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Original article

Exact irregular solutions to radial Schrödinger equation for the case of hydrogen-like atoms

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ABSTRACT This study propounds a novel methodology for obtaining the explicit/closed representation of the two linearly independent solutions of a large class of second order ordinary linear differential equation with special polynomial coefficients. The proposed approach is applied for obtaining the closed forms of regular and irregular solutions of the Coulombic Schrödinger equation for an electron experiencing the Coulomb force, and examples are displayed. The methodology is totally distinguished from getting these solutions either by means of associated Laguerre polynomials or confluent hypergeometric functions. Analytically, both the regular and irregular solutions spread in their radial distributions as the system energy increases from strongly negative values to values closer to zero. The threshold and asymptotic behavior indicate that the regular solutions have an r^{ℓ} dependence near the origin, while the irregular solutions diverge as $r^{-\ell-1}$. Also, the regular solutions drop exponentially in proportion to $r^{n-1}\exp(-r/n)$, in natural units, while the irregular solutions grow as $r^{-n-1}\exp(r/n)$. Knowing the closed form irregular solutions leads to study the analytic continuation of the complex energies, complex angular momentum, and solutions needed for studying bound state poles and Regge trajectories.

KEYWORDS second exact solutions, irregular exact solutions, Coulombic Schrödinger equation, Frobenius method, Coulombic interaction

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1. Introduction

Finding the closed-form of the first (regular) and the second (irregular) solutions to the quantum Coulomb problem for negative energies have not been well elucidated by the literature. Although, the regular solutions to the Coulombic Schrödinger equation have been more elucidated by an infinite power series representation, but the irregular solutions to the Schrödinger equation in the case of a bound electron experiencing a Coulomb force are being ignored for several reasons. Some of them indicate that irregular solutions are ill-behaved at the origin (due to the irregular singularity) and unbounded at infinity. But ignoring irregular solutions based on fancy reasons is worthless as they can be of great interest in problems describing hydrogenic bound electronic waves. The independent irregular solutions to the Coulomb Schrödinger equation for hydrogen like atoms can be effectively deployed for studying the complex poles for the bound, resonance and virtual states, hydrogenic wave functions, Regge trajectories, Pade extrapolation, and so on. If the electron potential energy is Coulombic only within a shell region around a central region, then irregular solutions can be accomplished in deriving shell region solutions on the boundaries of the shell. Geilhufe et al. [1] effectively constructed a Green function by taking into consideration the first (regular) and the second (irregular) solutions of the scattering (single site) problem and thereafter discussed the asymptotic behavior of the resulting spherical wave functions. Newton [2] studied the two linearly independent solutions of one dimensional Schrödinger equation (SE) and noted that the regular solution (in the form of Whittaker functions) that lies in the right half plane experiences analyticity near the origin whereas the irregular solution lying in the left half plane experiences logarithmic singularity and infinite derivative in the vicinity of the origin. Cantelaube [3] ruled out the necessity of the usual boundary condition imposed in extracting the radial part of the Coulombic SE in spherical polar coordinates and concluded that the first solutions are regular, but the second solutions are either singular or pseudo functions, the latter arises when the second solutions are derived by taking the Laplacian of the radial part. Khelashvili and Nadareishvili [4] exploited the singular behavior of the Laplacian operator and found that the radial wave function is less regular than $1/r$, owing to the delta like singularity at the origin.

Seaten [5] studied the asymptotic behavior of both regular and irregular solutions of radial SE with the Coulomb potential and remarked that the two solutions for attractive potentials decay exponentially whereas, for repulsive potentials, the regular (irregular) solutions grow (decay) exponentially. Khalilov and Mamsurov [6] constituted an expression for the radial Green's function after converting the regular and irregular solutions of radial Dirac equation into the form of Whittaker functions and found that the first (regular) solutions are R-integrable in the vicinity of the origin whereas the second (irregular) solutions are integrable at the point of infinity. Michel [7] compared the analytical and numerical computations of the first (regular) and the second (irregular) solutions of zero dimensional SE with the Coulomb potential. The authors concluded that, along the real axis, the numerical computation of the radial wave functions is quite difficult as they can vary significantly by many orders for absolute values of principal quantum numbers. Nevertheless, the analytic computation becomes more problematic when these wave functions are continued analytically in the complex plane. After solving coupled radial SE having regular singularity in the vicinity of the origin and irregular singularity at infinity, Galilev and Polupanov [8] rehabilitated irregular (logarithmic) solutions into the forms of asymptotic expansions and regular solutions as an algebraic combination of logarithmic function, power function, and power series.

Axel Schulze-Halberg [9] derived a finite normal series (order zero) solution of 1D radial SE with a large class of singular potentials having irregular singularity in the vicinity of infinity and/or the origin and thereafter computed energy eigenvalues corresponding to the SE. Gersten [10] rehabilitated the regular and irregular (logarithmic) solutions of the SE into the forms of spherical Bessel's functions and thereafter deployed backward recurrence relations and the Cauchy integral formula to achieve a 5-digit numerical accuracy of the resulting special functions. Based upon the numerical solutions of the SE with nuclear plus Coulomb potential, Mukhaamedzhanov et al. [11] established a novel procedure for obtaining the scattering pole parameters corresponding to the resonance(narrow and broad), virtual (anti bound) and bound states and utilized them to study asymptotic behavior of the Coulomb wave functions.

Cattapan and Maglione [12] numerically evaluated characteristic roots (eigenvalues) and corresponding characteristic vectors(eigenfunctions) of the SE and exploited them, by means of Pade extrapolation (approximant), to analytically continue the bound-states Coulomb wave function into the scattering region and finally achieved a larger numerical accuracy of the resonance parameters.

To overcome the limitations of the Milne-Thompson method, Midy et al. [13] deployed the enduring LT (Lanczes Tau) method to numerically approximate the regular and irregular solutions of 1D SE, intended to extract the complex poles for the bound states, resonance and virtual states and finally achieved a 12-digit numerical accuracy of the resulting solutions. Thompson and Barnnet [14] made analytic continuation of the hypergeometric series and obtained some continued fractions for the logarithmic derivatives of first(regular) and second(irregular) Coulomb wave functions of the 1D SE and rehabilitated the resulting solutions into the forms of Whittaker and Bessel's functions. The explicit representation of the independent irregular solutions at hand can help us in studying the analytic behavior of Coulomb scattered-wave amplitudes as the energy of the scattered electron is extended into the complex plane, and as the electron angular momentum quantum number ℓ takes on complex values, such as in Regge pole analysis(See Gaspard [16]). Furthermore, the closed-form expressions for the irregular solutions, rather than the usual Laurent series representation, provide explicit answers to how the irregular solutions behave for the electron waves at large distances from the nucleus, useful in presentations of the quantum Coulomb problem.Toli and Zou [17] obtained a Taylor series expansion of the regular Coulomb wave functions and concluded that the exact solutions of the SE, having the Coulomb potential for molecules consisting of more than two particles, cannot be achieved. Simos [19] developed multiderivative methods for comparing the numerical solution of the 1D SE with the existing exponentially- fitted Raptis-Allison method and Ixaru-Rizea method. Parke and Maximon [20] deployed the extended version of the Cauchy integral formula for obtaining the closed- form second independent solutions of the confluent hypergeometric difference equation for the degenerate case. Liu and Mei [21] applied the Laplace transform method as well as the transcendental integral function method for obtaining the second independent infinite series solution of the time dependent SE for hydrogen like atoms.

Many times the Frobenius coefficients, required for the explicit power series representation of a solution to a 2^{nd} order differential equation, obey a three-term recursion relation which cannot be easily utilized. The difficultly comes from the fact that three-term recursion relations have two linearly independent solutions. While attempting to compute the first solution from the recursion, numerical contamination from the second solution can grow, destroying the accuracy of the first solution. We here consider a large class of ordinary second-order differential equations which yield, via the Frobenius method, two-term recursion relations that have explicit solutions. We derive simplifying results for the Forbenius coefficients. These are applied to find the irregular solution of the radial Schödinger equation for the case of hydrogen-like atoms. The irregular solution, having an $1/r^{l+1}$ as well as a logarithmic singularity at the origin, is not ordinarily considered. However, it could be used, for instance, in a 'toy' problem wherein the nucleus is given a finite size, say radius r_a, and there is a different potential energy for the electron at a radius $r_b > r_a$, such as a screened electron potential energy proportional to $e^{-r/b}/r$. Between the radius r_a and r_b, both the first and the second Coulombic solutions would enter the steady bound-state wave function solution to match boundary conditions at r_a and r_b. (These boundary conditions are that the wave function, determining electron probabilities, and its derivative, determining the electron charge flux, must match on the boundaries.) However, under realistic conditions, r_a is more than 10,000 times smaller than the RMS radius $\sqrt{\int_0^\infty r^2 \left|R(r)\right|^2 r^2 dr}$, so that the contribution of the second solution is also extremely small. Moreover, theoretical quantum chemists have developed far more sophisticated techniques for getting good wave functions for inner electrons in atoms. This is why we call the problem a 'toy'.

The rest of this research paper is organized as follows: Section 2 addresses the concept of the Frobenius method required for the subsequent development of the proposed work. Section 3 discusses attempts to develop a novel procedure for obtaining the explicit representation of the two exact solutions of a large class of second order ordinary linear homogeneous differential equation with polynomials coefficients. Section 4 validates the applicability of the proposed procedure by solving the Coulombic Schrödinger equation. Some example expressions, plots and asymptotic behavior of both the regular and the irregular solutions to the Coulombic SE are given in Section 5. Finally, Section 6 summarizes the concrete conclusions and future scope of the work done in this paper.

2. Frobenius method

A large class of 2^{nd} order homogeneous linear differential equations with polynomial coefficients and regular singularity at the origin can be expressed as:

$$LR \equiv r^2(\alpha_0 + \alpha_s r^s)R'' + r(\beta_0 + \beta_s r^s)R' + (\gamma_0 + \gamma_s r^s)R = 0, \tag{1}$$

where α_i, β_i, γ_i $(i = 0, s)$ are real constants with the additional provision that $\alpha_0 \neq 0$, and s needs not be positive nor any negative integer. The most commonly utilized procedure for obtaining the power series solutions to (1), under the situations, when the polynomial $r^2(\alpha_0 + \alpha_s r^s)$ and $r(\beta_0 + \beta_s r^s)$ possess regular singularity in the vicinity of $x = 0$, was first exploited by Frobenius [15]. Thus, following the work of Frobenius [15], equation (1) will admit at least one infinite series solution of the form:

$$R(r, m) = r^m \sum_{k=0}^{\infty} b_{sk}(m) r^{sk}. \tag{2}$$

Here, the factor r^m reflects the threshold behavior of the resulting solutions to (1) and the exponent 'm' is chosen so that the leading coefficient $b_0(m)$ is a non-zero constant. The Frobenius series on the right of equation (2) can be differentiated term by term and converges on some interval $(0, d)$ where d is the distance from the origin to the nearest zero of the polynomial $(\alpha_0 r + \alpha_s r^s)$ of arbitrary degree in the complex plane and has no zeros on $(0, d)$. Further, the coefficients $b_0(m), b_s(m), b_{2s}(m), \cdots$ and the exponent 'm' are independent of r and the term r^m may be complex for the negative powers of r or undefined at the regular singularity. Due to this reason, we shall consider only those solutions which are defined for positive values of r since solutions for negative powers of r can be similarly obtained by using the well-known result which states that if $r^m \sum_{k=0}^{\infty} b_{sk}(m) r^{sk}$ is a power series solution of $LR \equiv 0$ on the interval $(0, d)$, then $|r|^m \sum_{k=0}^{\infty} b_{sk}(m) r^{sk}$ is also a solution on the intervals $(-d, 0)$ and $(0, d)$, respectively. Moreover, the coefficients $b_{sk}(m_1)$ can be determined recursively for $k > 0$ and for $k = 0$, an "indicial" equation must be satisfied. If the roots m_1, m_2 with $m_1 \geq m_2$, of the indicial equation differ by an integer, that is, when $(m_1 - m_2)/s = t$, $t \in \mathbb{Z}^+$, then the two resulting solutions for $y(x)$ will not be independent.

3. Procedure

Finding the closed-form of the first (regular) and the second (irregular) solutions to equation (1) have been well elucidated by developing a novel procedure. The proposed procedure is then applied for obtaining the explicit representation of the two independent solutions as well as some radial wave functions related to the Coulombic Schrödinger equation. The underlying procedure of getting these solutions is totally distinguished from getting them either by means of associated Laguerre polynomials or functions of hypergeometric nature. We observe that the series on the right of equation (2) is a positive term series and hence it is uniformly as well as absolutely convergent, which in turn, possesses first order partial derivatives with respect to the argument r. Thus, term by term partial differentiation of equation (2) w.r.t. r yields

$$R'(r, m) = \sum_{k=0}^{\infty} (sk + m) b_{sk}(m) r^{sk+m-1}; \tag{3}$$

$$R''(r, m) = \sum_{k=0}^{\infty} (sk + m)(sk + m - 1) b_{sk}(m) r^{sk+m-2}, \tag{4}$$

where the primes indicate partial derivatives of R with respect to r. Define

$$f_i(m) = \alpha_i m(m - 1) + \beta_i m + \gamma_i, \tag{5}$$

where $i = 0$ or s and m is any number (real or complex) such that $f_0(sk + m)$ is defined for all positive integer values of k. A practical way to compute the coefficients $b_{sk}(m)\, \forall k \geq 1$, is through the following theorem.

Theorem 1. If $R = R(r,m) = r^m \sum_{k=0}^{\infty} b_{sk}(m) r^{sk}$ is a power series solution of $LR \equiv 0$. Then

$$LR \equiv f_0(m) b_0(m) r^m. \tag{6}$$

Proof: Insert expressions (3) and (4) into (1) to get

$$LR \equiv \sum_{k=0}^{\infty} \Big[\alpha_0(sk+m)(sk+m-1) + \beta_0(sk+m) + \gamma_0\Big] b_{sk}(m) r^{sk+m} + \sum_{k=0}^{\infty} \Big[\alpha_s(sk+m)(sk+m-1) + \beta_s(sk+m) + \gamma_s\Big] b_{sk}(m) r^{s(k+1)+m}. \tag{7}$$

Plugging the notations defined by (5) in the forgoing equation (7) yields

$$LR \equiv \sum_{k=0}^{\infty} f_0(sk+m) b_{sk}(m) r^{sk+m} + \sum_{k=0}^{\infty} f_s(sk+m) b_{sk}(m) r^{s(k+1)+m}. \tag{8}$$

The index of the second summation in (8) is a dummy parameter and hence, without loss of generality, it can be shifted from k to $k-1$ to obtain

$$LR \equiv \sum_{k=0}^{\infty} f_0(sk+m) b_{sk}(m) r^{sk+m} + \sum_{k=1}^{\infty} f_s(s(k-1)+m) b_{s(k-1)}(m) r^{sk+m}.$$

To obtain more clarity on the successive coefficients $b_{sk}(m)$ $\forall k \geq 1$, extracting the first non zero term and combining the rest with the second summation yields

$$LR \equiv f_0(m) b_0(m) r^m + \sum_{k=1}^{\infty} \Big[f_0(sk+m) b_{sk}(m) + f_s(s(k-1)+m) b_{s(k-1)}(m)\Big] r^{sk+m}. \tag{9}$$

For $LR = 0$ to be satisfied, the coefficient of r^m in the first term and of r^{sk+m} in the bracket of the summation must be vanished and hence it becomes necessary to define

$$b_{sk}(m) = -\frac{b_{s(k-1)}(m) f_s(s(k-1)+m)}{f_0(sk+m)} \quad \forall k \geq 1, \tag{10}$$

which completes the proof.

The equation $f_0(m) = 0$, so-called indicial equation, is quadratic in m and determines possible values of 'm' for a solution of the assumed Frobenius form to exist. The two-term recursion relation (10), with a given starting value for $b_0(m)$, will give one all the subsequent coefficients for larger values of k. We now see that the form of the original differential equation (1) allows for a two-term (rather than a three-term) recursion relation for the coefficients in a Frobenius series. Having this two-term recursion relation, it is straight forward to solve $b_{sk}(m)$ in terms of $b_0(m)$.

Thus, giving k the values, $1, 2, 3, ...$ to the recurrence relation (10) yields

$$b_s(m) = \frac{b_0(m)(-1)^1 f_s(m)}{f_0(s+m)}, \quad b_{2s}(m) = \frac{b_0(m)(-1)^2 f_s(s+m) f_s(m)}{f_0(2s+m) f_0(s+m)},$$

$$b_{3s}(m) = \frac{b_0(m)(-1)^3 f_s(2s+m) f_s(s+m) f_s(m)}{f_0(3s+m) f_0(2s+m) f_0(s+m)}$$

and so on. Recursively, we have

$$b_{sk}(m) = \frac{b_0(m)(-1)^k \prod_{j=1}^{k} (f_s(s(j-1)+m)}{\prod_{j=1}^{k} f_0(sj+m)} \quad \forall k \geq 1, \tag{11}$$

where $1 \leq j \leq k$ and $\prod_{j=k_1}^{k_2} b_j = 1$ if $k_2 < k_1$ for any expression b_j. The result (11) has been furnished to compute the coefficient $b_{sk}(m)$ in our procedure.

To understand our procedure, let us denote the two possible solutions for 'm' of the indicial equation $f_0(m) = 0$ as m_1, m_2 with $m_1 \geq m_2$. Here, we briefly discuss the situation when the roots differ by an integer, that is, when $(m_1 - m_2)/s = t$, $t \in \mathbb{Z}^+$. Since

$$f_0(sk+m_1) = \alpha_0 sk(sk+st) = \alpha_0 s^2 k(k+t) \neq 0 \quad \forall \alpha_0 \neq 0, \;\; s, m, t \in \mathbb{Z}^+,$$

it follows that $b_{sk}(m_1)$ is defined for each $k \geq 1$ and therefore, the method of Frobenius permits us to obtain the first power series solution of (1) as

$$R_1 = R(r, m_1) = \sum_{k=0}^{\infty} b_{sk}(m_1) r^{sk+m_1}.$$

But $f_0(sk + m_2) = \alpha_0 s^2 k(k - t)$ vanishes for $k = t$ and hence the coefficient $b_{sk}(m_2)$ can not be computed for $k \geq t$. In such situation, we construct the second solution as a linear combination of w_1 and w_2 as discussed in the following theorems.

Theorem 2. Let

$$w_1 = \left.\frac{\partial R}{\partial m}\right|_{m=m_1} = R(r, m_1) \log r + \sum_{k=0}^{\infty} b'_{sk}(m_1) r^{sk+m_1}$$

with the additional provision that $b_0(m_1) = 1$. Then

$$L(w_1) = L\left.\left(\frac{\partial(R)}{\partial m}\right)\right|_{m=m_1} = \alpha_0 s t r^{m_1}. \tag{12}$$

Proof: The series on the right hand side of (2) can be differentiated partially with respect to the argument m to obtain

$$\frac{\partial R}{\partial m} = \frac{\partial}{\partial m}\left(r^m \sum_{k=0}^{\infty} b_{sk}(m) r^{sk}\right) = r^m \log r \sum_{k=0}^{\infty} b_{sk}(m) r^{sk+m} + \sum_{k=0}^{\infty} b'_{sk}(m) r^{sk+m} =$$

$$R(r, m) \log r + \sum_{k=0}^{\infty} b'_{sk}(m) r^{sk+m}.$$

Let the primes indicate partial differentiation with respect to r, such that $\frac{dR}{dr} = \frac{\partial R}{\partial r}$; $\frac{d^2 R}{dr^2} = \frac{\partial^2 R}{\partial r^2}$. The resulting Theorem 1 yields

$$r^2(\alpha_0 + \alpha_s r^s)\frac{\partial^2 R}{\partial r^2} + r(\beta_0 + \beta_s r^s)\frac{\partial R}{\partial r} + (\gamma_0 + \gamma_s r^s)R = f_0(m) b_0(m) r^m. \tag{13}$$

Both sides of equation (13) can be partially differentiated with respect to the argument m, which yields

$$r^2(\alpha_0 + \alpha_s r^s)\frac{\partial^2}{\partial r^2}\left(\frac{\partial R}{\partial m}\right) + r(\beta_0 + \beta_s r^s)\frac{\partial}{\partial r}\left(\frac{\partial R}{\partial m}\right) + (\gamma_0 + \gamma_s r^s)\frac{\partial R}{\partial m} =$$

$$L\left[\frac{\partial R}{\partial m}\right] = f'_0(m) b_0(m) r^m + f_0(m) b'_0(m) r^m + f_0(m) b_0(m) r^m \log r.$$

Setting $m = m_1$ yields the desired result.

Theorem 3. Assume the coefficients $b_s(m_2), b_{2s}(m_2), \ldots\ b_{s(t-1)}(m_2)$ are suitable chosen. Let $w_2 = \sum_{k=0}^{t-1} b_{sk}(m_2) r^{sk+m_2}$ with the provision that $b_0(m_2) = 1$, then

$$L(w_2) = f_s(m_1 - s) b_{s(t-1)}(m_2) r^{m_1}. \tag{14}$$

Proof: Since w_2 is a polynomial of degree $t - 1$, we can, suitably, choose $b_{st}(m_2) = b_{s(t+1)}(m_2) = \ldots = 0$. Under these restricted conditions, we have

$$w_2 = \sum_{k=0}^{t-1} b_{sk}(m_2) r^{sk+m_2} = \sum_{k=0}^{t-1} b_{sk}(m_2) r^{sk+m_2} + \sum_{k=t}^{\infty} b_{sk}(m_2) r^{sk+m_2} = \sum_{k=0}^{\infty} b_{sk}(m_2) r^{sk+m_2}.$$

With the aid of equation (9), the foregoing equation yields

$$\begin{aligned}
L(w_2) &= \sum_{k=1}^{\infty} \left(f_0(sk + m_2) b_{sk}(m_2) + f_s(s(k-1) + m_2) b_{s(k-1)}(m_2)\right) r^{sk+m_2} \\
&= \sum_{k=1}^{t-1} \left(f_0(sk + m_2) b_{sk}(m_2) + f_s(s(k-1) + m_2) b_{s(k-1)}(m_2)\right) r^{sk+m_2} \\
&+ \left(f_0(st + m_2) b_{st}(m_2) + f_s(s(t-1) + m_2) b_{s(t-1)}(m_2)\right) r^{st+m_2} \\
&+ \sum_{k=t+1}^{\infty} \left(f_0(sk + m_2) b_{sk}(m_2) + f_s(s(k-1) + m_2) b_{s(k-1)}(m_2)\right) r^{sk+m_2}.
\end{aligned}$$

Since $f_0(sk+m_2) = \alpha_0 s^2 k(k-t) \neq 0 \, \forall 1 \leq k \leq t-1$, we can use (10) to choose the coefficients $b_s(m_2)$, $b_{2s}(m_2)$, ... $b_{s(t-1)}(m_2)$ to satisfy

$$b_{sk}(m_2) = -\frac{f_s(s(k-1)+m_2)b_{s(k-1)}(m_2)}{f_0(sk+m_2)} = (-1)^k \prod_{j=1}^{k} \frac{f_s(s(j-1)+m_2)}{f_0(sj+m_2)} \quad \forall\, 1 \leq k \leq t-1. \tag{15}$$

With the aid of newly introduced formula (15) and employing the conditions $f_0(st+m_2) = f_0(m_1) = 0$ and $b_{st}(m_2) = b_{s(t+1)}(m_2) = ... = 0$, we finally have

$$L(w_2) = \big(f_s(s\,(t-1)+m_2)b_{s(t-1)}(m_2)\big)\, r^{st+m_2} = f_s(m_1-s)b_{s(t-1)}(m_2)r^{m_1}.$$

We next move to compute the coefficients $b'_{sk}(m_1) \, \forall k \geq 1$, which will strengthen the subsequent development of the proposed procedure.

3.1. Computation of $b'_{sk}(m_1)$

In finding the coefficient $b'_{sk}(m_1)$, it is legitimate to take logarithm of each member of equation (11) and write

$$\log\big|b_{sk}(m)\big| = \sum_{j=1}^{k} \log\big|f_s\,(s(j-1)+m)\,\big| - \sum_{j=1}^{k} \log\big|f_0(sj+m)\big| + \log\big|b_0(m)\big|.$$

Term by term logarithmic differentiation of each term of the foregoing series with respect to m yields

$$\frac{b'_{sk}(m)}{b_{sk}(m)} = \sum_{j=1}^{k} \frac{f'_s\,(s(j-1)+m)}{f_s\,(s(j-1)+m)} - \sum_{j=1}^{k} \frac{f'_0(sj+m)}{f_0(sj+m)} + \frac{b'_0(m)}{b_0(m)}.$$

The last term on the right in above vanishes, since $b_0(m_1) = 1$. Thus, setting $m = m_1$, we discover that

$$b'_{sk}(m_1) = b_{sk}(m_1)J_{sk}(m_1), \tag{16}$$

where

$$J_{sk}(m_1) = \sum_{j=1}^{k} \frac{f'_s\,(s(j-1)+m_1)}{f_s\,(s(j-1)+m_1)} - \sum_{j=1}^{k} \frac{f'_0(sj+m_1)}{f_0(sj+m_1)}. \tag{17}$$

The expression, formed by pair of equations (16) and (17), will act as an important formula for obtaining the second exact power series solution of (1). Next, we turn to establish one more important formula involved in obtaining the linear combination $L(Cw_1+w_2)$ which will put us in a better position to construct obtain the desired second exact solution to Coulombic Schrödinger equation. With the aid of equations (12) and (14), we finally have

$$L(Cw_1+w_2) = CL(w_1) + L(w_2) = C\alpha_0 st r^{m_1} + f_s(m_1-s)b_{s(t-1)}(m_2)r^{m_1}.$$

Lastly, We choose C such that

$$C = -\frac{f_s(m_1-s)b_{s(t-1)}(m_2)}{\alpha_0 st} \text{ so that } L(Cw_1+w_2) = 0,$$

which shows that $R_2 = R\,(r,m_2) = Cw_1 + w_2$ is the second exact power series solution of (1). However, if $C = 0$, then there is no need to compute w_1 and hence, the second solution in this case becomes $R_2 = R\,(r,m_2) = w_2$.

4. Two exact solutions of the Coulombic Schrödinger equation

To exemplify the procedure, we consider the case when $s = 1$. (The resulting differential equation is then of hypergeometric type.) We apply the proposed procedure for obtaining two exact solutions to the Coulombic Schrödinger equation:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2m}{\hbar^2}\left(E - V(r) - \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right)R = 0, \tag{18}$$

where the non negative integer ℓ represents the angular momentum quantum number, $\hbar = h/(2\pi)$, h is Planck's constant, E represents the total energy of the system and $V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$ represents the potential energy. Incidentally, the Coulomb potential energy, $V(r)$, admits continuous states for $E > 0$, describing electron- nucleus scattering, and discrete bound states for $E < 0$. We shall confine our discussion to the latter. Therefore, the values of $\kappa \equiv \left|\frac{\sqrt{-2mE}}{\hbar}\right|$ will be taken as a positive real number with the units of inverse length.

Under these restrictions, equation (18) reduces to the following form:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left(-\kappa^2 + 2\left(\frac{Zme^2}{4\pi\epsilon_0\hbar^2}\right)\cdot\frac{1}{r} - \frac{\ell(\ell+1)}{r^2}\right)R = 0.$$

Dividing throughout by κ^2 and defining $\kappa_0 = \dfrac{Zme^2}{4\pi\epsilon_0\hbar^2}$ in the foregoing equation, we obtain

$$\frac{1}{(\kappa r)^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left(-1+\frac{2\kappa_0}{\kappa}\frac{1}{(\kappa r)}-\frac{\ell(\ell+1)}{(\kappa r)^2}\right)R=0, \tag{19}$$

which can be further simplified as

$$r^2\frac{d^2R}{dr^2}+2r\frac{dR}{dr}+\Big(-\kappa^2r^2+2\kappa_0 r-\ell(\ell+1)\Big)R=0. \tag{20}$$

The parameter κ_0 is the inverse of the Bohr radius a. We first examine the asymptotic behavior of the solutions of (20) for large value of r. For this, take $\rho=\kappa r$ so that $\dfrac{d\rho}{dr}=\kappa$. Thus,

$$\frac{dR}{dr}=\frac{dR}{d\rho}\cdot\frac{d\rho}{dr}=\kappa\frac{dR}{d\rho};\ \frac{d}{dr}\left(r^2\frac{dR}{dr}\right)=\rho^2\frac{d^2R}{d\rho^2}+2\rho\frac{dR}{d\rho}.$$

Inserting these derivatives into (20) yields

$$\frac{d^2R}{d\rho^2}+\frac{2}{\rho}\frac{dR}{d\rho}+\left(-1+\frac{2\kappa_0}{\kappa}\frac{1}{\rho}-\frac{\ell(\ell+1)}{\rho^2}\right)R=0. \tag{21}$$

For large values of ρ, the coefficient in parenthesis can be approximated by -1, so equation (21) reduces to

$$\frac{d^2R}{d\rho^2}\cong R. \tag{22}$$

The general solution of (22) is given by $R\cong c_1e^{\rho}+c_2e^{-\rho}$, but e^{ρ} blows up for large value of ρ, which is an unbounded solution. Therefore, we must have $c_1=0$. That leaves $R\cong c_2e^{-\rho}$. Matters are simplified if we extract the asymptotic behavior from R. Thus, we define a new function $u(r)$ through

$$R(r)=e^{-\rho}u(r)=e^{-\kappa r}u(r). \tag{23}$$

Next, we have

$$\frac{dR}{dr}=e^{-\kappa r}\left(\frac{du}{dr}-\kappa u\right);\ \frac{d^2R}{dr^2}=e^{-\kappa r}\left(\frac{d^2u}{dr^2}-2\kappa\frac{du}{dr}+\kappa^2u\right).$$

Inserting these derivatives and (23) into (20) yields

$$r^2\frac{d^2u}{dr^2}+2r(1-\kappa r)\frac{du}{dr}+\left(-\ell(\ell+1)+2\left(\kappa_0-\kappa\right)r\right)u=0 \tag{24}$$

Here, we see that $r=0$ is a regular singular point. In our notations, we have

$$s=1,$$
$$\alpha_0=1,\quad \alpha_1=0;\quad \beta_0=2,\quad \beta_1=-2\kappa;\quad \gamma_0=-\ell(\ell+1),\quad \gamma_1=2(\kappa_0-\kappa).$$
$$f_0(m)=(m-\ell)(m+\ell+1),\quad f_0'(m)=2m+1;$$
$$f_1(m)=-2\kappa\left(m-\eta+1\right),\quad f_1'(m)=-2\kappa,\ \text{where } \kappa_0=\kappa\eta.$$

4.1. Comments and discussion

The roots of the indicial equation $f_0(m)=0$ are $m=\ell,-\ell-1$. Take $m_1=\ell, m_2=-\ell-1$ so that $m_1-m_2=2\ell+1=t$ where t is a positive integer. Thus, by Frobenius method, equation (20) has at least one solution of the form

$$R(r,m)=e^{-\kappa r}\sum_{k=0}^{\infty}b_k(m)r^{k+m}. \tag{25}$$

Since $e^{-\kappa r}=1-\kappa r+\dfrac{\kappa^2r^2}{2}+\cdots$, the radial wave function $R(r)$ behaves as $b_0(m)r^m$ for small r. Therefore, for $m=\ell$, $R(r)$ is not singular at the origin. But for $m=-\ell-1$, $R(r)\propto 1/r^{\ell+1}$ for small r. Since $\ell=0,1,2,3,\cdots$, the root $m=-\ell-1$ makes the term $1/r^{\ell+1}$ infinite at the origin. But, for the bound state eigenfunction to be normalized, we should have

$$\int_0^{\infty}R^2r^2dr\propto\int_0^{a}\frac{1}{r^{2\ell}}dr\propto\left.\frac{1}{r^{2\ell-1}}\right|_0^a, \tag{26}$$

where a is a small number. The $m=-\ell-1$ case gives states unnormalizable when $\ell>0$. When $\ell=0$, the divergence of the $R(r)$ near the origin gives one a radial function which no longer satisfies the original SE, since the diverge at the origin is strong enough to make $LR(r)=-(4\pi/r^2)\delta(r)$, where $\delta(r)$ is the Dirac delta function (see Messiah [18, p.352]). For this reason, standard references reject this root. Little effort is seen in the literature for obtaining the second exact solution of the Coulombic Schrödinger equation.

4.2. First exact solution of Coulombic Schrödinger equation

By the Frobenius method, equation (24) has at least one solution of the form

$$u(r,m) = \sum_{k=0}^{\infty} b_k(m) r^{k+m}. \tag{27}$$

Calculating the coefficients by successive differentiating a differential equation may be excellent in theory, but it is usually not a practical computational procedure. Rather, one might try to evaluate $b_k(m)$ recursively, one by one by writing the recurrence relation (10) first for $k = 1$, then $k = 2$, and so forth. Alternatively, we can convert the general formula for $b_k(m)$ in terms of $b_0(m)$. Thus, equation (10) gives one

$$b_k(m) = -\frac{f_1(k-1+m)b_{k-1}(m)}{f_0(k+m)} = \frac{2\kappa\,(k+m-\eta)\,b_{k-1}(m)}{(k+m-\ell)(k+m+\ell+1)} \quad \forall k \geq 1.$$

Giving k the values $1, 2, 3, ...,$

$$\begin{aligned} b_1(m) &= \frac{(2\kappa)^1\, b_0(m)\,(1+m-\eta)}{(1+m-\ell)(1+m+\ell+1)}, \\ b_2(m) &= \frac{(2\kappa)^2\, b_0(m)\,(2+m-\eta)\,(1+m-\eta)}{(2+m-\ell)(1+m-\ell)(2+m+\ell+1)(1+m+\ell+1)}, \\ &\dots \\ b_k(m) &= (2\kappa)^k\, b_0(m) \prod_{j=1}^{k} \frac{(j+m-\eta)}{(j+m-\ell)(j+m+\ell+1)} \quad \forall\ k \geq 1. \end{aligned} \tag{28}$$

Setting $m = m_1 = \ell$ in equation (28) yields

$$b_k(\ell) = \frac{(2\kappa)^k\, b_0(\ell)}{k!} \prod_{j=1}^{k} \frac{j+\ell-\eta}{j+2\ell+1}. \tag{29}$$

Changing k to $k+1$ in the resulting equation (29) to obtain

$$b_{k+1}(\ell) = \frac{(2\kappa)^{k+1}\, b_0(\ell)}{(k+1)!} \prod_{j=1}^{k+1} \frac{j+\ell-\eta}{j+2\ell+1} = \frac{2\kappa(k+1+\ell-\eta)}{(k+1)(k+2\ell+2)} b_k(\ell). \tag{30}$$

Suppose $B_k(m)$ represents the k^{th} term of the series represented by (27). Using (30), the ratio of $(k+1)^{th}$ term to k^{th} term of this series for the case $m = m_1 = \ell$ is represented as

$$\frac{B_{k+1}(\ell)}{B_k(\ell)} = \frac{b_{k+1}(\ell)}{b_k(\ell)} r = \frac{2\kappa\,(k+1+\ell-\eta)}{(k+1)(k+2\ell+2)} r \cong \frac{2\kappa r}{k} \text{ for large } k.$$

This means that the first solution $u_1(r) = u(r,\ell)$ is asymptotically equals to $e^{2\kappa r}$. This implies $R_1(r) = R(r,\ell) = e^{-\kappa r} u_1(r) \cong e^{\kappa r}$ which blows up for large value of r. This means the series solution $u_1(r) = u(r,\ell)$ must terminate. This implies there must exist some maximum integer k such that $b_k \neq 0$, and $b_{k+1} = 0, b_{k+2} = 0$ and so on. This is possible only if we can choose $k+\ell+1-\eta = 0$ so that $\eta = k+\ell+1$ (so called principal quantum number) This suggests that $R_1(r)$ is a polynomial of maximum degree $\eta - \ell - 1$. Setting $b_0(m_1) = 1$, and using $\eta \equiv \kappa_0/\kappa$, the first exact series solution represented by (25) is finally expressed as

$$R\,(r, m_1) = e^{-\kappa r} u(r) = e^{-\frac{Zr}{\eta a}} \sum_{k=0}^{\eta-\ell-1} b_k(\ell) r^{k+\ell} = e^{-\frac{Zr}{\eta a}} r^\ell \sum_{k=0}^{\eta-\ell-1} \frac{1}{k!} \prod_{j=1}^{k} \frac{(j+\ell-\eta)}{(j+2\ell+1)} \left(\frac{2Zr}{\eta a}\right)^k. \tag{31}$$

The sum factor is the associated Laguerre polynomial $L^{2\ell+1}_{\eta-\ell-1}(2Zr/(\eta a)$.

4.3. Second exact solution of the Coulombic Schrödinger equation

We first establish the fact that two solutions of the indicial equation give a set of linearly dependent solutions to equation (25). For this, changing k to $k+1$ in (28) to obtain

$$b_{k+1}(m) = \frac{(2\kappa)^{k+1}\,(k+1+m-\eta)\,b_0(m)}{(k+1+m-\ell)(k+1+m+\ell+1)} \cdot \prod_{j=1}^{k} \frac{(j+m-\eta)}{(j+m-\ell)(j+m+\ell+1)}. \tag{32}$$

Setting $m = \ell,\ b_0(\ell) = 1$, the foregoing equation (32) yields

$$b_{k+1}(\ell) = \frac{(2\kappa)^{k+1}\,(k+1+\ell-\eta)}{(k+1)(k+2\ell+2)} \cdot \frac{1}{k!} \cdot \frac{\prod_{j=1}^{k}(j+\ell-\eta)}{\prod_{j=1}^{k}(j+2\ell+1)}.$$

But

$$\prod_{j=1}^{k}(j+2\ell+1)=\frac{(k+2\ell+1)!}{(2\ell+1)!}$$

and

$$\prod_{j=1}^{k}(j+\ell-\eta)=(k+\ell-\eta)! \text{ and vanishes for } j\leq\eta-\ell.$$

Therefore

$$b_{k+1}(\ell)=\frac{(2\kappa)^{k+1}(k+1+\ell-\eta)!(2\ell+1)!}{(k+1)!(k+2\ell+2)!}. \tag{33}$$

Similarly, setting, $m=-\ell-1$, $b_0(-\ell-1)=\dfrac{(2\ell+1)!}{(2\kappa)^{2\ell+1}}$ in equation (32) to get

$$b_{k+1}(-\ell-1)=\frac{(2\kappa)^{k+1}(k-\ell-\eta)\,(2\ell+1)!}{(k+1)!(k-2\ell)\,(2\kappa)^{2\ell+1}}\cdot\frac{\prod_{j=1}^{k}(j-\ell-\eta-1)}{\prod_{j=1}^{k}(j-2\ell-1)}.$$

Changing k to $k+2\ell+1$, we get

$$b_{k+2\ell+1+1}(-\ell-1)=\frac{(2\kappa)^{k+2\ell+2}(k+\ell+1-\eta)\,(2\ell+1)!}{(k+1)!(k+2\ell+2)!\,(2\kappa)^{2\ell+1}}\cdot\frac{\prod_{j=1}^{k+2\ell+1}(j-\ell-\eta-1)}{\prod_{j=1}^{k+2\ell+1}(j-2\ell-1)}.$$

But

$$\prod_{j=1}^{k+2\ell+1}(j-2\ell-1) \text{ will vanish for } j\leq 2\ell+1, \text{ and otherwise}$$
$$\prod_{j=2\ell+2}^{k+2\ell+1}(j-2\ell-1)=k!.$$

Also, $\prod_{j=1}^{k+2\ell+1}(j-\ell-1-\eta)$ vanishes for $j\leq\eta+\ell+1$, and otherwise

$$\prod_{j=\eta+\ell+2}^{k+2\ell+1}(j-\ell-1-\eta)=(k+\ell-\eta)(k+\ell-\eta-1)...(1)=(k+\ell-\eta)!.$$

Therefore

$$b_{k+2\ell+1+1}(-\ell-1)=\frac{(2\kappa)^{k+1}(k+\ell+1-\eta)!(2\ell+1)!}{(k+1)!(k+2\ell+2)!}, \tag{34}$$

which is exactly the same as (33). This suggests that the two solutions of the indicial equation yield a set of two linearly dependent solutions to the Coulombic Schrödinger equation (18). In other words, out of these two, only one of them is useful and the other one can be dropped. Interestingly, discarding one of the solution has nothing to do with the regular singularity at $r=0$. Incidentally, we will construct another linearly independent solution of the Coulombic SE (24) by employing the general procedure proposed in Section 3.

4.3.1. Computation of $b'_k(\ell)\;\forall\; k\geq\eta-\ell$. Employing the resulting equations (16) and (17) for the case $m=\ell$, $b_0(\ell)=1$ and $\kappa=\dfrac{Z}{\eta a}$ to get

$$b'_k(\ell)=b_k(\ell)J_k(\ell), \tag{35}$$

where

$$\begin{aligned} b_k(\ell) &= \frac{1}{k!}\prod_{j=1}^{k}\frac{(j+\ell-\eta)}{(j+2\ell+1)}\left(\frac{2Z}{\eta a}\right)^k \;\forall\, k\geq 1;\\ J_k(\ell) &= \sum_{j=1}^{k}\frac{f_1'(j-1+\ell)}{f_1(j-1+\ell)}-\sum_{j=1}^{k}\frac{f_0'(j+\ell)}{f_0(j+\ell)}=\sum_{j=1}^{k}\left(\frac{1}{j-\eta+\ell}-\frac{1}{j}-\frac{1}{j+2\ell+1}\right), \end{aligned}$$

which becomes an indeterminate for $j = \eta - \ell$. To overcome this situation, we re-write equation (28) as

$$b_k(m) = b_0(m)\frac{\prod_{j=1}^{\eta-\ell}(m-\eta+j)\prod_{j=\eta-\ell+1}^{k}(j+m-\eta)}{\prod_{j=1}^{k}(j+m-\ell)(j+m+\ell+1)}\left(\frac{2Z}{\eta a}\right)^k$$
$$= b_0(m)\frac{(m-\eta+1)(m-\eta+2)\cdots(m-\ell-1)(m-\ell)\prod_{j=\eta-\ell+1}^{\eta-\ell}(j+m-\eta)}{\prod_{j=1}^{k}(j+m-\ell)(j+m+\ell+1)}\left(\frac{2Z}{\eta a}\right)^k,$$

which vanishes for $m = \ell$. Therefore, we re-write the foregoing equation as

$$b_k(m) = (m-\ell)\, C_k(m), \tag{36}$$

where

$$C_k(m) = b_0(m)\frac{(m-\eta+1)(m-\eta+2)\cdots(m-\ell-1)\prod_{j=\eta-\ell+1}^{k}(j+m-\eta)}{\prod_{j=1}^{k}(j+m-\ell)(j+m+\ell+1)}\left(\frac{2Z}{\eta a}\right)^k.$$

Differentiating the resulting equation (36) with respect to m yields

$$b'_k(m) = (m-\ell)C'_k(m) + C_k(m). \tag{37}$$

Plugging the root $m = \ell$, $b_0(\ell) = 1$ into (37) yields

$$b'_k(\ell) = C_k(\ell) = \frac{(\ell-\eta+1)(\ell-\eta+2)\cdots(\ell-\ell-2)(\ell-\ell-1)\prod_{j=\eta-\ell+1}^{k}(j+m-\eta)}{\prod_{j=1}^{k}(j)(j+2\ell+1)}\left(\frac{2Z}{\eta a}\right)^k$$
$$= \frac{(-1)^{\eta-\ell-1}(\eta-\ell-1)!\prod_{j=\eta-\ell+1}^{k}(j+\ell-\eta)}{k!\prod_{j=1}^{k}(j+2\ell+1)}\left(\frac{2Z}{\eta a}\right)^k.$$

But

$$\prod_{j=1}^{k}(j+2\ell+1) = (1+2\ell+1)(2+2\ell+1)\cdots(k-1+2\ell+1)(k+2\ell+1) = \frac{(k+2\ell+1)!}{(2\ell+1)!}.$$

Also

$$\prod_{j=\eta-\ell+1}^{k}(\ell-\eta+j) = (\ell-\eta+\eta-\ell+1)(\ell-\eta+\eta-\ell+2)(\ell-\eta+\eta-\ell+3)\cdots(\ell-\eta+k)$$
$$= 1\cdot 2\cdot 3\cdots(\ell-\eta+k) = (k-\eta+\ell)!.$$

Therefore

$$b'_k(\ell) = \frac{(-1)^{\eta-\ell-1}(\eta-\ell-1)!(k-\eta+\ell)!(2\ell+1)!}{k!(k+2\ell+1)!}\left(\frac{2Z}{\eta a}\right)^k \quad \forall k \geq \eta-\ell.$$

4.3.2. Computation of $b'_k(\ell)$ $\forall 1 \leq k \leq \eta-\ell-1$. Re-writing equation (28) as

$$b_k(m) = \frac{b_0(m)(m-\eta+k)(m-\eta+k-1)\cdots(m-\eta+3)(m-\eta+2)(m-\eta+1)\left(\frac{2Z}{\eta a}\right)^k}{(m-\ell+k)(m-\ell+k-1)\cdots(m-\ell+1)(m+\ell+1+k)(m+\ell+1+k-1)\cdots(m+\ell+2)}$$
$$= \frac{b_0(m)(m-\eta+k)!(m-\ell)!(m+\ell+1)!}{(m-\ell+k)!(m+\ell+1+k)(m-\eta)!}\left(\frac{2Z}{\eta a}\right)^k.$$

Setting $m = \ell$, $b_0(\ell) = 1$, in the foregoing equation, in this case, yields

$$b'_k(\ell) = \frac{\partial}{\partial m}\frac{(m-\eta+k)!(m-\ell)!(m+\ell+1)!}{(m-\ell+k)!(m+\ell+1+k)(m-\eta)!}\left(\frac{2Z}{\eta a}\right)^k\bigg|_{m=\ell}. \tag{38}$$

The expression on the right hand side of (40) can be further simplified as shown in the following theorem.
Theorem 4. The coefficient

$$\frac{\partial}{\partial m}\frac{(m-\eta+k)!}{(m-\eta)!}\frac{(m-\ell)!}{(m-\ell+k)!}\frac{(m+\ell+1)!}{(m+\ell+1+k)!}\bigg|_{m=\ell}$$

simplifies to

$$\frac{(-1)^{k+1}}{k!}\left(\prod_{j=1}^{k}\frac{\eta-\ell-j}{2\ell+1+j}\right)\sum_{j=1}^{k}\left(\frac{1}{\eta-\ell-j}+\frac{1}{2\ell+1+j}+\frac{1}{j}\right). \tag{39}$$

Proof: Define

$$c(\eta,\ell,k) = \frac{\partial}{\partial m}\frac{(m-\eta+k)!}{(m-\eta)!}\frac{(m-\ell)!}{(m-\ell+k)!}\frac{(m+\ell+1)!}{(m+\ell+1+k)!}\bigg|_{m=\ell}$$
$$= \frac{\partial}{\partial m}\left(\prod_{j=1}^{k}\frac{m-\eta+j}{(m-\ell+j)(m+\ell+1+j)}\right)\Bigg|_{m=\ell} = \frac{\partial}{\partial m}F(\eta,\ell,k,m)\bigg|_{m=\ell}, \quad (40)$$

where

$$F(\eta,\ell,k,m) = \prod_{j=1}^{k}\frac{m-\eta+j}{(m-\ell+j)(m+\ell+1+j)}.$$

Define a logarithmic derivative of $F(\eta,\ell,k,m)$ through

$$G(\eta,\ell,k,m) \equiv \frac{1}{F(\eta,\ell,k,m)}\frac{\partial}{\partial m}F(\eta,\ell,k,m) = \frac{\partial}{\partial m}\left(\ln F(\eta,\ell,k,m)\right),$$

with the advantage that products in $F(\eta,\ell,k,m)$ become sums. We have

$$G(\eta,\ell,k,m) = \frac{\partial}{\partial m}\ln\prod_{j=1}^{k}\left(\frac{m-\eta+j}{(m+\ell+1+j)(m-\ell+j)}\right)$$
$$= \frac{\partial}{\partial m}\sum_{j=1}^{k}\left(\ln(m-\eta+j) - \ln(m+\ell+1+j) - \ln(m-\ell+j)\right)$$
$$= \sum_{j=1}^{k}\left(\frac{1}{m-\eta+j} - \frac{1}{m+\ell+1+j} - \frac{1}{m-\ell-j}\right).$$

Therefore (41) gives one

$$c(\eta,\ell,k) = F(\eta,\ell,k,m)\,G(\eta,\ell,k,m)|_{m=\ell}$$
$$= \left(\prod_{j=1}^{k}\frac{m-\eta+j}{(m-\ell+j)(m+\ell+1+j)}\right)\sum_{j=1}^{k}\left(\frac{1}{m-\eta+j} - \frac{1}{m-\ell-j} - \frac{1}{m+\ell+1+j}\right)\Bigg|_{m=\ell}$$
$$= \frac{(-1)^{k+1}}{k!}\left(\prod_{j=1}^{k}\frac{\eta-\ell-j}{2\ell+1+j}\right)\sum_{j=1}^{k}\left(\frac{1}{\eta-\ell-j} + \frac{1}{j} + \frac{1}{2\ell+1+j}\right).$$

With the aid of resulting equation (40), the undergoing equation (39) yields

$$b'_k(\ell) = \frac{(-1)^{k+1}}{k!}\left(\prod_{j=1}^{k}\frac{\eta-\ell-j}{2\ell+1+j}\right)\sum_{j=1}^{k}\left(\frac{1}{\eta-\ell-j} + \frac{1}{2\ell+1+j} + \frac{1}{j}\right)\left(\frac{2Z}{\eta a}\right)^{k} \quad \forall 1 \le k \le \eta-\ell-1. \quad (41)$$

Here, we assume $b'_k(\ell) = 0\ \forall 1 \le k \le 0$.

4.3.3. Computation of w_1. For obtaining the second exact solution of (24), the resulting expressions for $b'_k(\ell)$ represented by (38) and (42) and Theorem 2 suggest us to write

$$w_1 = u(r,\ell)\log r + r^{\ell}\sum_{k=1}^{\eta-\ell-1} b'_k(\ell)r^k + r^{\ell}\sum_{k=\eta-\ell}^{\infty} b'_k(\ell)r^k.$$

4.3.4. Computation of C. Setting $b_0(m_2) = b_0(-\ell-1) = 1$ into the resulting equation (28) yields

$$b_k(-\ell-1) = \left(\frac{2Z}{\eta a}\right)^{k}\frac{\prod_{j=1}^{k}(\eta+\ell+1-j)}{k!\prod_{j=1}^{k}(2\ell+1-j)}.$$

In particular, setting $k = 2\ell$ into the undergoing equation yields

$$b_{2\ell}(-\ell-1) = \left(\frac{2Z}{\eta a}\right)^{2\ell}\frac{1}{(2\ell)!}\frac{\prod_{j=1}^{2\ell}(\eta+\ell+1-j)}{\prod_{j=1}^{2\ell}(2\ell+1-j)}. \quad (42)$$

But

$$\prod_{j=1}^{2\ell}(2\ell+1-j) = (2\ell)(2\ell-1)\cdots 3\cdot 2\cdot 1 = (2\ell)!.$$

Also

$$\prod_{j=1}^{2\ell}(\eta+\ell+1-j) = (\eta+\ell+1-1)(\eta+\ell+1-2)...(\eta+\ell+1-2\ell+1)(\eta+\ell+1-2\ell)$$
$$= \frac{(\eta+\ell)(\eta+\ell-1)...(\eta-\ell+2)(\eta-\ell+1)(\eta-\ell)!}{(\eta-\ell)!} = \frac{(\eta+\ell)!}{(\eta-\ell)!}.$$

Plugging the resulting expressions into (43) yields

$$b_{2\ell}(-\ell-1) = \frac{(\eta+\ell)!}{(\eta-\ell)!(2\ell)!(2\ell)!}\left(\frac{2Z}{\eta a}\right)^{2\ell}.$$

Therefore by definition

$$C = -\frac{f_1(m_1-1)b_{t-1}(m_2)}{\alpha_0 stb_0(m_1)} = -\frac{f_1(\ell-1)b_{2\ell}(-\ell-1)}{2\ell+1}$$
$$= -\frac{2Z}{\eta a}\frac{(\eta-\ell)b_{2\ell}(-\ell-1)}{2\ell+1} = -\frac{(\eta+\ell)!}{(2\ell+1)!(2\ell)!(\eta-\ell-1)!}\left(\frac{2Z}{\eta a}\right)^{2\ell+1}. \tag{43}$$

4.3.5. Computation of w_2. By definition,

$$w_2 = \sum_{k=0}^{2\ell} b_k(-\ell-1)r^{k-\ell-1} = r^{-\ell-1}\sum_{k=0}^{2\ell}\frac{\prod_{j=1}^{k}(\eta+\ell+1-j)}{k!\prod_{j=1}^{k}(2\ell+1-j)}\left(\frac{2Zr}{\eta a}\right)^k.$$

Finally, the second exact solution to Coulombic Schrödinger equation (18) is

$$S^Z_{\eta\ell}(r) = R(r,m_2) = e^{-\frac{Zr}{\eta a}}u(r,m_2) = e^{-\frac{Zr}{\eta a}}(w_2+Cw_1)$$
$$= e^{-\frac{Zr}{\eta a}}\left[r^{-\ell-1}\sum_{k=0}^{2\ell}\frac{1}{k!}\prod_{j=1}^{k}\frac{\eta+\ell+1-j}{2\ell+1-j}\left(\frac{2Zr}{\eta a}\right)^k\right.$$
$$-\frac{(\eta+\ell)!r^\ell}{(2\ell+1)!(2\ell)!(\eta-\ell-1)!}\left(\frac{2Z}{\eta a}\right)^{2\ell+1}\left\{\left(\sum_{k=0}^{\eta-\ell-1}\frac{1}{k!}\prod_{j=1}^{k}\frac{(j+\ell-\eta)}{(j+2\ell+1)}\left(\frac{2Zr}{\eta a}\right)^k\right)\log r\right.$$
$$+\sum_{k=1}^{\eta-\ell-1}\frac{(-1)^{k+1}}{k!}\left(\prod_{j=1}^{k}\frac{\eta-\ell-j}{2\ell+1+j}\right)\sum_{j=1}^{k}\left(\frac{1}{\eta-\ell-j}+\frac{1}{j}+\frac{1}{2\ell+1+j}\right)\left(\frac{2Zr}{\eta a}\right)^k$$
$$\left.\left.+\sum_{k=\eta-\ell}^{\infty}\frac{(-1)^{\eta-\ell-1}(\eta-\ell-1)!(k-\eta+\ell)!(2\ell+1)!}{k!(k+2\ell+1)!}\left(\frac{2Zr}{\eta a}\right)^k\right\}\right].$$

We are now in a position to provide some example expressions and plots of the Coulombic radial wave functions of the second kind (and of the first kind) in the following section 5.

5. Examples of radial wave functions of second kind

Case 1. If $\eta = 1$, then $\ell = 0$. In this case, the graphical representation of the radial wave function of the second kind (and of first kind) are represented in Figs. 1 and 2 and mathematically, employing equation (45), is

$$S^Z_{10}(r) = e^{-\frac{Zr}{a}}\left\{\frac{1}{r}-\frac{2Z}{a}\left(\log r+\sum_{k=1}^{\infty}\frac{(k-1)!}{k!(k+1)!}\left(\frac{2Zr}{a}\right)^k\right)\right\}.$$

Case II. If $\eta = 2$, then $\ell = 0, 1$. In this case, the graphical representation is displayed in Figs. 3 and 4, and , mathematically, using equation (45), is

$$S^Z_{20}(r) = e^{-\frac{Zr}{2a}}\left\{\frac{1}{r}-\frac{2Z}{a}\left(\left(1-\frac{Zr}{2a}\right)\log r+\frac{5Zr}{4a}-\sum_{k=2}^{\infty}\frac{(k-2)!}{k!(k+1)!}\left(\frac{Zr}{a}\right)^k\right)\right\},$$
$$S^Z_{21}(r) = e^{-\frac{Zr}{2a}}\left\{\frac{1}{r^2}+\frac{3Z}{2ar}+\frac{3Z^2}{2a^2}-\frac{Z^3r}{2a^3}\left(\log r+\sum_{k=1}^{\infty}\frac{6(k-1)!}{k!(k+3)!}\left(\frac{Zr}{a}\right)^k\right)\right\}.$$

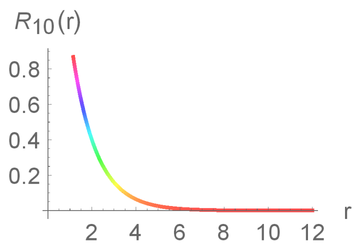

FIG. 1. Radial wave function $R_{10}(r)$

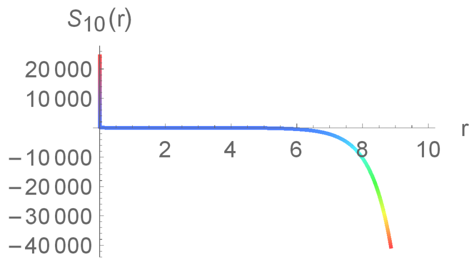

FIG. 2. Radial wave function $S_{10}(r)$

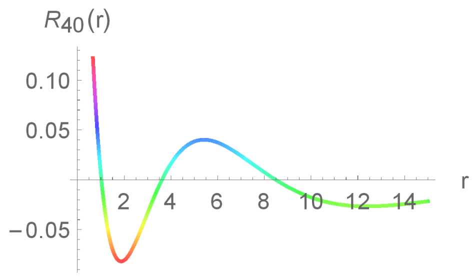

FIG. 3. Radial wave function $R_{40}(r)$

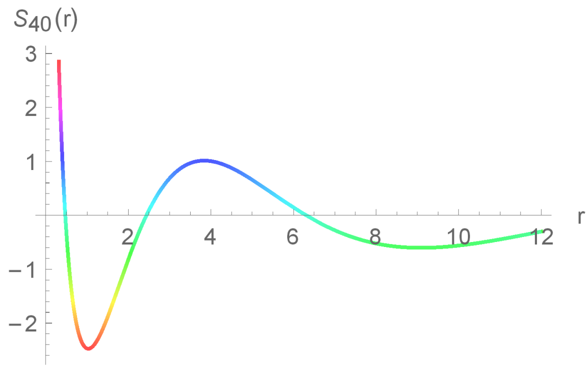

FIG. 4. Radial wave function $S_{40}(r)$

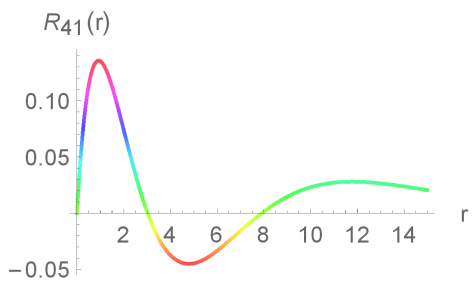

FIG. 5. Radial wave function $R_{41}(r)$

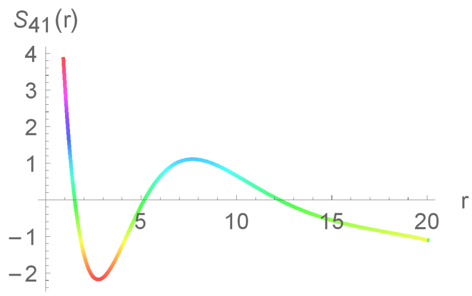

FIG. 6. Radial wave function $S_{41}(r)$

Case III. If $\eta = 3$, then $\ell = 0, 1, 2$, In this case, the graphical representation is displayed in Figs. 5 and 6, and mathematically,

$$S_{30}^{Z}(r) = e^{-\frac{Zr}{3a}} \left\{ \frac{1}{r} - \frac{2Z}{a} \left(\left(1 - \frac{2Zr}{3a} + \frac{2Z^2r^2}{27a^2} \right) \log r + \frac{4Zr}{3a} - \frac{23Z^2r^2}{81a^2} + \sum_{k=3}^{\infty} \frac{2(k-3)!}{k!(k+1)!} \left(\frac{2Zr}{3a} \right)^k \right) \right\},$$

$$S_{31}^{Z}(r) = e^{-\frac{Zr}{3a}} \left\{ \frac{1}{r^2} + \frac{4Z}{3ar} + \frac{4Z^2}{3a^2} - \frac{16Z^3r}{27a^3} \left(\left(1 - \frac{Zr}{6a} \right) \log r + \frac{3Zr}{8a} - \sum_{k=3}^{\infty} \frac{6(k-2)!}{k!(k+3)!} \left(\frac{2Zr}{3a} \right)^k \right) \right\},$$

$$S_{32}^{Z}(r) = e^{-\frac{Zr}{3a}} \left\{ \frac{1}{r^3} + \frac{5Z}{6ar^2} + \frac{10Z^2}{27a^2r} + \frac{10Z^3}{81a^3} + \frac{10Z^4r}{243a^4} - \frac{4Z^5r^2}{729a^5} \left(\log r + \sum_{k=1}^{\infty} \frac{5!(k-1)!}{k!(k+5)!} \left(\frac{2Zr}{3a} \right)^k \right) \right\}.$$

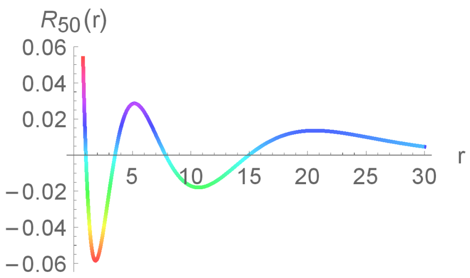

FIG. 7. Radial wave function $R_{50}(r)$

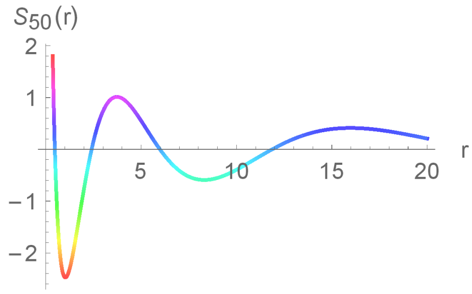

FIG. 8. Radial wave function $S_{50}(r)$

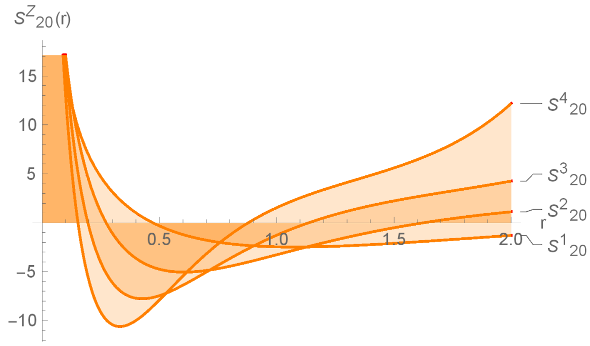

FIG. 9. Radial wave functions $S_{\eta\ell}(r)$ with Z increases

Case IV. If $\eta = 4$, then $\ell = 0, 1, 2, 3$. In this case, the graphical representation is displayed in Figs. 7 and 8, and mathematically

$$S_{40}^{Z}(r) = e^{-\frac{Zr}{4a}} \left\{ \frac{1}{r} - \frac{2Z}{a} \left(\left(1 - \frac{3Zr}{4a} + \frac{Z^2r^2}{8a^2} - \frac{Z^3r^3}{192a^3} \right) \log r + \frac{11Zr}{8a} - \frac{19Z^2r^2}{48a^2} + \frac{19Z^3r^3}{768a^3} - \sum_{k=4}^{\infty} \frac{6(k-4)!}{k!(k+1)!} \left(\frac{Zr}{2a} \right)^k \right) \right\},$$

$$S_{41}^{Z}(r) = e^{-\frac{Zr}{4a}} \left\{ \frac{1}{r^2} + \frac{5Z}{4ar} + \frac{5Z^2}{4a^2} - \frac{5Z^3r}{8a^3} \left(\left(1 - \frac{Zr}{4a} + \frac{Z^2r^2}{80a^2} \right) \log r + \frac{7Zr}{16a} - \frac{69Z^2r^2}{1600a^2} + \sum_{k=3}^{\infty} \frac{12(k-3)!}{k!(k+3)!} \left(\frac{Zr}{2a} \right)^k \right) \right\},$$

$$S_{42}^{Z}(r) = e^{-\frac{Zr}{4a}} \left\{ \frac{1}{r^3} + \frac{3Z}{4ar^2} + \frac{5Z^2}{16a^2r} + \frac{5Z^3}{48a^3} + \frac{5Z^4r}{128a^4} - \frac{Z^5r^2}{128a^5} \left(\left(1 - \frac{Zr}{12a} \right) \log r + \frac{13Zr}{72a} - \sum_{k=2}^{\infty} \frac{5!(k-2)!}{k!(k+5)!} \left(\frac{Zr}{2a} \right)^k \right) \right\},$$

$$S_{43}^{Z}(r) = e^{-\frac{Zr}{4a}} \left\{ \frac{1}{r^4} + \frac{7Z}{12ar^3} + \frac{7Z^2}{40a^2r^2} + \frac{7Z^3}{192a^3r} + \frac{7Z^4}{1152a^4} + \frac{7Z^5r}{7680a^5} + \frac{7Z^6r^2}{46080a^6} - \frac{Z^7r^3}{92160a^7} \left(\log r + \sum_{k=1}^{\infty} \frac{7!(k-1)!}{k!(k+7)!} \left(\frac{Zr}{2a} \right)^k \right) \right\}.$$

Case V. If $\eta = 5$, then $\ell = 0, 1, 2, 3, 4$. In this case, we have

$$S_{50}^{Z}(r) = e^{-\frac{Zr}{5a}} \left\{ \frac{1}{r} - \frac{2Z}{a} \left(\left(1 - \frac{4Zr}{3a} + \frac{4Z^2r^2}{25a^2} - \frac{4Z^3r^3}{375a^3} + \frac{2Z^4r^4}{9375a^4} \right) \log r + \frac{7Zr}{5a} - \frac{7Z^2r^2}{15a^2} + \frac{16Z^3r^3}{375a^3} - \frac{109Z^4r^4}{93750a^4} + \sum_{k=5}^{\infty} \frac{4!(k-5)!}{k!(k+1)!} \left(\frac{2Zr}{5a} \right)^k \right) \right\},$$

$$S_{51}^{Z}(r) = e^{-\frac{Zr}{5a}} \left\{ \frac{1}{r^2} + \frac{6Z}{5ar} + \frac{6Z^2}{5a^2} - \frac{16Z^3r}{25a^3} \left(\left(1 - \frac{3Zr}{10a} + \frac{3Z^2r^2}{125a^2} - \frac{Z^3r^3}{1875a^3} \right) \log r + \frac{19Zr}{40a} - \frac{167Z^2r^2}{2500a^2} + \frac{257Z^23r^3}{112500a^3} - \sum_{k=4}^{\infty} \frac{36(k-4)!}{k!(k+3)!} \left(\frac{2Zr}{5a} \right)^k \right) \right\}.$$

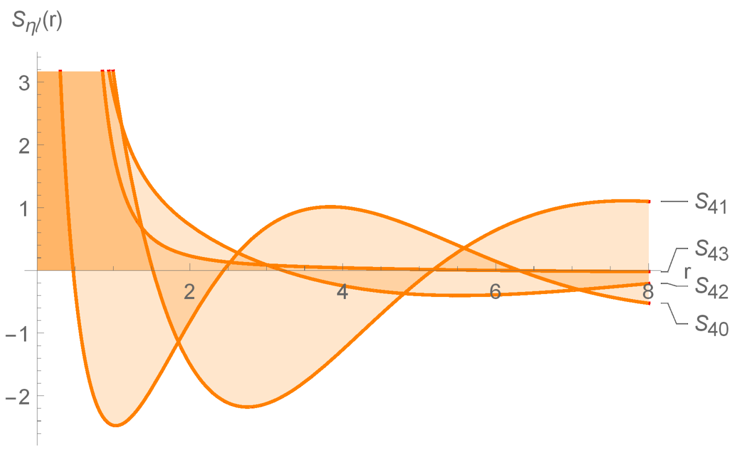

FIG. 10. Radial wave functions $S_{\eta\ell}(r)$ with ℓ increases

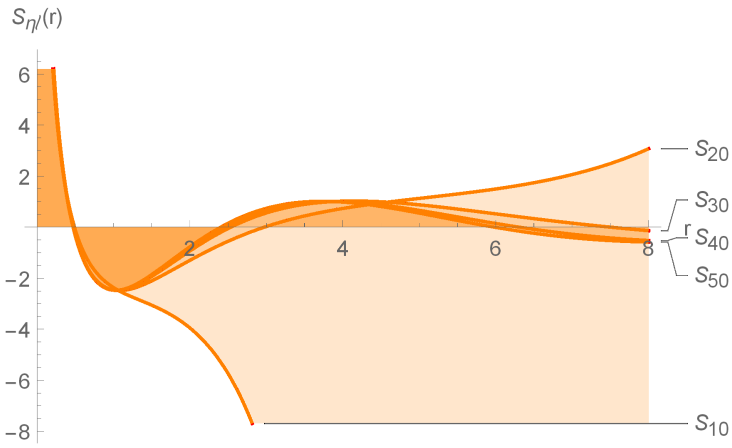

FIG. 11. Radial wave functions $S_{\eta\ell}(r)$ with η increases

5.1. Properties of the Coulombic radial solutions

As expected, Figs. 9–11 reveal that both the regular and the irregular solutions to the Coulombic radial SE spread in their radial distribution as the system energy increases from strongly negative values to values closer to zero. Also, both distributions move away from the origin as the angular momentum of the electron increases. However, the threshold and asymptotic behavior are quite different. The regular solutions have an r^{ℓ} dependence near the origin, while the irregular solutions diverge as $r^{-\ell-1}$. Asymptotically, the regular solutions drop exponentially in proportion to $r^{n-1}\exp(-r/n)$, in natural units, while the irregular solutions grow as $r^{-n-1}\exp(r/n)$.

6. Conclusions and future scope

We have shown that a large class of second-order linear differential equations with polynomial coefficients determine two-term recursion relations which can be solved explicitly, and also yield second (irregular) solutions. The procedure is applied to find the regular and irregular (second) solutions to the Coulombic Schrödinger equation for an electron experiencing a Coulomb force, and examples are displayed. Even though second solutions are ordinarily rejected in the Coulombic case because of their unbound character, having explicit expressions for them has utility for several reasons. One is in the study of the analytic behavior of general solutions as a function of the energy and angular momentum of the electron-nucleus system (See Gaspard [16]). Another is in the study of numerical-solution techniques when three-term recurrence relations are used to solve 2^{nd} order differential equations. In such cases, the second solution may invade the wanted first solution through truncation errors during iteration. Asymptotically, the regular solutions drop exponentially while the irregular solutions grow exponentially. Moreover, knowledge of the behavior of the second solution can be used to control the errors in the first. With these techniques at hand, exploration of second solutions to other important linear differential equations is possible.

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