THE
PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 154, NO. 5 25 FEBRUARY 1967

Bound-State Solutions of the Schrödinger Equation

LEONARD EYGES
Air Force Cambridge Research Laboratories, Office of Aerospace Research, Bedford, Massachusetts
(Received 20 September 1966)

We present a new method for solving the Schrödinger equation for attractive potentials. The basic idea is to use in conjunction both the differential and integral forms of the equation. In one dimension, for example, a formal solution for $\psi(x)$ can be found from the differential equation; since this is of second order, the solution is fixed, in principle, by $\psi(0)$ and $\psi'(0)\equiv d\psi/dx|_{x=0}$. These quantities are in fact unknown, but from the integral equation we can calculate integral expressions for them. We insert the formal solution into the integrands of these expressions and eliminate $\psi(0)$ and $\psi'(0)$ from the resulting equations to get an equation for the energy eigenvalues. In three dimensions, the method works much the same way. In terms of $Q_l(r)$, where the radial wave function $R_l(r)$ for the lth angular momentum state is $R_l(r)=r^lQ_l(r)$, it leads to the basic equation for the eigenvalues,

$$1=-\frac{Kv_0(ik)^l}{1\times3\times5\times\cdots\times(2l+1)}\int_0^\infty h_l(iKr')u(r')Q_l(r')r'^{l+2}dr',$$

where K^2 is essentially the magnitude of the energy, and the potential is written as $-v_0u(r)$. For nonsingular potentials, the formal solution for $Q_l(r)$ can be put in the form

$$Q_l(r)=S_l(r)+\sum_s S_{l,s}(r)U_0^{(s)}+\sum_{st}S_{l,st}(r)U_0^{(s)}U_0^{(t)}+\cdots,$$

where $U(r)=v_0u(r)-K^2$, and where $U_0^{(s)}$ is the sth derivative of $U(r)$ at the origin. The functions $S_l(r)$ and $S_{l,s}(r)$ are calculated, and then the results are applied to the case of a Gaussian potential. A modification of these ideas for singular potentials is also discussed, and is applied to the Yukawa potential.

I. INTRODUCTION

THE problem of solving the Schrödinger equation for one or another potential arises in many branches of physics. Unfortunately, there is only a small number of potentials for which an exact solution is known. In one dimension there are, for example,[1] the square-well (or, more generally, any "staircase" potential), the harmonic-oscillator, triangular potentials,[2] and a small number of less well-known ones. In three dimensions, the square-well and oscillator potentials are still solvable, and there is, in addition, the Coulomb potential, and a few others, such as the exponential, which can be solved exactly for S states only.[1]

In this paper, we present a method of solution which applies to a wide variety of potentials and equally to one, two, or three dimensions. For the sake of clarity, however, we shall begin by explaining it for the one-dimensional case since the multiple integrations and spherical harmonics that three dimensions introduces are complications that are irrelevant to the basic idea.

We consider then the one-dimensional Schrödinger equation for a potential $V(x)$ and for a bound state with energy $E=-|E|$:

$$d^2\psi/dx^2=[\epsilon-v_0u(x)]\psi, \tag{1}$$

where

$$\epsilon=2m|E|/\hbar^2, \quad v(x)\equiv-v_0u(x)=2mV(x)/\hbar^2.$$

There is an integral counterpart of this which we can write using the Green's function $G_K(x,x')$,

$$G_K(x,x')=(1/2K)e^{-K|x-x'|}, \quad K^2=\epsilon,$$

which satisfies

$$((d^2/dx^2)-K^2)G_K(x,x')=-\delta(x-x').$$

[1] For a fairly complete presentation of most known cases see P. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953).

[2] The triangular potential is discussed (for the scattering problem) in N. F. Mott and I. N. Sneddon, *Wave Mechanics and Its Applications* (Oxford University Press, London, 1948).

This integral equation is

$$\psi(x)=\frac{v_0}{2K}\int_{-\infty}^{\infty}\psi(x')u(x')e^{-K|x-x'|}dx'. \tag{2}$$

Now each of the two equivalent forms (1) and (2) has a special virtue that merits a comment. The virtue of Eq. (1) is that it has a formal solution. If, for example, the potential is nonsingular, such a solution can be constructed in the form of a Taylor series and, since the equation is of second order, the series is determined, in principle, by fixing the value of ψ and $d\psi/dx\equiv\psi'(x)$ at some point, say the origin. The solution can be constructed in practice by computing the higher derivatives of ψ in terms of $\psi(0)$ and $\psi'(0)$ from the equation itself, by repeated differentiation. There is, of course, a catch: Eq. (1) is not really defined, since one does not know the value of ϵ in advance, and it is in this sense that the solution is a formal one. For an arbitrary choice of ϵ, a solution for ψ which is constructed out from the origin in the above or any other way will, in general, blow up at infinity. It is only for special values of ϵ, the eigenvalues, that the eigenfunction will have the acceptable form at large distances of a decaying exponential.

The integral Eq. (2) has the virtue of not suffering from this defect, for if one computes ψ from its left-hand side using even an approximate or formal expression for $\psi(x')$ in the integrand, it automatically gives the correct form at large $|x|$ of a decaying exponential, although the exponent may not be known. On the other hand, this equation is not so easy to attack as the differential equation is; there is no analogous formal solution. Perhaps the only truly general method is to expand it in some set of orthogonal functions, and so convert it to an infinite set of linear equations and a corresponding infinite, and in general untractable, determinant for the eigenvalues.

In this paper, we present a method which, using both Eqs. (1) and (2), combines their virtues and, we believe, minimizes their defects. Although we apply it only to the bound-state (homogeneous) problem, it is clear that a similar technique can be used for the scattering (inhomogeneous) problem.

II. ONE DIMENSION

The method goes, in general, like this. From Eq. (2) for $\psi(x)$, we calculate ψ' as

$$\psi'(x)=-\tfrac{1}{2}v_0\int_{-\infty}^{x}\psi(x')u(x')e^{-K(x-x')}dx' +\tfrac{1}{2}v_0\int_{x}^{\infty}\psi(x')u(x')e^{-K(x'-x)}dx'. \tag{3}$$

We evaluate (2) and (3) at some convenient point x_0, and then expand $\psi(x')$ in the integrands in a formal Taylor series about that point, systematically using (1) to reduce the higher derivatives $d^n\psi/dx^n$ to linear combinations of $\psi(x_0)$ and $\psi'(x_0)$. We end up then with two homogeneous linear equations in $\psi(x_0)$ and $\psi'(x_0)$, whose vanishing determinant fixes the energy eigenvalues. Having found these, we can then calculate the corresponding eigenfunctions either from the formal solution, or in other ways, as we discuss below.

Now we fill in some details. In this paper, we shall use a Taylor series about the origin, that is, take $x_0=0$, but there may be cases in which other values are more appropriate. For compactness, we relabel ψ and its derivative at the origin according to

$$\psi(0)\equiv a,\quad \psi'(0)\equiv b.$$

Then Eqs. (2) and (3) become

$$a=\frac{v_0}{2K}\int_{-\infty}^{\infty}\psi(x')u(x')e^{-K|x'|}dx', \tag{4}$$

$$b=-\tfrac{1}{2}v_0\left[\int_{-\infty}^{0}\psi(x')u(x')e^{Kx'}dx' -\int_{0}^{\infty}\psi(x')u(x')e^{-Kx'}dx'\right]. \tag{5}$$

Since the formal solution is determined by a and b, it can be written as

$$\psi(x)=a\psi_a(x)+b\psi_b(x), \tag{6}$$

where $\psi_a(x)$ and $\psi_b(x)$ are definite functions, calculable from (1) and involving the energy ϵ. We shall shortly discuss them in detail but, assuming for the moment that they are known, we see on putting (6) into (5) and (4) that the energy eigenvalues of the system are determined from

$$\begin{aligned} a&=T_a a+T_b b,\\ b&=T_a' a+T_b' b,\end{aligned}$$

or

$$\begin{vmatrix} T_a-1 & T_b \\ T_a' & T_b'-1 \end{vmatrix}=0, \tag{7}$$

where

$$T_a=\frac{v_0}{2K}\int_{-\infty}^{\infty}\psi_a(x')u(x')e^{-K|x'|}dx',$$

$$T_a'=-\tfrac{1}{2}v_0\int_{-\infty}^{0}\psi_a(x')u(x')e^{Kx'}dx' +\tfrac{1}{2}v_0\int_{0}^{\infty}\psi_a(x')u(x')e^{-Kx'}dx'.$$

The problem now is to calculate ψ_a and ψ_b. We begin by writing (1) more compactly as

$$\psi''=-U\psi,\quad U(x)=v_0u(x)-\epsilon. \tag{8}$$

We shall have to deal with various functions and their derivatives evaluated at the origin. For a typical function, call it $Z(x)$, we shall use the notation

$$\frac{d^nZ}{dx^n}\equiv Z^{(n)},\quad \left.\frac{d^nZ}{dx^n}\right|_{x=0}\equiv Z_0{}^{(n)}. \tag{9}$$

The Taylor series is then

$$\psi(x)=\sum_{n=0}^{\infty}\psi_0{}^{(n)}\frac{x^n}{n!}. \tag{10}$$

To calculate the coefficients $\psi_0{}^{(n)}$, we simply differentiate (1) repeatedly. If we adopt the normalization

$$u(0)\equiv u_0=1,$$

we get, for example

$$\psi_0{}^{(2)}=-U_0a,$$
$$\psi_0{}^{(3)}=-U_0{}^{(1)}a-U_0b,$$
$$\psi_0{}^{(4)}=(U_0{}^2-\cdots U_0{}^{(2)})a-2U_0{}^{(1)}b,$$

From derivatives like these, we then find for $\psi_a(x)$ up to terms in x^7,

$$\psi_a(x)=1-\frac{x^2}{2!}U_0-U_0{}^{(1)}\frac{x^3}{3!}+(U_0{}^2-U_0{}^{(2)})\frac{x^4}{4!}+(4U_0U_0{}^{(1)}-U_0{}^{(3)})\frac{x^5}{5!}+(-U_0{}^3+(4U_0{}^{(1)})^2+7U_0U_0{}^{(2)}-U_0{}^{(4)})\frac{x^6}{6!}$$
$$+(-9U_0{}^{(1)}U_0{}^2+15U_0{}^{(1)}U_0{}^{(2)}+11U_0U_0{}^{(3)}-U_0{}^{(5)})\frac{x^7}{7!}+\cdots, \tag{11}$$

and for $\psi_b(x)$,

$$\psi_b(x)=x-\frac{U_0x^3}{3!}-\frac{2U_0{}^{(1)}x^4}{4!}+(U_0{}^2-3U_0{}^{(2)})\frac{x^5}{5!}+(6U_0U_0{}^{(1)}-4U_0{}^{(3)})\frac{x^6}{6!}$$
$$+(-U_0{}^3+10(U_0{}^{(1)})^2+13U_0U_0{}^{(2)}-5U_0{}^{(4)})\frac{x^7}{7!}+\cdots. \tag{12}$$

The question of the convergence of the series above is, of course, an important, even crucial one. It will turn out that, in some simpler applications, the series converge well enough to be useful as they stand. In this connection, one should note from (2) that the series are used only in the region where the potential is nonvanishing.

To get some idea of the convergence, we work out a simple example. We take first a symmetric potential, for which $u(x)=u(-x)$. Then, each state as a function of x is either even or odd about the origin. For the even states, $\psi_0{}^{(1)}\equiv b$ is zero, T_a' is zero, and Eq. (7) becomes

$$T_a=1,\quad \text{even parity.} \tag{13}$$

Similarly, for odd states, we have

$$T_b'=1,\quad \text{odd parity.} \tag{14}$$

It is instructive to try these equations out on the square-well potential:

$$u(x)=1,\quad -a<x<a$$
$$=0\quad \text{elsewhere.}$$

All the derivatives $U_0{}^{(n)}$ are then zero; and from (11) we see that $\psi_a(x)$ simply becomes $\cos((v_0-\epsilon)^{1/2}x)$. Thus, (13) becomes

$$1=\frac{v_0}{K}\int_0^a\cos(U_0{}^{1/2}x)e^{-Kx'}dx'.$$

Integrating this equation, we get the well-known exact result

$$(y-z)^{1/2}\tan(y-z)^{1/2}=(z)^{1/2},$$

where

$$y=v_0a^2,\quad z=\epsilon a^2.$$

Similarly, from Eq. (14) for the odd states, we get

$$(y-z)^{1/2}\cot(y-z)^{1/2}=-(z)^{1/2}.$$

To get some idea of the convergence of the series expression for $\psi(x)$, we compare the results of term-by-term integration with exact ones. For the even state, for example, if we keep only the first constant term in the Taylor expansion, we get

$$1=(y/z)(1-\exp[-z^{1/2}]). \tag{15}$$

Similarly, with the first two terms we find,

$$1=\frac{y}{z}\left\{1-\exp(-z^{1/2})+\tfrac{1}{2}\left(1-\frac{y}{z}\right)\right.$$
$$\left.\times[2-\exp(-z^{1/2})](2+2z^{1/2}+z)\right\}. \tag{16}$$

In Table I, we compare results from these formulas with the exact ones. We see that even the lowest order approximation gives results accurate to within about 10%.

So much for the moment on the eigenvalues; we now would like to comment on the calculation of the eigenfunctions. With the eigenvalues known, the eigenfunctions are, of course, determinate and are, in fact,

TABLE I. Exact and approximate results for ground state of one-dimensional square well. $y=v_0a^2$, $z=\epsilon a^2$.

		y	
		One term in Taylor series:	Two terms in Taylor series:
z	Exact	Eq. (15)	Eq. (16)
0.1685	0.5285	0.5004	0.5290
0.6784	1.318	1.209	1.323
2.4254	3.425	3.074	3.454
3.3507	4.453	3.992	4.500
4.6712	5.881	5.280	5.962

given in series form in (11) and (12). There is another possibility however: we can use the integral expression (2) for calculating the eigenfunction. Now at first sight there might seem to be no advantage in doing so, since to evaluate the integral for $\psi(x)$, one must already know $\psi(x)$, say from the exact series form itself, to put into the integrand. There may, however, be an advantage in practice, since the series can really be used only as a truncated one, which may or may not converge well. If, however, we use this approximate form in the right-hand side of (2), we can then look on this integral equation as a device for iterating and, hopefully, improving it. Thus, instead of tediously calculating higher order terms in the series (11), it may be simpler and more accurate to stop at some reasonable point and to iterate the resultant function. It is impossible, of course, to prescribe how and when this should be done in general, but to illustrate it, let us take a very simple example.

We consider the ground state of the square-well for which the approximation of the wave function in the well by a constant leads to the results in Table I. Let us now iterate this to find a new approximation to the wave function. If then, we put $\psi(x')=1$ in the integrand on the right-hand side of (2), we find for the iterated wave function, with $\zeta=x/a$

$$1-\tfrac{1}{2}\{\exp[-z^{1/2}(1+\zeta)]+\exp[-z^{1/2}(1-\zeta)]\}, \quad |\zeta|<1$$

to which, of course, is joined the function $\exp(-z^{1/2}|\zeta|)$ for $|\zeta|>1$.

We plot this, normalized to unity at the origin, in Fig. 1 and compare with the exact wave function. The iteration improves the wave function to a surprising degree.

III. THREE DIMENSIONS

A. General Results

We now consider the problem in three dimensions. We proceed along much the same lines as in one di-

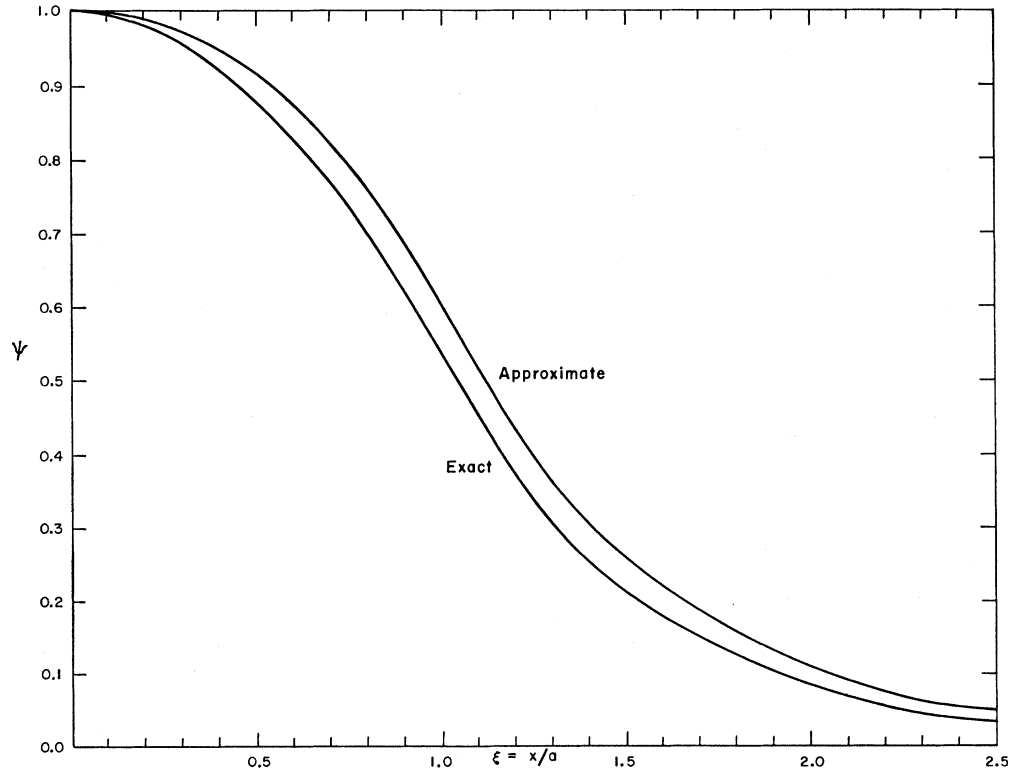

FIG. 1. The exact solution for the ground state of the one-dimensional square well and the first-order approximation obtained by using the integral equation (2) to iterate once the zeroth-order approximation $\psi(x)=$constant, $|x|<a$. $y=3.4254$. $z=2.4254$ exactly and $z=2.779$ approximately.

mension, that is, by using the appropriate differential and integral equations in conjunction. We shall consider the potential v to be spherically symmetric: $v=v(r)$. The Schrödinger equation is then

$$[\nabla^2+v_0u(r)]\psi(\mathbf{r})=\epsilon\psi(\mathbf{r}), \tag{17}$$

where, as in one dimension,

$$\epsilon=K^2=2m|E|/\hbar^2 \quad \text{and} \quad v(r)=-v_0u(r) \tag{18}$$

with the normalization $u(0)\equiv u_0=1$.

The equivalent integral equation contains the three-dimensional Green's function

$$G_K(\mathbf{r},\mathbf{r}')=\frac{1}{4\pi}\frac{e^{-K|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}$$

and is

$$\psi(\mathbf{r})=v_0\int u(r')\psi(\mathbf{r}')G_K(\mathbf{r},\mathbf{r}')d\mathbf{r}'. \tag{19}$$

For the assumed spherically symmetric potential, the wave function $\psi(\mathbf{r})$ is an eigenfunction of angular momentum, and we need only consider one such eigenfunction at a time. For the lth state, then

$$\psi(\mathbf{r})=R_l(r)Y_{lm}(\Omega). \tag{20}$$

The radial function $R_l(r)$ satisfies the well-known differential equation,

$$\frac{d^2R_l}{dr^2}+\frac{2}{r}\frac{dR_l}{dr}+\left\{v_0u(r)-\epsilon-\frac{l(l+1)}{r^2}\right\}R_l=0. \tag{21}$$

We can get the corresponding integral equation by using the expansion

$$G_K(\mathbf{r},\mathbf{r}')=-\frac{K}{4\pi}\sum_{l=0}^{\infty}(2l+1)P_l(\cos\gamma)\Gamma_l(r,r'), \tag{22}$$

where

$$\begin{aligned}\Gamma_l(r,r')&=j_l(iKr')h_l(iKr), \quad r'<r \\ &=j_l(iKr)h_l(iKr'), \quad r<r'\end{aligned} \tag{23}$$

and γ is the angle between $\mathbf{r}$ and $\mathbf{r}'$. If we put (20) and (22) into (19), and use the addition theorem for spherical harmonics on $P_l(\cos\gamma)$, we get in a straightforward way

$$R_l(r)=-Kv_0\int_0^{\infty}R_l(r')u(r')\Gamma_l(r,r')r'^2dr'. \tag{24}$$

Now, we cannot usefully evaluate (24) at the origin since it vanishes there; it is well known that R_l behaves like r^l for small r. But we can then write

$$R_l(r)=r^lQ_l(r), \tag{25}$$

and consider the differential and integral equations for $Q_l(r)$, since $Q_l(r)$ is finite at the origin. Using (25) in (21), we find that $Q_l(r)$ satisfies

$$rQ_l''+2(l+1)Q_l'+r[v_0u(r)-\epsilon]Q_l=0. \tag{26}$$

We first discuss the formal solution of this equation. This solution, which expresses Q_l in terms of $Q_l(0)$ and $Q'_l(0)$, is in some ways simpler for the present case than for the one-dimensional case, since $Q_l'(0)$ is not, in general, independent of $Q_l(0)$. We shall discuss this in detail for two important cases: $u(r)$ regular at the origin as for a Gaussian or exponential potential, and $u(r)$ singular as $1/r$, as in a Yukawa potential. For the former case, we see directly, on evaluating (26) at the origin and recognizing that $Q_l(0)$ and $Q_l''(0)$ are finite, that

$$Q_l'(0)=0, \quad u(r) \text{ regular at the origin.}$$

Thus, the formal solution of (26), is determined completely by $Q_l(0)$. For the case that $u(r)$ is singular, we write

$$u(r)=w(r)/r, \tag{27}$$

where $w(r)$ is finite at the origin and, in fact, can be taken to be unity there. Again evaluating (26) at the origin, we see that

$$Q_l'(0)=-\frac{v_0}{2(l+1)}Q_l(0), \quad u(r) \text{ singular at the origin.}$$

For this case also then, $Q_l'(0)$ is fixed, so the formal solution is in terms of $Q_l(0)$ only. Since Eq. (26) for Q_l is homogeneous, the value of $Q_l(0)$ drops out of consideration and we can conveniently take

$$Q_l(0)=1. \tag{28}$$

The calculation of $Q_l(r)$ will take a fair amount of discussion, and we shall leave it for the next section. We turn then to the integral equation satisfied by Q_l; we want to evaluate it at the origin. We begin by substituting (25) in (24), when it becomes

$$r^lQ_l(r)=-Kv_0\int_0^{\infty}r'^lQ_l(r')u(r')\Gamma_l(r,r')r'^2dr'.$$

To extract $Q_l(0)$ from this, we write it out as

$$\begin{aligned}r^lQ_l(r)=-Kv_0\Big\{&h_l(iKr)\int_0^r j_l(iKr')u(r')Q_l(r')r'^{l+2}dr' \\ &+j_l(iKr)\int_r^{\infty}h_l(iKr')u(r')Q_l(r')r'^{l+2}dr'\Big\}.\end{aligned} \tag{29}$$

Now, for small r

$$h_l(iKr)\to-\frac{i\times1\times1\times3\times5\times\cdots(2l-1)}{(iKr)^{l+1}},$$

$$j_l(iKr)\to\frac{(iKr)^l}{1\times3\times5\times\cdots(2l+1)}$$

and with these expressions in (29), we see that the first integral vanishes in the limit $r\to0$, and a factor

r^l arises in the second which just cancels the r^l on the left-hand side. Thus, we have, remembering (28),

$$1=-\frac{Kv_0(iK)^l}{1\times3\times5\times\cdots(2l+1)}\times\int_0^\infty h_l(iKr')u(r')Q_l(r')r'^{l+2}dr'. \quad (30)$$

All that remains then is to determine $Q_l(r)$.

B. Potentials Regular at the Origin

In this section, we discuss the formal solution for $Q_l(r)$ for potentials which are regular at the origin; those with a $1/r$ singularity are discussed in the next section.

There are at least two possibilities. First, we might simply expand Q_l in a Taylor series, as we did in one dimension. In fact, the results are already at hand for one special case which is instructive to look at. Namely, if for $l=0$, we make the substitution

$$Q_0(r)=\chi(r)/r,$$

then the equation for $\chi(r)$ is identical to the one-dimensional Eq. (1),

$$\chi''=-[v_0u(r)-\epsilon]\chi.$$

The formal solution of this is then given by Eqs. (6), (11), and (12). To apply these results to the present case, we must however satisfy one further condition. That is, we know Q_0 must be finite at the origin, which means that $\chi(0)$ must be zero. Thus, $Q_0(r)$ is given by the one-dimensional formal series with $a=0$, or

$$Q_0(r)=\psi_b(r)/r. \quad (31)$$

If we put this into (30), we have the basic equation for s states,

$$1=v_0\int_0^\infty \psi_b(r')u(r')e^{-Kr'}dr'. \quad (32)$$

There is, however, another way we can go about finding a formal solution, without prejudice against the straightforward series form. To be concrete, let us look in detail at the solution for $Q_0(r)=\psi_b(r)/r$. This is of the form of a series of powers of r each times a coefficient which is a function of the U_0, $U_0^{(1)}$, $U_0^{(2)}$, $\cdots$. Moreover, although we have not remarked on it, it is clear that this series can be partially summed. For it is evident that for the special case that all $U_0^{(n)}$ are zero the potential is simply a constant and the series must represent the odd solution in a constant potential. That is, the series must represent $\sin(U_0^{1/2}r)/r$ and, in fact, in (11) one can pick out the terms, among others, which constitute the expansion of this function. This then suggest that the other terms in the series may be summable in a similar way into known, or at least universal, functions. Thus, there is, for example, in ψ_b, a term in which $U_0^{(1)}$ multiplies powers of r^4 and r^6, and this suggests the beginning of a series of even powers of r multiplying $U_0^{(1)}$, and similarly for a series of odd powers of r multiplying $U_0^{(2)}$.

We can get at these series from a more basic viewpoint if we look at the problem in the following way. The equation for Q_l is a *function* of r; it is also a *functional* of the quantity $U(r)$; we can take this to mean that it is a function of U_0 and of the infinite number of derivatives $U_0^{(1)}$, $U_0^{(2)}$, $\cdots$

$$Q_l=Q_l(r;\,U_0,\,U_0^{(1)},\,U_0^{(2)},\,\cdots). \quad (33)$$

We can imagine Q_l expanded in power series in either of two ways. We can consider it as a power series in r in which the coefficients are functions of the $U_0^{(n)}$; this is just the form in which we have presented the one-dimensional solution and the solution above for Q_0. Alternatively, we could expand it in an infinite-dimensional power series in the quantities $U_0^{(1)}$, $U_0^{(2)}$, $U_0^{(3)}$ $\cdots$ and their powers and products in which the "coefficients" are functions of r. That is, we could write

$$Q_l(r;\,U_0,\,U_0^{(1)},\,U_0^{(2)},\,\cdots)=S_l(r)+\sum_{s=1}^\infty \frac{U_0^{(s)}S_{l,s}(r)}{s!}+\sum_{\substack{s=1\\ t\geq s}}^\infty \frac{S_{l,st}(r)U_0^{(s)}U_0^{(t)}}{s!t!}+\cdots. \quad (34)$$

Such a series has at least one important advantage. We know the solution when all the derivatives $U_0^{(n)}$ are zero; as we have discussed above, it is just $j_l(U_0^{1/2}r)$ for R_l and this times r^{-l} for Q_l. Thus, the first term in the series corresponds to approximating the potential by a constant. One would, therefore, expect good convergence for potentials close to square wells.

The basic question now is whether the functions S_l, $S_{l,s}$, etc., can be calculated. A second, and equally important, question is that of the convergence of (34). The answer to the first question is yes; the details of construction of the series are given in the Appendix. From it we find, for example, for the case $l=0$, for which we shall shortly work out a numerical example.

$$S_0(r)=\frac{\sin(U_0^{1/2}r)}{U_0^{1/2}r} \quad (35)$$

and

$$S_{0,s}(r)=-\frac{s!}{(s+3)!}r^{s+2}B_s(U_0^{1/2}r). \quad (36)$$

Here

$$B_s(w)=\sum_{m=0}^\infty \frac{(s+3)!}{(s+2m+3)!}(-)^m\beta(s,m)w^{2m} \quad (37)$$

and $\beta(s,m)$ is expressed in terms of binomial coefficients

$$\beta(s,m)=\binom{s+1}{s}+\binom{s+3}{s}+\cdots\binom{s+2m+1}{s}.$$

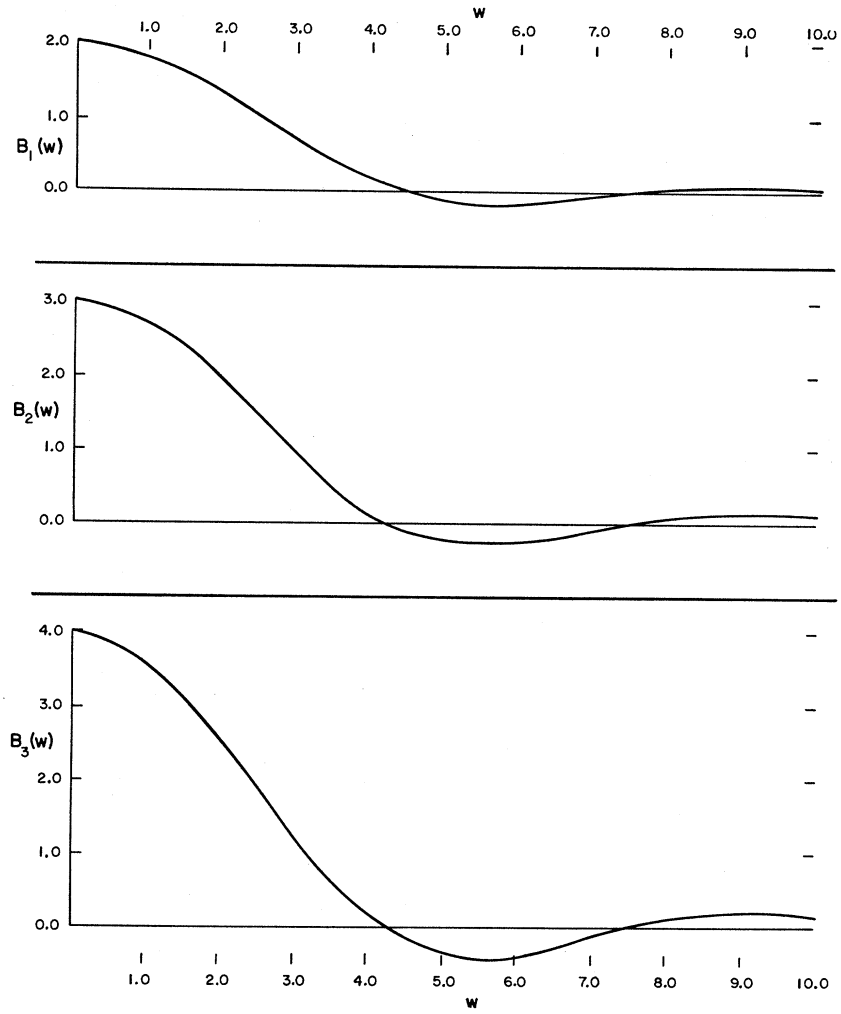

FIG. 2. The functions $B_s(w)$ for $s=1, 2, 3$.

The question of the convergence of the expansion (34) is not unrelated to the problem of explicitly calculating the higher functions $S_{l,st}$, etc., for if the expansion does converge well, the more complicated of these do not enter into practical calculations, and so do not need to be worked out at all. We have already begged this question somewhat above in that we have written out only the expression for $S_{0,s}$; this corresponds, in (34), to keeping only terms linear in the $U_0^{(n)}$. We shall shortly see, however, for the numerical example we adopt, that this is fairly good and hopefully it will be so for other cases as well.

We turn then to a numerical example. We consider the potential

$$u(r)=e^{-(r/a)^2}, \tag{38}$$

since there are quite exact variational calculations by Svartholm[3] with which to compare. For this potential, all $U_0^{(n)}$ with n odd are zero and

$$U_0^{(2)}=-\frac{2v_0}{a^2}, \quad U_0^{(4)}=\frac{12v_0}{a^4}, \quad U_0^{(6)}=-\frac{120v_0}{a^6}.$$

We then put (34), (35), and (36) into (30), use the reduced variables

$$y=v_0a^2, \quad z=\epsilon a^2,$$

and then rather arbitrarily truncate the formula by keeping only the terms involving the first two non-vanishing derivatives: $U_0^{(2)}$ and $U_0^{(4)}$. We get

$$1=\frac{y}{(y-z)^{1/2}}\int_0^\infty \sin((y-z)^{1/2}s)\exp(-s^2-z^{1/2}s)ds$$
$$+\frac{2y^2}{5!}\int_0^\infty B_2((y-z)^{1/2}s)s^5\exp(-s^2-z^{1/2}s)ds$$
$$-\frac{12y^2}{7!}\int_0^\infty B_4((y-z)^{1/2}s)s^7\exp(-s^2-z^{1/2}s)ds. \tag{39}$$

[3] N. Svartholm, Hakan Ohlssons, Lund, thesis, 1945 (unpublished).

Numerical results from this formula are given in Table II and compared with what appear to be the quite accurate variational calculations of Svartholm.[3] We see that the results are good to within several percent, which clearly leaves room for improvement but which is also good enough to indicate that there is nothing seriously wrong. To make this method into a really precise one some numerical experiments are now needed to determine, for example, the relative importance of keeping in (34) the higher derivatives $U_0^{(6)}$, etc. and of keeping terms nonlinear in the $U_0^{(n)}$, as $(U_0^{(2)})^2$, $U_0^{(2)}\,U_0^{(4)}$, etc.

C. Singular Potentials

Now we consider singular potentials, as defined by Eq. (27). With this definition, Eq. (26) becomes

$$rQ_l''+2(l+1)Q_l'+W(r)Q_l=0\,,\qquad W(r)=v_0w(r)-\epsilon r\,. \tag{40}$$

We want now to find the formal solution of this equation. As in the previous case, we can derive it in either of two ways: We can simply write it as a power series in r, with coefficients that are functions of the quantities $W_0^{(1)}, W_0^{(2)}\cdots$; or we can write it as a series of powers, and products of powers, of these quantities, with coefficients that are functions of r.

We first consider the former kind of series. We can simply consider this a Taylor series in r, i.e., can write

$$Q_l(r)=\sum_{n=0}^{\infty}(Q_l^{(n)})_0\frac{r^n}{n!}, \tag{41}$$

where we use the notation of Eq. (9). We can calculate the coefficients from Eq. (40), by differentiating it n times and evaluating it at the origin. If we do this, we get

$$(Q_l^{(n+1)})_0=P(n,l)(WQ_l)_0^{(n)}\,, \tag{42}$$

where

$$P(n,l)=-\frac{1}{n+2(l+1)}\,.$$

By successively setting $n=0, 1, 2, \cdots$ in (42), we can calculate the coefficients $(Q_l^{(n)})_0$, and so derive however many of the terms in the series (41) that we wish. We find in this way:

$$\begin{aligned}Q_l(r)=1&+W_0P(0,l)r+P(1,l)[(W_0)^2P(0,l)+W_0^{(1)}](r^2/2!)\\&+P(2,l)[(W_0)^3P(0,l)P(1,l)+W_0W_0^{(1)}(P(1,l)+2P(0,l))+W_0^{(2)}](r^3/3!)\\&+P(3,l)[(W_0)^4P(0,l)P(1,l)P(2,l)+W_0^2W_0^{(1)}\langle 3P(1,l)P(0,l)+P(2,l)[P(1,l)+2P(0,l)]\rangle\\&+3(W_0^{(1)})^2P(1,l)+W_0W_0^{(2)}(3P(0,l)+P(2,l))+W_0^{(3)}](r^4/4!)+\cdots.\end{aligned} \tag{43}$$

This series is obviously somewhat more complicated than the analogous one for potentials regular at the origin. Moreover, if we set all the derivatives $W_0^{(n)}$ equal to zero, the series does not approach that for a constant potential, as was the case previously. The reason is, of course, that for potentials regular at the origin, the first term in the Taylor-series expansion of the potential is a constant; in the present case, by contrast, potentials with a $1/r$ singularity have no Taylor series expansion around the origin.

There is, however, a limiting case of (43) which it is instructive to consider. Consider a pure Coulomb potential for which $w(r)=1$. We then have,

$$W_0=v_0\,,\qquad W_0^{(1)}=-\epsilon\,,\qquad W_0^{(n)}=0,\quad n=2, 3, 4\cdots.$$

Thus, those terms in (43) which involve only W_0 and $W_0^{(1)}$ and their powers represent the formal solution to the pure Coulomb case. We might proceed by writing this in terms of the hypergeometric function, and then sum the remaining terms which involve the $W_0^{(2)}$, $W_0^{(3)}\cdots$. This would be then quite analogous to the treatment of regular potentials where we took the solution to be that for a constant potential, plus a series in the $U_0^{(n)}$ which represented the deviation from constancy.

Partly for variety and partly because it appears easier for a beginning, we shall proceed in a different way in which we still can exhibit explicitly the Coulomb limit. We do this by writing the wave function for some level in the potential $w(r)$ as the product of the Coulomb wave function which would obtain if $w(r)$ were unity times a series which we can calculate from (43). Consider, for example, the ground state in a Yukawa potential $w(r)=e^{-r/r_0}$. For $r_0\to\infty$, we have the pure Coulomb case; if we use atomic units in the Schrödinger equation, we have for this case

$$v_0=2,\quad w(r)=1,\quad K^2\equiv\epsilon=1$$

and the ground-state wave function $Q_0(r)$ is just e^{-r}. For the Yukawa potential, also in these units, we can

TABLE II. The relation between $y=v_0a^2$ and $z=\epsilon a^2$ for the Gaussian potential $v(r)=-v_0e^{-r^2/a^2}$ as calculated from Eq. (39) and as given by the variation method of Svartholm.

z	y(Svartholm)	y[Eq. (39)]
0	2.69	2.84
0.5	5.33	5.61
1.5	7.84	8.40
3.0	10.9	11.8

TABLE III. Ground-state energies for the Yukawa potential $v(r)=-2e^{-\delta r}/r$: Length in atomic units, energy in Rydbergs; $\delta=0$ corresponds to the hydrogen atom.

δ	ϵ (Harris)[a]	ϵ from Eq. (47)
0.15	0.7309	0.7272
0.30	0.5153	0.5089
0.50	0.2962	0.2916
0.80	0.0894	0.0806

[a] G. Harris, Phys. Rev. **125**, 1131 (1962).

write, with δ dimensionless

$$w(r)=e^{-\delta r}. \tag{44}$$

For $Q_0(r)$, we can then assume

$$Q_0(r)=e^{-r}C(r), \tag{45}$$

and know now that as $\delta\to 0$, $C(r)\to 1$. We can get a formal power series for $C(r)$ by simply multiplying out the series (43) (with $l=0$) for $Q_0(r)$ and the series for e^r. If we do this, we get

$$C(r)=\left[1+\frac{r^2}{2}\left(\frac{\delta}{3}+\frac{\epsilon}{6}-\frac{1}{6}\right)+r^3\left(-\frac{\delta^2}{12}+\frac{\delta}{9}+\frac{\epsilon}{18}-\frac{1}{18}\right)+\frac{r^4}{120}(3\delta^3+\delta^2+4\delta\epsilon+\epsilon^2-1)+\cdots\right]. \tag{46}$$

We then put (45) and (46) back into (30), and do the integrals to get an explicit formula for δ versus K. For example, keeping only the first three terms in Eq. (46) for $C(r)$, we get the transcendental equation

$$1=\frac{2}{K+\delta+1}\left[1+\frac{\frac{2}{3}(\delta+\frac{1}{2}K^2-\frac{1}{2})}{(K+\delta+1)^2}+\frac{(-\frac{1}{2}\delta^2+\frac{2}{3}\delta+\frac{1}{3}K^2-\frac{1}{3})}{(K+\delta+1)^2}+\cdots\right]. \tag{47}$$

In Table III, we compare the results from this formula with variational results due to Harris. We see, as we would expect, that the results get worse for large values of δ, but presumbaly this could be improved by taking more terms in the series. These results are, however, enough to illustrate our present points.

ACKNOWLEDGMENT

I would like to thank Paul Tsipouras of the Data Analysis Branch of AFCRL for very able programming aid.

APPENDIX

We consider Eq. (26) of the text, which we rewrite in the form

$$Q_l''+U(r)Q_l=-\frac{2(l+1)Q_l'}{r}, \tag{A1}$$

where

$$U(r)=v_0u(r)-\epsilon. \tag{A2}$$

We assume that $U(r)$ is regular at the origin and can, therefore, be expanded in the Taylor series,

$$U(r)=\sum_{s=0}^{\infty}\frac{U_0^{(s)}r^s}{s!}. \tag{A3}$$

It will be convenient to define $F(s)$ by

$$F(s)=U_0^{(s)}/s!, \tag{A4}$$

and in terms of this, the form of the solution that we shall seek for Q_l is, from Eq. (34),

$$Q_l(r;U_0,U_0^{(1)},U_0^{(2)}\cdots)=S_l(r)+\sum_{s=1}^{\infty}S_{l,s}(r)F(s)+\sum_{\substack{s=1\\ t\geq s}}^{\infty}S_{l,st}(r)F(s)F(t)+\cdots. \tag{A5}$$

To express Q_l in this form, we shall first derive a formal power series solution of (A1), and then pick out from it the factors of $F(s)$, of $F(s)F(t)$, etc.; these factors will then be the functions $S_{l,s}$, $S_{l,st}$, etc. In (A1) then, we put

$$Q_l=\sum_{n=0}^{\infty}D_l(n)r^n \tag{A6}$$

as well as the expansion (A3) to get

$$\sum_{n=2}^{\infty}n(n-1)D_l(n)r^{n-2}+\sum_{s=0}^{\infty}\frac{U_0^{(s)}r^s}{s!}\sum_{m=0}^{\infty}D_l(m)r^m=-2(l+1)\sum_{n=1}^{\infty}nD_l(n)r^{n-2}.$$

If we equate coefficients of r^n in this equation, letting $s+m=n$ in the double summation, we get the infinite-term recursion relation

$$D_l(n+2)=-\frac{1}{(n+2)[(n+1)+2(l+1)]}\times\sum_{m=0}^{n}\frac{U_0^{(n-m)}}{(n-m)!}D_l(m).$$

It is convenient to replace $n+2$ by n in the last equation, and to define $H(n,l)$ by

$$H(n,l)=-n[n+2l+1],$$

in which case it becomes, on relabeling the summation variable,

$$D_l(n)=\frac{1}{H(n,l)}\sum_{n_1=0}^{n-2}F(n-2-n_1)D_l(n_1). \tag{A7}$$

We write out this last equation as follows, remembering

that $D_l(1)=0$, since $Q_l'(0)=0$, and $D_l(0)\equiv 1$,

$$D_l(n)=\frac{1}{H(n,l)}\left\{F(n-2)+\sum_{n_1=2}^{n-2}F(n-2-n_1)D_l(n_1)\right\}.$$

We iterate this once, i.e., we form $D_l(n_1)$ from it and then put the result back into its own right-hand side. We get

$$D_l(n)=\frac{1}{H(n,l)}\left\{F(n-2)+\sum_{n_1=2}^{n-2}\frac{F(n-2-n_1)F(n_1-2)}{H(n_1,l)}\right.$$
$$\left.+\sum_{n_1=2}^{n-2}\frac{F(n-2-n_1)}{H(n_1,l)}\sum_{n_2=2}^{n_1-2}F(n_1-2-n_2)D_l(n_2)\right\}. \quad \text{(A8)}$$

If we continue to iterate in this way, we end up with an infinite formal expression for $D_l(n)$, viz.,

$$D_l(n)=\frac{F(n-2)}{H(n,l)}+\sum_{n_1=2}^{n-2}\frac{F(n-2-n_1)F(n_1-2)}{H(n,l)H(n_1,l)}$$
$$+\sum_{n_1=2}^{n-2}\sum_{n_2=2}^{n_1-2}\frac{F(n-2-n_1)F(n_1-2-n_2)F(n_2-2)}{H(n,l)H(n_1,l)H(n_2,l)}+\cdots. \quad \text{(A9)}$$

We want to use (A9) to construct the functions $S_l(r)$, $S_{l,s}(r)\cdots$ defined by (A5). Since Q_l is a power series in r, the functions S_l, $S_{l,s}$, etc., will also be power series in r; the right-hand side of (A5) can be considered to be a rearranged version of the original series (A6). We can then write

$$S_l(r)=\sum_{n=0}^{\infty}d_l(n)r^n,$$

$$S_{l,s}(r)=\sum_{n=0}^{\infty}d_l(n,s)r^n,$$

$$S_{l,st}(r)=\sum_{n=0}^{\infty}d_l(n,st)r^n$$

$$\cdots$$

If we combine these equations with Eqs. (A5) and (A6), we have

$$D_l(n)=d_l(n)+\sum_{s=1}^{\infty}F(s)d_l(n,s)$$
$$+\sum_{\substack{s=1\\ t\geq s}}^{\infty}F(s)F(t)d_l(n,st)+\cdots. \quad \text{(A10)}$$

Consider first $S_l(r)$. To construct this is to find the coefficients $d_l(n)$. To do this, we choose a value of n and then pick out from the expression for $D_l(n)$ that part which is independent of any of the derivatives $U_0^{(s)}$, i.e., that involves only $F(0)$. This part is then just $d_l(n)$. We find, for example, with the normalization $d_l(0)=1$, corresponding to $D_l(0)=1$,

$$d_l(n)=0, \quad n \text{ odd}$$

$$d_l(2)=\frac{F(0)}{H(2,l)},$$

$$d_l(4)=\frac{F(0)^2}{H(2,l)H(4,l)},$$

$$\cdots$$

$$d_l(2n)=\frac{F(0)^n}{H(2,l)H(4,l)\cdots H(2n,l)}.$$

Thus, $S_l(r)$ is

$$S_l(r)=1+\frac{F(0)r^2}{H(2,l)}+\frac{F(0)^2r^4}{H(2,l)H(4,l)}$$
$$+\frac{F(0)^3r^6}{H(2,l)H(4,l)H(6,l)}+\cdots, \quad \text{(A11)}$$

and if we put in the defining expressions for $F(0)$ and for $H(n,l)$, it is straightforward to find that this series is related, as we would expect, to that for the spherical Bessel function $j_l(x)$. We find, in fact

$$S_l(r)=\frac{1\times 3\times 5\times\cdots(2l+1)}{(U_0^{1/2}r)^l}j_l(U_0^{1/2}r).$$

Now we work out the functions $S_{l,s}(r)$. We begin with $S_{l,1}$; the calculation of the general $S_{l,s}$ then follows the same lines. We imagine the formal expression (A9) for $D_l(n)$ substituted in the left-hand side of Eq. (A10). We then take $n=0, 1, 2, \cdots$ successively in the resulting equation and for each n pick out the factor of $F(1)$ on the left-hand side; this factor is just $d_l(n,1)$. It is easy to see that there is no such factor for $n=0$, 1, and 2, so $d_l(0,1)$, $d_l(1,1)$ and $d_l(2,1)$ are zero. For $n=3$, however, the left-hand side reduces to the single term

$$D_l(3)=\frac{F(1)}{H(3,l)}$$

so that

$$d_l(3,1)=\frac{1}{H(3,l)}.$$

We get no factors of $F(1)$ from Eq. (A9) for $n=4$, but for $n=5$ it becomes

$$D_l(5)=\frac{F(3)}{H(5,l)}+\frac{1}{H(5,l)}\sum_{n_1=2}^{3}\frac{F(3-n_1)F(n_1-2)}{H(n_1,l)}. \quad \text{(A12)}$$

A factor $F(1)$ arises in the summation for $n_1=2$ and

for $n_1=3$. We have then

$$d_l(5,1)=\frac{F(0)}{H(5,l)}\left[\frac{1}{H(2,l)}+\frac{1}{H(3,l)}\right]. \tag{A13}$$

Likewise, for $n=7$, we find

$$d_l(7,1)=\frac{F(0)^2}{H(7,l)}\left[\frac{1}{H(2,l)H(4,l)}+\frac{1}{H(2,l)H(5,l)}+\frac{1}{H(3,l)H(5,l)}\right].$$

Proceeding this way, it soon becomes clear that the general term is of the form, for $m\geq 1$,

$$d_l(2m+1,\,1)=\frac{F(0)^{m-1}M_l(m,1)}{H(2m+1,\,l)}$$

where the factor $M_l(m,1)$ is formed as follows: For $m=1$, we define $M_l(1,1)$ to be unity; for $m>1$, we form the sequence

$$2,\,4,\,6,\,8,\,\cdots\,2(m-1). \tag{A14}$$

We then form a set of sequences, of which the first of the set is just (A14). The next sequence of the set is got by increasing the *first* and all succeeding members of (A14) by unity, and the next sequence after that by increasing the *second* member and all succeeding members of (A14) by unity, and so on. Thus, we generate the set of sequences

$$\begin{array}{llll} 2,\,4,\,6,\,8, & \cdots & \cdots & 2(m-1), \\ 3,\,5,\,7,\,9, & \cdots & \cdots & 2m-1, \\ 2,\,5,\,7,\,9, & \cdots & \cdots & 2m-1, \\ 2,\,4,\,7,\,9, & \cdots & \cdots & 2m-1, \\ 2,\,4,\,6,\,8, & \cdots & 2m-2, & 2m-1. \end{array} \tag{A15}$$

Now, if $p_1,p_2\cdots p_q$ is any one of these sequences, we form an associated factor

$$1/H(p_1,l)H(p_2,l)\cdots H(p_q,l)$$

and add together all such factors, one for each sequence; the result is the factor $M_l(m,1)$. We can write this then

$$M_l(m,1)=\sum_{\substack{\text{All}\\ \text{sequences}\\ \text{in (A15).}}}\frac{1}{H(p_1,l)H(p_2,l)H(p_3,l)\cdots H(p_q,l)}.$$

With this definition, the coefficients $d_l(n,1)$ are now well defined. The series for $S_{l,1}(r)$ in terms of these coefficients is then

$$S_{l,1}(r)=\sum_{m=0}^{\infty}\frac{F(0)^m r^{2m+3}}{H(2m+3,\,l)}M_l(m+1,\,1).$$

In exactly the same manner, we find for the general case

$$S_{l,s}(r)=\sum_{m=0}^{\infty}\frac{F(0)^m r^{2m+s+2}}{H(2m+s+2,\,l)}M_l(m+1,\,s). \tag{A16}$$

Here, $M_l(m,s)$ is formed according to the same prescription as $M_l(m,1)$ except that in forming the related sequences like (A15), one adds s where one added unity in forming $M_l(m,1)$.

If now we specialize these results to the case $l=0$, using $H(n,0)=-n(n+1)$ and the definition of $F(s)$, it is not difficult to show that Eq. (A16) becomes the result in the text quoted as Eq. (36). Similarly, Eq. (A11), for $l=0$ becomes Eq. (35).