to this extent nonrigorous). Such a system can be solved readily, according to the work of Pierce.[13]

It is convenient to change the notation so that the equations have the same form as those of Pierce. Set $p^i=x^{2i}$ and $F^i=x^{2i-1}$, $i=1,\ 2\cdots N$.

Then $$(dx^{2i-1}/ds)=x^{2i},\quad (dx^{2i}/ds)=[(4\alpha^i+(15/4))/s^2]x^{2i-1}-Ex^{2i-1}-\sum_j[B(2i-1,\ 2j-1)/s]x^{2j-1}. \tag{13}$$

[10] The exponent $\gamma=-1$ gives an infinite variational integral, and must hence be excluded.
[11] J. F. Ritt, Trans. Amer. Math. Soc. **18**, 27 (1917).
[12] See also the summary of work in this field by R. D. Carmichael, Bull. Amer. Math. Soc. **42**, 193 (1936).
[13] J. Pierce, Amer. Math. Monthly **43**, 530 (1936).

This can be written as

$$(dx^k/ds)=\sum_l(\theta_{kl}/s^2)x^l, \quad (k, l=1, 2\cdots 2N), \tag{14}$$

where

$$\theta_{2i-1,\,2i}=s^2,$$
$$\theta_{2i,\,2i-1}=4\alpha^i+(15/4)-Es^2-B_{2i-1,\,2i-1}s,$$
$$\theta_{2i,\,2j-1}=-B_{2i-1,\,2j-1}s \quad (j\neq i),$$
$$\theta_{2i-1,\,2i-1}=0.$$

According to Pierce, the solution of the system (14) is expressible as a series of definite integrals, as follows:

$$x^i=\sum_{h=1}^{\infty}y_{ih}, \tag{15}$$

where

$$y_{ih}=\int_{s_0}^{s}\sum_j(\theta_{ij}/t^2)y_{j,\,h-1}dt, \tag{16}$$

and the integration is to avoid the origin. One is also to start by setting $y_{i1}=c_i$, which are arbitrary constants. For purposes of visualization, it is perhaps best to write down the matrix

$$(\theta_{ij})=\begin{Bmatrix} 0 & s^2 & 0 & 0 & 0 & 0 & \cdots \\ \theta_{21} & 0 & \theta_{23} & 0 & \theta_{25} & 0 & \cdots \\ 0 & 0 & 0 & s^2 & 0 & 0 & \cdots \\ \theta_{41} & 0 & \theta_{43} & 0 & \theta_{45} & 0 & \cdots \end{Bmatrix}.$$

The equations (16) may be set down in more detail:

$$y_{1h}=\int_{s_0}^{s}y_{2,\,h-1}dt \quad (\text{since } \theta_{ij}=\theta_{12}\delta_{2j}), \tag{16a}$$

$$y_{2h}=\int_{s_0}^{s}\sum_{j=1}^{N}(\theta_{2,\,2j-1}/t^2)y_{2j-1,\,h-1}dt, \tag{16b}$$

$$y_{3h}=\int_{s_0}^{s}y_{4,\,h-1}dt, \quad \text{etc.} \tag{16c}$$

The coefficients $\theta_{2,\,2j-1}$ are

$$\theta_{21}=(4\alpha_1+(15/4))-B_{11}s-Es^2$$
$$\theta_{23}=\qquad -B_{13}s \qquad, \text{ etc.}$$

Then

$$y_{2j-1,\,2}=\int_{s_0}^{s}(\theta_{2j-1,\,2j}/t^2)y_{2j,\,1}dt=\int_{s_0}^{s}c_{2j}dt=c_{2j}(s-s_0), \tag{17}$$

$$y_{2j,\,2}=\int_{s_0}^{s}[\theta_{2j,\,1}c_1+\theta_{2j,\,3}c_3+\theta_{2j,\,5}c_5+\cdots](dt/t^2)$$

$$=\int_{s_0}^{s}[(4\alpha^j+(15/4)-Et^2)c_{2j-1}-\sum_{i=1}^{N}B_{2j-1,\,2i-1}tc_{2i-1}](dt/t^2)$$

$$=\left[-(4\alpha^j+(15/4))\left(\frac{1}{s}-\frac{1}{s_0}\right)-E(s-s_0)\right]c_{2j-1}-\left(\log\frac{s}{s_0}\right)\sum_{i=1}^{N}B_{2j-1,\,2i-1}c_{2i-1}, \tag{18}$$

$$y_{2j-1,\,3}=\int_{s_0}^{s}(\theta_{2j-1,\,2j}/t^2)y_{2j,\,2}dt=\int_{s_0}^{s}y_{2j,\,2}dt, \tag{19}$$

$$y_{2j,\,3}=\int_{s_0}^{s}(\theta_{2j,\,1}y_{12}+\theta_{2j,\,3}y_{32}+\cdots)(dt/t^2). \tag{20}$$

The general formulae are

$$y_{2j-1,\,i}=\int_{s_0}^{s}y_{2j,\,i-1}dt, \tag{21}$$

$$y_{2j,\,i}=\int_{s_0}^{s}[(4\alpha^j+(15/4)-Et^2)y_{2j-1,\,i-1}-\sum_{k=1}^{N}B_{2j-1,\,2k-1}ty_{2k-1,\,i-1}](dt/t^2). \tag{22}$$

By applying first (22) and then (21), we may proceed from $y_{2k-1,\,i-1}$ to $y_{2j-1,\,i+1}$ or from $y_{2k-1,\,i}$ to $y_{2j-1,\,i+2}$. By mathematical induction, then, we can find the form of all the y_{ih}'s. From formula (19), we see that $y_{2j-1,\,3}=a^j+b^j\log s+c^js+d^js^2$, where a^j, b^j, c^j, and d^j are constants. Applying (22), we have

$$y_{2j,\,4}=\frac{A^j}{s}+\frac{B^j\log s}{s}+C^j\log s+D^j(\log s)^2(+\text{ascending power series in } s).$$

The application of (21) now gives $y_{2j-1,\,5}$ and this is of the same form as $y_{2j-1,\,3}$ except for higher powers of s and $\log s$. In a similar fashion, one may find from $y_{2j-1,\,2}$ the expressions for $y_{2j,\,3}$ and $y_{2j-1,\,4}$. The same results hold, so that the x^i in (15) will be ascending power series in t (or s), except for logarithmic terms. This would imply that the wave function is of the form $\sum_{k=0}^{\infty}c^{(k)}(s,\beta,\varphi)(\log s)^k$, where the $c^{(k)}$'s are of the same nature as the ψ of Eq. (2). This conclusion is legitimate subject to two assumptions: (1) that ψ can be expanded in a series of the type G(10), and (2) that the infinite system of equations has qualitatively the same behavior as any finite system.

Discussion

If, at the origin, the solution of the equation with a small electronic interaction were not very different from the corresponding solution of the unperturbed (separable) equation, then we should expect that a solution of the form (2) would be possible. Since this does not appear to be so (Part I), we must conclude that, if a solution of (1) exists, it differs essentially from the separable solution at the origin. Hence we see that the ordinary continuity assumption of perturbation theory cannot be generally legitimate, at least at such a singular point.

Even though the eigenfunctions may exist, the continuity property does not always need to hold. Rellich[14] gives an example in which the eigenvalues vary continuously when a small perturbation is introduced, but the eigenfunctions do not.

For the present, then, we see that there are serious difficulties in the way of finding a solution to the helium wave equation, if such exists. If the properties of continuity in the parameter are to be preserved, then no solution can exist. If a solution does exist, then the continuity requirement must be abandoned, at least in certain regions of phase space. It is conceivable that retention of the continuity

[14] F. Rellich, Math. Annalen **113**, 600 (1936). I am indebted to Professor Weyl for referring me to this paper.

requirement except at the singularities may allow one to find a solution quadratically integrable over all space. This is beyond the scope of the present paper, but is worthy of further investigation.

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Appendix

1. Solution of Eq. (5), verification

Given: $a^1=a_0{}^1+(1/2Z)(1-\cos\varphi\sin\beta)^{\frac{1}{2}}$, where $a_0{}^1$ satisfies (5) if $Z=\infty$.
To show: a^1 satisfies (5) for any Z.
Demonstration: Let $b^1=a^1-a_0{}^1$.

$$b^1{}_\beta=-(1/2Z)\tfrac{1}{2}\cos\varphi\cos\beta(1-\cos\varphi\sin\beta)^{-\frac{1}{2}};\qquad b^1{}_\varphi=(1/2Z)\tfrac{1}{2}\sin\varphi\sin\beta(1-\cos\varphi\sin\beta)^{-\frac{1}{2}},$$

$$b^1{}_{\beta\beta}=-(1/2Z)\tfrac{1}{2}\cos\varphi\left\{\frac{1}{2}\frac{\cos\varphi\cos^2\beta}{(1-\cos\varphi\sin\beta)^{\frac{3}{2}}}-\frac{\sin\beta}{(1-\cos\varphi\sin\beta)^{\frac{1}{2}}}\right\},$$

$$b^1{}_{\varphi\varphi}=(1/2Z)\tfrac{1}{2}\sin\beta\left\{-\frac{1}{2}\frac{\sin^2\varphi\sin\beta}{(1-\cos\varphi\sin\beta)^{\frac{3}{2}}}+\frac{\cos\varphi}{(1-\cos\varphi\sin\beta)^{\frac{1}{2}}}\right\},$$

$$(b^1{}_{\varphi\varphi}/\sin^2\beta)+b^1{}_{\beta\beta}=(1/4Z)\left\{-\frac{1}{2}\frac{\sin^2\varphi+\cos^2\varphi\cos^2\beta}{(1-\cos\varphi\sin\beta)^{\frac{3}{2}}}+\frac{\cos\varphi(1+\sin^2\beta)}{\sin\beta(1-\cos\varphi\sin\beta)^{\frac{1}{2}}}\right\},\tag{23}$$

$$2\cot 2\beta b^1{}_\beta=-(1/4Z)(\cos^2\beta-\sin^2\beta)(\cos\varphi/\sin\beta)(1-\cos\varphi\sin\beta)^{-\frac{1}{2}},\tag{24}$$

$$(23)+(24)=(1/4Z)[1-\tfrac{1}{2}(1+\cos\varphi\sin\beta)+3\sin\beta\cos\varphi](1-\cos\varphi\sin\beta)^{-\frac{1}{2}},$$
$$fa^0=(1/4Z)[-2(1-\cos\varphi\sin\beta)^{-\frac{1}{2}}],$$
$$(23)+(24)+fa^0=(1/4Z)[-\tfrac{5}{2}(1-\cos\varphi\sin\beta)^{\frac{1}{2}}]=-\tfrac{5}{4}b^1.$$

Since (25) is the same as (5), the verification is complete. As stated in the text, we have needed only to compare the terms involving Z.

2. Computation of $\int_0^1 t^{\frac{1}{2}}dt\int_0^{2\pi}\cos\varphi fa^1d\varphi$

$$f=[2(1+t^{\frac{1}{2}}\sin\varphi)]^{-\frac{1}{2}}+[2(1-t^{\frac{1}{2}}\sin\varphi)]^{-\frac{1}{2}}-(1/2Z)(1-t^{\frac{1}{2}}\cos\varphi)^{-\frac{1}{2}},$$
$$a^1=-(1/\sqrt{2})\{(1+t^{\frac{1}{2}}\sin\varphi)^{\frac{1}{2}}+(1-t^{\frac{1}{2}}\sin\varphi)^{\frac{1}{2}}\}+(1/2Z)(1-t^{\frac{1}{2}}\cos\varphi)^{\frac{1}{2}},$$
$$fa^1=-1-(1/2Z)^2+(1/2Z\sqrt{2})\{(1-t^{\frac{1}{2}}\cos\varphi)^{\frac{1}{2}}[(1+t^{\frac{1}{2}}\sin\varphi)^{-\frac{1}{2}}+(1-t^{\frac{1}{2}}\sin\varphi)^{-\frac{1}{2}}]$$
$$+(1-t^{\frac{1}{2}}\cos\varphi)^{-\frac{1}{2}}[(1-t^{\frac{1}{2}}\sin\varphi)^{\frac{1}{2}}+(1-t^{\frac{1}{2}}\sin\varphi)^{\frac{1}{2}}]\}.$$

Now, if $h(\varphi)$ is a function of period 2π,

$$\int_0^{2\pi}h(\varphi)d\varphi=-\int_{2\pi}^{0}h(2\pi-\varphi)d\varphi=\int_0^{2\pi}h(-\varphi)d\varphi.$$

In particular, $$\int_0^{2\pi}\cos\varphi d\varphi\left(\frac{1-t^{\frac{1}{2}}\cos\varphi}{1+t^{\frac{1}{2}}\sin\varphi}\right)^{\frac{1}{2}}=\int_0^{2\pi}\cos\varphi d\varphi\left(\frac{1-t^{\frac{1}{2}}\cos\varphi}{1-t^{\frac{1}{2}}\sin\varphi}\right)^{\frac{1}{2}}.$$

Also, $$\int_0^{2\pi}\cos\varphi d\varphi\left(\frac{1-t^{\frac{1}{2}}\cos\varphi}{1-t^{\frac{1}{2}}\sin\varphi}\right)^{\frac{1}{2}}=\int_0^{2\pi}\cos(\varphi+\pi/2)d(\varphi+\pi/2)\left(\frac{1-t^{\frac{1}{2}}\cos(\varphi+\pi/2)}{1-t^{\frac{1}{2}}\sin(\varphi+\pi/2)}\right)^{\frac{1}{2}}$$
$$=\int_0^{2\pi}-\sin\varphi d\varphi\left(\frac{1+t^{\frac{1}{2}}\sin\varphi}{1-t^{\frac{1}{2}}\cos\varphi}\right)^{\frac{1}{2}}=\int_0^{2\pi}\sin\varphi d\varphi\left(\frac{1-t^{\frac{1}{2}}\sin\varphi}{1-t^{\frac{1}{2}}\cos\varphi}\right)^{\frac{1}{2}}.$$

Therefore

$$I=\int_0^{2\pi}fa^1\cos\varphi d\varphi=(1/Z\sqrt{2})\int_0^{2\pi}(\cos\varphi+\sin\varphi)d\varphi\left(\frac{1-t^{\frac{1}{2}}\sin\varphi}{1-t^{\frac{1}{2}}\cos\varphi}\right)^{\frac{1}{2}}.$$

The quickest and most convenient procedure is to evaluate $I(t)$ numerically. It is also useful to know how I behaves near the end points $t=0$ and $t=1$.

(a) For $t=0$, expand the integrand in a Taylor's series.

$$\sqrt{2}ZI=\int_0^{2\pi}(\cos\varphi+\sin\varphi)d\varphi[1-\tfrac{1}{2}t^{\frac{1}{2}}\sin\varphi-\tfrac{1}{8}t\sin^2\varphi-\tfrac{1}{16}t^{\frac{3}{2}}\sin^3\varphi-\cdots][1+\tfrac{1}{2}t^{\frac{1}{2}}\cos\varphi+\tfrac{3}{8}t\cos^2\varphi+\tfrac{5}{16}t^{\frac{3}{2}}\cos^3\varphi+\cdots]$$
$$=\int_0^{2\pi}(\cos\varphi+\sin\varphi)d\varphi[1+\tfrac{1}{2}t^{\frac{1}{2}}(-\sin\varphi+\cos\varphi)+t(\tfrac{3}{8}\cos^2\varphi-\tfrac{1}{4}\cos\varphi\sin\varphi-\tfrac{1}{8}\sin^2\varphi)$$
$$+t^{\frac{3}{2}}(\tfrac{5}{16}\cos^3\varphi-\tfrac{3}{16}\cos^2\varphi\sin\varphi-\tfrac{1}{16}\cos\varphi\sin^2\varphi-\tfrac{1}{16}\sin^3\varphi)+\cdots].$$

Only the odd powers of $t^{\frac{1}{2}}$ will have nonvanishing coefficients. The coefficient of $t^{\frac{1}{2}}$ itself is zero, and if we consider values of t for which $t^2 \ll 1$, then

$$\begin{aligned}\sqrt{2}ZI &\cong t^{\frac{3}{2}}\int_0^{2\pi}(\cos\varphi+\sin\varphi)d\varphi(\tfrac{5}{16}\cos^3\varphi-\tfrac{3}{16}\cos^2\varphi\sin\varphi-\tfrac{1}{16}\cos\varphi\sin^2\varphi-\tfrac{1}{16}\sin^3\varphi)\\ &=t^{\frac{3}{2}}\int_0^{2\pi}d\varphi(\tfrac{5}{16}\cos^4\varphi+\tfrac{1}{8}\cos^3\varphi\sin\varphi-\tfrac{1}{4}\cos^2\varphi\sin^2\varphi-\tfrac{1}{8}\cos\varphi\sin^3\varphi-\tfrac{1}{16}\sin^4\varphi)\\ &=\pi/8t^{\frac{3}{2}}.\end{aligned}$$

(b) As $t \rightarrow 1$, I becomes infinite, as may be seen from inspection. The infinity is due to the behavior of the integrand near $\varphi=0$, and it is therefore obvious that I becomes infinite in the same way as

$$J=\int_0^{2\pi}\cos\varphi d\varphi(1-t^{\frac{1}{2}}\cos\varphi)^{-\frac{1}{2}}=\text{const. } t^{\frac{1}{2}}F(\tfrac{3}{4},\tfrac{5}{4},2,t). \qquad \text{(See "G".)}$$

If $t \rightarrow 1$, J behaves as $-t^{\frac{1}{2}}\log(1-t)$, which is positive.

(c) Numerical integration yields positive values of I for values of t between 0 and 1. The following values of cI (c a constant) show the run of the function:

$$t=0.09,\quad cI=0.15;\quad t=0.25,\quad cI=0.80;\quad t=0.64,\quad cI=5.5;\quad \text{and}\quad t=0.95\quad cI=23.$$

It is therefore to be concluded that I is positive throughout the interval $0 \leq t \leq 1$, and that the integral $\int_0^1 t^{\frac{1}{2}}dtI(t)$ cannot possibly vanish.

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On the Connection Formulas and the Solutions of the Wave Equation

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Part 1 gives a general discussion of asymptotic representations of the solutions of the one-dimensional wave equation. The forms ordinarily used in the so-called W. K. B. method are multiple valued and consequently necessitate a consideration of the Stokes' phenomenon, in any region about a turning point, i.e., a point in which the kinetic energy changes sign. Except under restrictive hypotheses they give no description of the solutions near the turning points. The author's method for representing the solutions of such differential equations by means of single valued functions is discussed, and the formulas applicable to the wave equation are given. These formulas are usable over the whole of an interval which includes a turning point. The Stokes' phenomenon is not involved. It need be considered only if expressions of the older type are desired, and then the connection formulas of the W. K. B. method are immediately evolved. An appropriate formal development of the solutions of the wave equation as power series in $\hbar$ is given.

Part 2 deals with the radial wave equation for motion in a central field of force. Both the attractive and repulsive Coulomb field are considered. It is shown that the application of the W. K. B. analysis to this equation as it has generally been made is uncritical and in error. The solution commonly identified thereby as the wave function is in fact not the wave function. The "failure" of the W. K. B. formulas, and the apparent necessity for modifying them by replacing the number $l(l+1)$ by $(l+\frac{1}{2})^2$, has been noted by many investigators. This is traced to the misapplication of the theory. When correctly applied the theory naturally yields the formulas which have been found to be called for on other grounds.

Finally the case is discussed in which a turning point lies too near the point $r=0$ for the W. K. B. method to be effectively applicable. It is shown how the solutions are describable in this case, the formulas given specializing, when the field is an attractive field and the energy is zero, to formulas which were given for that special case by Kramers.

PART 1. THE ONE-DIMENSIONAL WAVE EQUATION

THE wave equation for a mechanical system of one degree of freedom is familiarly of the form

$$d^2u/dx^2+Q^2(x)u=0, \qquad (1)$$

with

$$Q^2(x)=\frac{2m}{\hbar^2}\{E-V(x)\}.$$

m, E and $V(x)$ representing respectively the mass, the total energy and the potential energy,