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Closed-form solutions of the Schrödinger equation for a class of smoothed Coulomb potentials

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Abstract. An infinite family of closed-form solutions is exhibited for the Schrödinger equation for the potential $V(\mathbf{r}) = -Z/\sqrt{|\mathbf{r}|^2 + a^2}$. Evidence is presented for an approximate dynamical symmetry for large values of the angular momentum l.

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1. Introduction

A recent paper [1] demonstrated the existence of a family of closed-form solutions to the one-dimensional Schrödinger equation for the potential

$$V_1(x) = -\frac{1}{\sqrt{x^2 + a^2}} \tag{1}$$

which is widely used [2, 3, 4, 5, 6, 7, 8] in the modeling of atomic response to strong time-dependent radiation fields. The approach used in Ref. [1] was somewhat analogous to the Sturmian method [9] for generating a complete basis set of Coulomb wavefunctions, in which the energy E is held fixed and the nuclear charge Z is determined as an eigenvalue. Ref. [1] determined "eigenvalues" a_n of the cutoff parameter a, for which the eigenenergies E_n of the Schrödinger equation for the potential Eq. (1) take the values

$$E_n = -\frac{1}{2n^2}; \tag{2}$$

these are the energies of the states of the three- dimensional hydrogen atom, in the usual system of atomic units (used throughout the present paper) in which the numerical value of unity is assigned to the mass m and charge e of the electron and to the reduced Planck's constant $\hbar$. The associated eigenfunctions $\Psi_n(x)$ were found to have a closed-form expression:

$$\Psi_n(x) = x^\nu e^{-\kappa\chi} f_n(\chi), \tag{3}$$

where: $\nu = 0$ or 1 for cases of even and odd parity respectively; $\chi = \sqrt{x^2 + {a_n}^2}$; f_n is a polynomial of degree $n \geq 1 - \nu$; $\kappa = 1/n$; and ${a_n}^2$ is a root of an n^{th}-degree polynomial.

In the present work a similar approach is applied to the three-dimensional smoothed Coulomb potential

$$V(\mathbf{r}) = -\frac{Z}{\sqrt{|\mathbf{r}|^2 + a^2}}. \tag{4}$$

This potential arises in the Kramers-Hennenberger transformation of the equations of motion of a hydrogen atom in a radiation field [10, 11], and it is qualitatively similar to some pseudopotentials used in density-functional calculations of electronic structure (e.g. Ref. [12]). It is shown here that, subject to an assumption similar to one made in Ref. [1], the Schrödinger equation for this potential admits an infinite number of closed-form solutions for each value of the angular momentum l. The lowest-energy solutions for each l are quite simple, so knowledge of these exact results may be useful for calibrating numerical methods that must be used to solve general equations of this type. To the best of the author's knowledge, these are the first exact results for Schródinger eigenvalues and eigenfunctions for potenials of the class described by Eq. (4).

2. Method of solution

The extension of the method of [1] is straightforward. We proceed from the Schrödinger equation

$$-\frac{1}{2}\nabla^2\Psi(\mathbf{r}) - \frac{Z}{\sqrt{|\mathbf{r}|^2 + a^2}}\Psi(\mathbf{r}) = E\Psi(\mathbf{r}), \tag{5}$$

and invoke the usual spherical coordinate factorization $\Psi(\mathbf{r}) = \psi_l(r)Y_{lm}(\theta, \phi)$. With the definitions $\alpha = Za$, $\rho = \sqrt{(Zr)^2 + \alpha^2}$, $\epsilon = E/Z^2 = -\kappa^2/2$, and

$$\psi_l(r) = r^l\phi_l(\rho), \tag{6}$$

the equation

$$\left(1 - \frac{\alpha^2}{\rho^2}\right)\frac{\partial^2\phi_l(\rho)}{\partial\rho^2} + \left(\frac{\alpha^2}{\rho^3} + \frac{2l+2}{\rho}\right)\frac{\partial\phi_l(\rho)}{\partial\rho} + \left(\frac{2}{\rho} - \kappa^2\right)\phi_l(\rho) = 0. \tag{7}$$

is obtained. We now postulate a solution of the form

$$\phi_l(\rho) = e^{-\kappa\rho}\sum_{i=0}^{n} c_i\rho^i, \tag{8}$$

where n is an integer to be determined. For economy of expression the dependence of κ and c_i upon n and l is not made explicit in the notation, but it is held to be implicit.

We now show that Eq. (8) does not provide a general solution, but that it is applicable for discrete values of α. To see this, we substitute eq. (8) in the l.h.s. of Eq. (7), and require the net coefficient of each power of ρ to vanish identically. The coefficient of ρ^j that emerges from this operation is

$$\begin{aligned}&-\alpha^2(j+4)(j+2)c_{j+4} + \alpha^2\kappa(2j+5)c_{j+3} + \\ &\left((j+2)(j+2l+3) - \alpha^2\kappa^2\right)c_{j+2} + 2\left(1 - \kappa(j+l+2)\right)c_{j+1} = 0\end{aligned} \tag{9}$$

for $j = -3, -2, -1, ..., n-1$. Thus we must solve the $n+3$ simultaneous equations (9) in the $n+2$ variables $\{c_1, c_2, ..., c_n, \kappa, \alpha\}$.

We proceed by treating Eq. (9) as a *four-term* recurrence relation, and solve for c_j sequentially downwards from $j = n-1$. Because $c_j = 0$ for $j > n$, the solution for $j = n-1$ gives

$$\kappa = \frac{1}{n+l+1}. \tag{10}$$

Thus κ is uniquely determined by n and l. Eq. (10) describes exactly the spectrum of the three-dimensional Coulomb potential, i.e. the limiting case of Eq. (5) with $a = 0$; in that case n coresponds to the number of nodes in the radial eigenfunction. We shall see subsequently that, for $\alpha \neq 0$, we must have $n \geq 1$, and the maximum number of radial nodes in the wavefunction described by Eqs. (8) and (10) is $n-1$. The potential of Eq. (4) has a long-range Coulomb tail and a non-Coulombic component at small r, so its Schrödinger spectrum is naturally described in the language of quantum defect theory [13]. In that terminology, Eq. (10) describes a state with an integer value of the quantum defect μ, which is necessarily negative for $a \neq 0$. The following development will indicate that all eigenfunctions with integral quantum defects obtained with potentials of the class Eq. (4) are described by Eq. (8).

Since Eq. (7) is homogeneous, we can set $c_n = 1$ without loss of generality. The values of c_i for $i < n$ are then determined in terms of c_n by downward recursion using Eq. (9). For $j = n-2$, we get

$$c_{n-1} = \frac{1}{2}\left(n(n+l+1)(n+2l+1) - \frac{\alpha^2}{n+l+1}\right) c_n = p_1(\alpha^2)c_n, \qquad (11)$$

where $p_1(x)$ designates a first-degree polynomial in x. From this equation it is apparent that there will be a solution for $n = 0$ only if $\alpha = 0$, which is the familiar Coulombic case.

Inspection of the structure of Eq. (9) shows that by continuing the recursion process downward in j we get

$$c_{n-m} = p_m(\alpha^2)c_n, \qquad (12)$$

with $p_m(\alpha^2)$ being a polynomial of degree m in α^2. So for $j = 0$ and $j = -1$ we find

$$c_1 = p_{n-1}(\alpha^2)c_n \qquad \text{and} \qquad c_0 = p_n(\alpha^2)c_n \qquad (13)$$

respectively. The last two cases to be considered are $j = -2$ and $j = -3$. These are found to give the *same* equation:

$$c_1 = \kappa c_0 = \frac{c_0}{n+l+1}. \qquad (14)$$

Thus, from Eqs. (13) and (14), we see that Eq. (8) will provide a valid solution if

$$q_n(\alpha^2) = p_n(\alpha^2) - (n+l+1)p_{n-1}(\alpha^2) = 0 \qquad (15)$$

or, in other words, if α^2 is a root of the n^{th} degree polynomial q_n.

The applicability of Eq. (8) thus depends upon some roots of Eq. (15) being positive real numbers. The investigation reported here has not uncovered a general proof that Eq. (15) has any such roots, but calculations carried out for $l \leq 10^6$ and $n \leq 20$ suggest that *all* its roots are positive real numbers and are nondegenerate. Let us adopt this as a hypothesis. If it is true, then the following statements hold:

i. *For each l, n there are $n+1$ values of α^2 for which Eq. (5) has solutions of the form Eqs. (6, 8).* This includes the previously-known (Coulombic) value $\alpha^2 = 0$, plus the n roots of the polynomial q_n.

ii. *The only potentials of the class eq. (4) which have bound states with Coulombic energies are just those with values of α^2 that are solutions to Eq. (15).* This is because Eq. (4) describes a monotonic function of α^2. Thus, for a given l, its associated discrete Schrödinger eigenvalues will increase uniformly towards zero as α increases. For a given l, Z, and Coulombic energy,

$$E_{nl} = -\frac{1}{2}\frac{Z^2}{(n+l+1)^2}, \tag{16}$$

there will be some maximum value of α^2 for which E_{nl} occurs as an eigenvalue, i.e., that for which it is the lowest eigenvalue. As α^2 is decreased from this maximum, E_{nl} will next occur in the spectrum when it is the second lowest eigenvalue, then as the third lowest, etc., until finally at $\alpha^2 = 0$, when it is the $(n+1)$-th lowest eigenvalue. Thus there are indeed only $n+1$ values of α^2 for which Eq. (16) occurs in the spectrum, which is consistent with the stated hypothesis, and if the hypothesis is true, these values must thus coincide with the roots of Eq. (15)

The argument ii. is illustrative of the actual results of computations of solutions of Eqs. (9) and (15), as will be described below. The largest value of α^2 for a given (n, l) is associated with a nodeless eigenfunction; the next largest value of α^2, with an eigenfunction with one node; and so on to the smallest nonzero value of α^2, which corresponds to an eigenfunction with $n-1$ nodes.

3. Results

The eigenvalues of α^2 can be easily be found for a given (n, l) by numerical solution of the polynomial equation (15). They have relatively simple closed forms for $n = 1$ and 2, which are presented here. Numerical tables are given below for $1 \le l \le 3$ and $n \le 10$.

3.1. $n = 1$

For $n = 1$ we obtain

$$\alpha^2 = 2(l+2)^3, \qquad c_0 = l+2, \qquad c_1 = 1, \tag{17}$$

so that the (nonnormalized) solution of Eq. (5) is

$$\psi_l(r) = r^l e^{-\rho/(l+2)}\,(l+2+\rho)\,, \tag{18}$$

with $\rho = \sqrt{(Zr)^2 + 2(l+2)^3}$, and $a^2 = Z^{-2}\alpha^2 = Z^{-2}2(l+2)^3$.

3.2. $n = 2$

For $n = 2$ there are two solutions for α^2:

$$\alpha^2 = \left[3 \pm \sqrt{\frac{l+15}{l+3}}\right](l+3)^3. \tag{19}$$

With the choice of $c_2 = 1$, we can write the expressions for the two sets of coefficients c_i in the common form:

$$c_0 = \frac{\alpha^2}{2} - (l+3)^2(2l+3), \qquad c_1 = \frac{c_0}{l+3}, \tag{20}$$

with the value of α^2 to be chosen as appropriate.

3.3. $n > 2$

Although closed-form expressions can be obtained for α^2 and c_i for $n = 3$ and 4, they have the typical cumbersome form of roots of cubic and quartic equations, and it does not seem particularly useful to record them here in full. However, a simplifying relationship is worth noting. For these values of n, the values of α^2 can be written as

$$\alpha^2 = (n+l+1)^3(n+1+\beta), \tag{21}$$

where β is a root of the polynomials,

$$\beta^3 - 4\frac{l+19}{l+4}\beta - 24\frac{l+14}{(l+4)^2} = 0 \tag{22}$$

$$\beta^4 - 10\frac{l+23}{l+5}\beta^2 - 48\frac{3l+50}{(l+5)^2}\beta + 9\frac{(l^3+51l^2+643l+945)}{(l+5)^3} = 0, \tag{23}$$

for $n = 3$ and 4, respectively. In the limit of large l, the solutions of Eqs. (22) and (23) tend respectively to $\beta = 0, \pm 2$ and $\beta = \pm 1, \pm 3$. Thus from Eqs. (17-23) we see that for large l, the smallest value of α^2 tends to $\alpha^2 = 2(n+l+1)^3$ for $n = 1$ through 4. This motivates the choice of Eq. (21) as a general representation for the values of α^2, and it has been used to record those values in the tables given below. It has been found that, to a high degree of numerical accuracy, the computed values of β for a given (n, l) sum to zero, so that substituting $\beta = 0$ in eq. 21 apparently locates $\alpha^2 = (n+l+1)^3(n+1)$ as the average of the values of α^2. No fundamental explanation of this apparent fact is advanced here.

Tables 1, 2, 3 give the values of β for $n \leq 10$ for $l = 1 - 3$. A similar set of values for $l = 0$ can be found in Table 1 of Ref. [1], so they are not repeated here [14].

3.4. Systematic behavior of wavefunctions

Numerical calculations indicate that the wavefunctions described by Eq. (8) exhibit the qualitative behavior discussed at the end of Sec. 2. For a given (n, l), denote by α_k the k^{th} smallest value of α obtained in solving Eq. (15), with $k = 1, 2, ..., n$. Numerical experiments indicate that the wavefunction corresponding to α_k has $n_r = n - k$ radial nodes, a pattern that was observed in the one-dimensional cases treated in ref. [1]. An example of this behavior is illustrated in Fig. 1 for the case $n = 10$, $l = 1$.

Fig. 2 depicts the values of α_k for $0 \leq l \leq 4$ as a function of $n_r + l + 2 = n^*$, the effective principal quantum number of atomic spectroscopy, which is related to the energy via Eq. (10). For a given (l, k), as labelled in Fig. 2, a discernable sequence of values of α_k is observed; these sequences are seen to approach definite limits as $n*$ increases. This is related to the well-known phenomenon in atomic spectroscopy in which quantum defects tend to constant values high in Rydberg series. The slow variations of high-n quantum defects are due to the presence of a fixed, short-range, non-Coulombic part of the potential experienced by a Rydberg electron. Correspondingly, the fixed value of quantum defect obtained in the present method is associated with slow variation of α_k at large n.

For large α^2 and large k, on the other hand, the eigenfunctions approach those of the three-dimensional harmonic oscillator. This can be seen by expanding $Z/\sqrt{r^2 + a^2}$ in powers of r/a for large a; retaining the lowest two terms gives the Schrödinger equation for the harmonic oscillator. If first-order perturbation theory is used to include the effects of the r^4 term in this expansion, we obtain the approximate spectrum,

$$\begin{aligned} E_{n_r l} \rightarrow & -\frac{Z}{a} + [2n_r + l + 3/2]\sqrt{\frac{Z}{a^3}} \\ & -\frac{3}{8a^2}\left[6n_r\left(n_r + l + 3/2\right) + \left(l + 5/2\right)\left(l + 3/2\right)\right], \end{aligned} \tag{24}$$

as $a \rightarrow \infty$. Fig. 3 is a correlation diagram that displays the connection between this limit and the hydrogenic limit $a = 0$, if one keeps the number of radial nodes, n_r, fixed as a varies. Two familiar cases of l-degeneracy are apparent in this figure: $n_\rho + l$ = constant for the hydrogen atom, and $2n_\rho + l$ = constant for the three-dimensional harmonic oscillator.

3.5. The spectrum for large values of l and a

In sec. 3.3 it was mentioned that as $l \rightarrow \infty$, we find $\alpha_n \rightarrow 2(n + l + 1)^3$ for $1 \leq n \leq 4$. Thus in this limit we recover a case of near-l-degeneracy similar to that encountered in hydrogen: there are values of α that support degenerate eigenfunctions with different values of l, described as a class by the equation $n_r + l$ = constant. The approach to this limit is relatively slow, apparently like l^{-1} as suggested by Eq. (19): e.g. for $l = 10,000$

and $n \leq 10$, the actual value of α changes by about a part in 10^4 for a unit change in n_r at constant $n_r + l$. Numerical experiments suggest that this approximate degeneracy is a general phenomenon at large l.

There is a simple effect of this kind of degeneracy for all potentials that have a long-range Coulomb tail and some non-Coulombic behavior localized at small r. In such systems, the centrifugal barrier presented to a high-l wavefunction - commonly called a "nonpenetrating orbital" - will prevent it from sampling the non-Coulombic region. Thus the Coulombic l-degeneracy is largely undisturbed for large l. The quantum defects μ_l of nonpenetrating orbitals tend to zero as $l \to \infty$, a phenomenon that is universal in actual atomic systems, where, apart from isolated instances of series perturbation, observed quantum defects are hardly greater than 0.01 for $l \geq 5$.

However, the effect encountered in the present system is quite different. The non-Coulombic behavior of the potential extends to very large r, so the large-l eigenfunctions are substantially modified from their Coulombic forms: their quantum defects are negative integers. The appearance of this novel l-degeneracy presumably derives from the existence of a constant of motion for the Schrödinger equation given by Eq. (5) that emerges in the large-l limit, but it has not been identified in the present work.

4. Conclusions

A simple algebraic method has been presented to generate an infinite number of parameters a for which closed-form solutions may be found to the Schrödinger equation for the class of smoothed Coulomb potentials described by Eq. (4). The procedure bears some superficial resemblances to the Sturmian approach. However, it is not based on a system of orthogonal polynomials, and because the functions it generates are obviously incomplete, it probably cannot be simply related to known orthogonal systems. These results should be useful for testing, to arbitrary numerical accuracy, methods that integrate the Schrödinger equation for Coulomb-like systems, such as are encountered in electronic structure and collision problems. The approach also points to the possibility of previously unknown integrals of motion in these systems.

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[14] The values of a in the “odd parity” section of Table 1 of Ref. [1] are identical to the values of α for $l = 0$ described in the present paper, because the odd-parity spectrum of the 1-dimensional potential of Eq. 1 is identical to the s-wave spectrum of Eq. (5).

Figure captions

Figure 1. Solutions for $n = 10$, $l = 1$: wavefunctions $\psi_1(\rho)$ (solid line) and scaled potentials $Z^2V(r) = -\left[\rho^2+\alpha^2\right]^{-\frac{1}{2}}$ (dashed line) vs. ρ (horizontal axis). The numerical value of α is displayed for each case. The horizontal range $0 \leq \rho \leq 350$ is the same for all figures, and the negative portion of the vertical axis that is displayed covers the range [-0.11,0] in all cases. The wavefunctions $\psi_1(\rho)$ are not normalized, and have each been scaled to fit the frame; they have also been chosen to be positive near $\rho = 0$, a convention that differs trivially from that used in the constructive procedure presented in sec. 2, where instead the long-range tail is taken to be positive.

Figure 2. Plot of α vs. $n^* = n_r + l + 2$ for $0 \leq l \leq 4$, $2 \leq n + l + 1 \leq 16$, and $\alpha \leq 100$. Key: plus: $l = 0$; x: $l = 1$; star: $l = 2$; square: $l = 3$; triangle: $l = 4$. The first few series (l,k) are explicitly labelled.

Figure 3. Correlation diagram for the spectrum of eq. (5) as a function of a (increasing schematically to the right), reflecting the conservation of n_r. The vertical position of a level is proportional to its effective principal quantum number n*, which determines the energy via $E = -Z^2/(2n^{*2})$ or $E = -Z/a + (n^* + 3/2)\sqrt{Z/a^3}$ for the hydrogenic and oscillator limits, respectively; the horizontal position corresponds to l as indicated. The values of n* for the two limits are displaced and on different scales to ease visualization of the reordering of levels.

Table 1. Values of β as defined in Eq. (21), for $l = 1$, $3 \leq n \leq 10$. The n values of β for each n are given in ascending order in the columns as labeled.

$n = 3$	4	5	6
-3.436527918374	-4.654288835724	-5.773876395778	-6.844547165256
-0.954320351864	-3.021850153582	-4.650636370300	-6.042758624724
4.390848270238	0.696058817445	-1.972562395354	-4.058664349356
	6.980080171861	2.712910374971	-0.480918834922
		9.684164786461	4.966113875958
			12.460775098300

$n = 7$	8	9	10
-7.888799456947	-8.917837293622	-9.937641169524	-10.951590892028
-7.298711510457	-8.472195004982	-9.593574030219	-10.680835341450
-5.793704911519	-7.307257906333	-8.675819112578	-9.946495139814
-3.007931174911	-5.101818236107	-6.904370845863	-8.505293514974
1.322982663950	-1.607950021737	-4.050370418227	-6.148266454200
7.380032760853	3.353214980339	0.059395253271	-2.710246349993
15.286131629031	9.908007968597	5.551945760159	1.934250402020
	18.145835513845	12.519780081038	7.879187144780
		21.030654481943	15.194895308886
			23.934394836774

Table 2. Values of β as defined in Eq. (21), for $l = 2$, $3 \leq n \leq 10$, presented as in Table 1

$n = 3$	4	5	6
-3.278125698868	-4.521965213374	-5.668426333247	-6.761249358836
-0.798234614319	-2.785523299847	-4.411763596407	-5.826275313135
4.076360313187	0.779586310517	-1.735936565934	-3.774065245823
	6.527902202704	2.700152211531	-0.287039774645
		9.115974284057	4.853558868056
			11.795070824383

$n = 7$	8	9	10
-7.822716061200	-8.864931236359	-9.894830804857	-10.916571653805
-7.110457925768	-8.311162452760	-9.456572802320	-10.564284465555
-5.507083989124	-7.038000908935	-8.431024341412	-9.727562574162
-2.723146982242	-4.785217058704	-6.586194666454	-8.200598472288
1.453378478484	-1.351453753382	-3.733658908457	-5.808927517424
7.172075276697	3.411667214518	0.271140940945	-2.413663893356
14.537951203153	9.611814936391	5.536500893854	2.092437435636
	17.327283259231	12.143135917875	7.791260127102
		20.151503770825	14.745312392743
			23.002598621108

Table 3. Values of β as defined in Eq. (21), for $l = 3$, $3 \leq n \leq 10$, presented as in Table 1

$n = 3$	4	5	6
-3.151022588503	-4.406309629179	-5.569879138144	-6.679108747771
-0.688273381129	-2.602022794423	-4.214093797042	-5.637934713748
3.839295969632	0.834376786655	-1.552972495811	-3.541460362647
	6.173955636947	2.678798505483	-0.137921230589
		8.658146925515	4.750180241001
			11.246244813755

$n = 7$	8	9	10
-7.754622190689	-8.808385081533	-9.847641443106	-10.876940137334
-6.939787368805	-8.160018019327	-9.324116930842	-10.448678615450
-5.263146046115	-6.801150749358	-8.209581772798	-9.524662708154
-2.490737352918	-4.517404302068	-6.309419903787	-7.929266399940
1.551042361196	-1.142156136416	-3.465931796518	-5.514770174927
6.987662691921	3.449539586975	0.443287284785	-2.162791993620
13.909587905409	9.350359497993	5.511558811618	2.219325513867
	16.629215203734	11.809781767444	7.703479769014
		19.392063983204	14.345470691179
			22.188834055364