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The Energy Spectra of Soluble Potentials Within the Framework of the Variational Method

***[1]Ekwevugbe Omugbe, [2]Etido P. Inyang and [3]Clement A. Onate**

[1]Department of Physics and Engineering Physics, Faculty of Science, Obafemi Awolowo University Ile-Ife, Osun State, Nigeria.
[2]Department of Physics, National Open University of Nigeria, Jabi-Abuja, Nigeria.
[3] Physics Department, Bowen University, Iwo, Osun State, Nigeria.

*Corresponding author's email: eomugbe@oauife.edu.ng

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ABSTRACT

In this article, we demonstrated the use of the variational approach in solving the bound state solutions of the Schrödinger equation for solvable potential functions. The method has been applied to determine the exact analytical excited states energy spectra for the Coulomb, and Pseudo-harmonic potentials. Also, the exact analytical ground state energy spectra for the Hulthén and hyperbolic potentials have been obtained in closed form. In addition, we obtained the approximate energy eigenvalues of an exponential potential which does not admit exact analytical closed form solution. Using a Gaussian trial wave function and comparing our solutions with exact numerical results of the Matrix-Numerov approach, we obtained an average percentage absolute deviation of 0.14%. The errors were larger with an exponential trial wave function and the WKB approximation where we found APAD values of 0.55% and 0.31% respectively. By minimizing the total variational energy, the variational parameters were derived. The results for these potential functions align perfectly with those obtained through other methods in the existing literature and numerical solution with the Matrix Numerov approach. The results demonstrate that the accuracy of the variational approach is strongly correlated with the use of accurate trial wave functions.

INTRODUCTION

The variational method is one of the approximation techniques used in quantum mechanics, theoretical condensed matter physics and quantum chemistry to determine the ground state energy and associated wave functions of quantum systems. The method may be applied in atomic and molecular physics, to approximate the ground and first excited state wave functions and energy levels. The variational method with the application of correlated wave function of the Hyllaraas type has proven useful in obtaining the energy solutions of the Helium atoms for different screening parameters (Gning et al., 2021). Gaiki & Gade (2019) employed a symbolic computational approach within the framework of the variational method to obtain the ground state energies of the anharmonic quartic and sextic potential functions. Their results agreed with the exact values further demonstrating the effectiveness of the variational technique. Additionally, other research works have focused on developing more advanced trial wave functions to further improve the accuracy of the variational method. The variational principle was applied to obtain the s-wave energy levels of the Yukawa potential where the trial wave function was expressed in terms of the Slater-type functions (Zuniga et al., 2012). Maiz (2020) investigated the ground state energy of the Schrödinger equation with anharmonic potentials within the variational approach. The calculated energies agreed with the energies obtained from Numerov method. The linear variational method has been applied to a particle confined in one-dimensional potentials (Van der vaart et al., 2025).

The variational method is focused on the solution of the ground states energy spectra, but it has also been extended to excited states. The method has been employed to determine the excited states energy levels and transition probabilities of the screened static Coulomb potential (Roussel & O'cornell, 1974). Using a

trial Gaussian wave function, Cooper et al., (1994) applied the supersymmetric-based variational approach to calculate the energy levels of the anharmonic oscillator, where their results for the first few quantum states match with the exact values. In the same manner, Filho & Ricotta (1995) ; (2000) combined both the variational and supersymmetric quantum mechanics approaches to calculate the energies of the screened Coulomb and Morse potentials with high precision. Mutuk (2019) used the variational and asymptotic iteration methods to obtain the energy spectra of the radial Schrödinger equation with an attractive Gaussian potential. The results of the energy levels showed good agreement with existing literature data. The variational approach has been applied to obtain the approximate ground and first excited state energies of the Gaussian potential (Fernandez, 2011). The method was also implemented into a numerical scheme to solve the time-independent Schrödinger equation with harmonic, rectangular and pseudo-coulomb potentials. For the harmonic oscillator, the results of the energy levels and probability density functions showed good agreement with the exact values (Alzate-Cardona et al., 2017). The variational method has been combined with computational techniques like Variational Quantum Monte Carlo methods, facilitating the study of many-electron systems (Foulkes et al., 2001). These approaches integrate the variational principle with stochastic sampling, offering robust tools for investigating electronic correlations and properties in condensed matter systems.

While the aforementioned literature entails computational and numerical solutions of the wave equation in the variational principle, in this work, we present the analytical bound state solutions of the wave equations for the ground and excited states using the variational approach. We used the approach to obtain the exact analytical bound state solutions of the Schrödinger equation with solvable potentials, notably the Coulomb and Pseudo-harmonic, Hulthén, the hyperbolic potentials. We will also demonstrate the approach for a step exponential potential owing to the absence of exact analytical closed-form solution of the energy spectrum. Our motivation is to show the effectiveness of the variational method in obtaining closed-form analytical solutions without transforming the Schrodinger equation. The results will be compared with other analytical methods (Rani et al., 2008; Amani & Ghorbanpour, 2012; Ikhdair & Sever, 2008; Omugbe et al., 2024; Bayrak & Boztosun, 2007) and numerical solutions (Pillai et al. 2012). The solutions provided here may serve as a resource tool for advanced undergraduate courses in quantum Physics.

MATERIALS AND METHODS

Theoretical Foundations

The radial part of the Schrödinger equation is obtained from the wave equation in spherical coordinates by separation of variables

$$-\frac{\hbar^2}{2\mu}\frac{d^2R_{nl}(r,\alpha_1,\alpha_2)}{dr^2}+V_{eff}(r)R_{nl}(r,\alpha_1,\alpha_2)=E_{nl}(\alpha_1,\alpha_2)R_{nl}(r,\alpha_1,\alpha_2) \quad (1)$$

where $\hbar$ and μ are the reduced Planck's constant and the reduced mass of the two-body system respectively. The functions $R_{nl}(r,\alpha_1,\alpha_2)$ and $V_{eff}(r)$ are the respective variational radial wave function and the effective potential. The parameters $\alpha_i\,(i=1,2)$ are the unknown variational parameters which will be obtained later from the minimization of the variational energy. The effective potential is given as

$$V_{eff}(r)=V(r)+\frac{l(l+1)\hbar^2}{2\mu r^2} \quad (2)$$

The variational approximation is an approach for obtaining the energy of the wave equations in quantum mechanics by using trial wave functions. The wave function must be guessed such that it shares the same properties and boundary conditions as the true wave function. The energy level ($E(\alpha_1,\alpha_2)$) in the variational method is an upper bound to the exact energy and satisfies the relations (Griffiths, 1995):

$$E_{nl}(\alpha_1,\alpha_2)\geq E_{nl} \quad (3)$$

$$\begin{cases}\dfrac{\partial E_{nl}(\alpha_1,\alpha_2)}{\partial\alpha_1}=0\\[2ex]\dfrac{\partial E_{nl}(\alpha_1,\alpha_2)}{\partial\alpha_2}=0\end{cases} \quad (4)$$

The most important aspect of the variational approach is the correctness of the wave function that satisfies the Schrödinger equation. Multiplying Eq. (**1**) by the complex conjugate of $R_{nl}(r,\alpha_1,\alpha_2)$ from the left and performing integration gives

$$E_{nl}(\alpha_1,\alpha_2)=\frac{\hbar^2}{2\mu}\left(\left\langle \hat{p}_{nl}^2(r)\right\rangle+l(l+1)\left\langle r^{-2}\right\rangle\right)+\left\langle V(r)\right\rangle \quad (5)$$

where $\hat{p}(r)\left(-i\hbar\frac{d}{dr}\right)$ is a momentum operator, $\left\langle r^{-2}\right\rangle$ and $\langle V(r)\rangle$ are the expectation values of the centrifugal barrier term and the potential function that describes the physical system. The equations that describe the mean values are given by

$$\left\langle \hat{p}_{nl}^2(r)\right\rangle=\int_0^\infty\left(\frac{dR_{nl}(r,\alpha_1,\alpha_2)}{dr}\right)^2dr \quad (6)$$

$$\left\langle r^{-2}\right\rangle=\int_0^\infty r^{-2}\left|R_{nl}(r,\alpha_1,\alpha_2)\right|^2dr \quad (7)$$

$$\left\langle V(r)\right\rangle=\int_0^\infty V(r)\left|R_{nl}(r,\alpha_1,\alpha_2)\right|^2dr \quad (8)$$

Bound State Solutions with Solvable Potential Functions

The Coulomb Potential

The Coulomb potential plays a significant role in the description of the binding energies of the hydrogen-like atoms in atomic physics. Other methods have been applied to obtain the analytical energy equation in the literature (Omugbe et al. 2024; Tezcan & Sever, 2009). The potential is given as

$$V(r) = -\frac{A}{r} \tag{9}$$

where A is a parameter that is related to the number of electrons of the hydrogen-like atoms. Substituting the potential into the Schrödinger equation, the wave function may be guessed using the Nikiforov-Uvarov method (Tezcan & Sever, 2009; Nikiforov & Uvarov, 1988) or from the transformation of the Schrödinger equation into a standard differential equation (Szego, 1939). However, solving the Schrödinger equation completely is not the primary aim of this current research, therefore we proposed the trial wave function of the form

$$R_{nl}(r,a,b) = N_{nl} r^{a+\frac{1}{2}} e^{-br} L_n^{2a}(2br) \tag{10}$$

In Eq. (10), N_{nl} is the normalization constant, the terms a and b are unknown variational parameters which would be determined from the minimization of the variational energy. The function $L_n^{2a}(2br)$ is the generalized Laguerre polynomial. The normalization factor may be obtained from the condition:

$$N_{nl}\int_0^\infty \left|R_{nl}(r,a,b)\right|^2 dr = 1 \tag{11}$$

Inserting the wave function into Eq. (11), with a change of variable $x = 2br$, the normalization equation turns out as

$$\frac{N_{nl}}{2b^{2a+2}}\int_0^\infty x^{2a+1} e^{-x} L_n^{2a}(x)\,dx = 1 \tag{12}$$

The integral in (12) is a standard whose solution is given by

$$\int_0^\infty x^{2a+1} e^{-x}\left(L_n^{2a}(x)\right)^2 dx = \frac{\Gamma(n+2a+1)(2n+2a+1)}{n!} \tag{13}$$

Comparing Eq. (12) and (13), the normalization constant is obtained as

$$N_{nl} = \sqrt{\frac{(2b)^{2a+2}\, n!}{\Gamma(n+2a+1)(2n+2a+1)}} \tag{14}$$

Utilizing the normalized wave function, the momentum moment in (6) may be written as

$$\mathbf{P}_{nl}^2(r,a,b) = N_{nl}^2\int_0^\infty\left(\frac{dR_{nl}(r,a,b)}{dr}\right)^2 dr = \left(\left(a+\frac{1}{2}\right)^2 I_0 + 2b\left(a+\frac{1}{2}\right)I_1 + b^2 I_2 - 4b\left(a+\frac{1}{2}\right)I_3 - 4b^2 I_4 + 4b^2 I_5\right) \tag{15}$$

where

$$I_0 = N_{nl}^2\int_0^\infty r^{2a-1} e^{-2br}\left(L_n^{2a}(2br)\right)^2 dr = \frac{N_{nl}^2\Gamma(n+2a+1)}{(2b)^{2a}\,2a\,n!} \tag{16}$$

$$I_1 = N_{nl}^2\int_0^\infty r^{2a} e^{-2br}\left(L_n^{2a}(2br)\right)^2 dr = \frac{N_{nl}^2\Gamma(n+2a+1)}{(2b)^{2a+1}\,n!} \tag{17}$$

$$I_2 = N_{nl}^2\int_0^\infty r^{2a+1} e^{-2br}\left(L_n^{2a}(2br)\right)^2 dr = \frac{N_{nl}^2\Gamma(n+2a+1)(2n+2a+1)}{(2b)^{2a+2}\,n!} \tag{18}$$

$$I_3 = N_{nl}^2\int_0^\infty r^{2a} e^{-2br} L_n^{2a+1}(2br) L_n^{2a}(2br)\,dr = \frac{N_{nl}^2\Gamma(n+2a+1)}{(2b)^{2a+1}\,n!} \tag{19}$$

$$I_4 = N_{nl}^2\int_0^\infty r^{2a+1} e^{-2br} L_n^{2a+1}(2br) L_n^{2a}(2br)\,dr = \frac{N_{nl}^2\Gamma(n+2a+2)}{(2b)^{2a+2}\,n!} \tag{20}$$

$$I_5 = N_{nl}^2\int_0^\infty r^{2a+1} e^{-2br}\left(L_n^{2a+1}(2br)\right)^2 dr = \frac{N_{nl}^2\Gamma(n+2a+2)}{(2b)^{2a+2}\,n!} \tag{21}$$

In Eq. (15), we have used the following properties of the Laguerre polynomial (Szego, 1939)

$$\frac{dL_n^{2a}(2br)}{dr} = -2bL_{n-1}^{2a+1}(2br) \tag{22}$$

$$L_{n-1}^{2a+1}(2br) = L_n^{2a+1}(2br) - L_n^{2a}(2br) \tag{23}$$

The standard integrals in (17) and (18) are obtained from the othonormality conditions, while the integrals in (16) and Eq. (19-21) have been deduced with the help of the Mathematica program.

The integral solutions in (7) and (8) are given as

$$\left\langle r^{-2}\right\rangle = N_{nl}^2\int_0^\infty r^{2a-1} e^{-2br}\left(L_n^{2a}(2br)\right)^2 dr = \frac{4b^2}{(2n+2a+1)\,2a} \tag{24}$$

$$\left\langle V(r)\right\rangle = -AN_{nl}^2\int_0^\infty r^{2a} e^{-2br}\left(L_n^{2a}(2br)\right)^2 dr = -\frac{2Ab}{(2n+2a+1)} \tag{25}$$

Inserting the integrals solutions in Eq. (16-21) with the normalization constant obtained in (14) into (15), the momentum moment is obtained as

$$\mathbf{P}_{nl}^2(r,a,b) = \frac{b^2(4an+2a+1)}{2a(2n+2a+1)} \tag{26}$$

Substituting Eq. (24-26) into (5) gives the total energy as

$$E_{nl}(a,b) = \frac{\hbar^2 b^2\left(a\left(n+\frac{1}{2}\right)+\left(l+\frac{1}{2}\right)^2\right) - 2Aab\mu}{a\mu(2n+2a+1)} \tag{27}$$

Using the minimization approach in (4), the variational parameters are obtained

$$\frac{\partial E_{nl}(a,\,b)}{\partial b} = 0 \tag{28}$$

$$b = \frac{4Aa\mu}{\left(4an+4l^2+2a+4l+1\right)\hbar^2} \tag{29}$$

Substituting b into the energy equation in (27) for a gives the relation

$$E_{nl}(a) = -\frac{4A^2 a\mu}{(2n+2a+1)\left(4an+4l^2+2a+4l+1\right)\hbar^2} \tag{30}$$

Minimizing the energy allows for the determination of a

$$\frac{\partial E_{nl}(a)}{\partial a} = 0 \tag{31}$$

$$a = \pm\left(l+\frac{1}{2}\right) \tag{32}$$

The acceptable solution that satisfies the wave function boundary conditions is $a_+ = l + \frac{1}{2}$. The other value $a_- = -l - \frac{1}{2}$ would lead to a blow-up or singular wave function at the origin which does not obey the law of quantum mechanics. Inserting a and b into (27) admits the exact energy spectra of the Coulomb potential for any radial and orbital quantum numbers;

$$E_{nl} = -\frac{A^2\mu}{2\hbar^2\left(n+l+1\right)^2} \tag{33}$$

Pseudo-Harmonic Potential

The Pseudo-harmonic potential is given by (Rani et al., 2008; Amani & Ghorbanpour, 2012; Ikhdair & Sever, 2008; Omugbe et al., 2024)

$$V(r) = D\left(\frac{r}{r_0} - \frac{r_0}{r}\right)^2 \tag{34}$$

The parameters D, r_0 and r represent the respective dissociation energy, equilibrium bond length and the inter-nuclear distance. The wave function of the Schrödinger with the Pseudo-harmonic potential may be guessed as

$$R_{nl}\left(r, a_1, b_1\right) = W_{nl} r^{a_1+\frac{1}{2}} e^{-b_1 r^2} L_n^{a_1}\left(2b_1 r^2\right) \tag{35}$$

where a_1 and b_1 are unknown variational parameters and W_{nl} is the normalization factor. Using the condition for normalization, W_{nl} may be obtained as follows:

$$W_{nl}^2 \int_0^\infty r^{2a_1+1} e^{-2b_1 r^2} \left(L_n^{a_1}\left(2b_1 r^2\right)\right)^2 dr = 1 \tag{36}$$

Using the change of variable $y = 2br^2$, (36) transforms into

$$\frac{W_{nl}^2}{2\left(2b_1\right)^{a_1+1}} \int_0^\infty y^{a_1} e^{-y} \left(L_n^{a_1}(y)\right)^2 dy = 1 \tag{37}$$

Using the standard integral;

$$\int_0^\infty y^{a_1} e^{-y} \left(L_n^{a_1}(y)\right)^2 dy = \frac{\Gamma\left(n+a_1+1\right)}{n!}, \tag{38}$$

the normalization factor may be obtained as

$$W_{nl} = \sqrt{\frac{2\left(2b_1\right)^{a_1+1} n!}{\Gamma\left(n+a_1+1\right)}} \tag{39}$$

The kinetic energy of the system may be derived from Eq. (5) as

$$\left\langle T_{nl}\left(a_1, b_1\right)\right\rangle = \frac{\hbar^2}{2\mu}\left(\left\langle \nabla^2(r)\right\rangle + l(l+1)\left\langle r^{-2}\right\rangle\right) \tag{40}$$

$$\left\langle T_{nl}\left(a_1, b_1\right)\right\rangle = \frac{\hbar^2}{2\mu}\left[\left(\left(a_1+\frac{1}{2}\right)^2 + l(l+1)\right) I_{s0} + 4b_1\left(a_1+\frac{1}{2}\right) I_{s1} + 4b_1^2 I_{s2} - 8b_1\left(a_1+\frac{1}{2}\right) I_{s3} - 16b_1^2 I_{s4} + 16b_1^2 I_{s5}\right] \tag{41}$$

Using the change of variable $y = 2b_1 r^2$, the following integrals Eq.(42- 50) are evaluated with the help of the standard solutions given in Eq. (16 - 21)

$$I_{s0} = W_{nl}^2 \int_0^\infty r^{2a_1-1} e^{-2b_1 r^2} \left(L_n^{a_1}\left(2b_1 r^2\right)\right)^2 dr = \frac{2b_1}{a_1} \tag{42}$$

$$I_{s1} = W_{nl}^2 \int_0^\infty r^{2a_1+1} e^{-2b_1 r^2} \left(L_n^{a_1}\left(2b_1 r^2\right)\right)^2 dr = 1 \tag{43}$$

$$I_{s2} = W_{nl}^2 \int_0^\infty r^{2a_1+3} e^{-2b_1 r^2} \left(L_n^{a_1}\left(2b_1 r^2\right)\right)^2 dr = \frac{2n+a_1+1}{2b_1} \tag{44}$$

$$I_{s3} = W_{nl}^2 \int_0^\infty r^{2a_1+1} e^{-2b_1 r^2} L_n^{a_1}\left(2b_1 r^2\right) L_n^{a_1+1}\left(2b_1 r^2\right) dr = 1 \tag{45}$$

$$I_{s4} = W_{nl}^2 \int_0^\infty r^{2a_1+3} e^{-2b_1 r^2} L_n^{a_1+1}\left(2b_1 r^2\right) L_n^{a_1}\left(2b_1 r^2\right) dr = \frac{n+a_1+1}{2b_1} \tag{46}$$

$$I_{s5} = W_{nl}^2 \int_0^\infty r^{2a_1+3} e^{-2b_1 r^2} \left(L_n^{a_1+1}\left(2b_1 r^2\right)\right)^2 dr = \frac{n+a_1+1}{2b_1} \tag{47}$$

The mean value of the potential is obtained as

$$\left\langle V(r)\right\rangle = \frac{D}{r_0^2} I_{s6} - 2D + Dr_0^2 I_{s7} \tag{48}$$

where

$$I_{s6} = \left\langle r^2\right\rangle = W_{nl}^2 \int_0^\infty r^{2a_1+3} e^{-2b_1 r^2} \left(L_n^{a_1}\left(2b_1 r^2\right)\right)^2 dr = \frac{2n+a_1+1}{2b_1} \tag{49}$$

$$I_{s7} = \left\langle r^{-2}\right\rangle = W_{nl}^2 \int_0^\infty r^{2a_1-1} e^{-2b_1 r^2} \left(L_n^{a_1}\left(2b_1 r^2\right)\right)^2 dr = \frac{2b_1}{a_1} \tag{50}$$

Substituting the values of the integrals in Eq. (42-47) for the mean kinetic energy, (49) and (50) for the average potential energy into (5), the total variational energy is obtained in closed-form

$$E_{nl}\left(a_1, b_1\right) = \frac{b\hbar^2}{a_1\mu}\left[\left(l+\frac{1}{2}\right)^2 + 2a_1 n + a_1\right] + \frac{D\left(2n+a_1+1\right)}{2r_0^2 b_1} - 2D + \frac{2Dr_0^2 b_1}{a_1} \tag{51}$$

Following the minimization approach in (4), the variational parameters (a_1, b_1) are obtained

$$a_1 = b_1\sqrt{\frac{2\hbar^2 r_0^2}{\mu D}}\sqrt{\frac{2\mu D r_0^2}{\hbar^2} + \left(l+\frac{1}{2}\right)^2} \tag{52}$$

$$b_1 = \sqrt{\frac{\mu D}{2\hbar^2 r_0^2}} \tag{53}$$

Finally, the energy is obtained after the substitution of a_1 into Eq. (51)

$$E_{nl} = -2D + \hbar\sqrt{\frac{8D}{\mu r_0^2}}\left(n+\frac{1}{2}+\frac{1}{2}\sqrt{\frac{2\mu D r_0^2}{\hbar^2} + \left(l+\frac{1}{2}\right)^2}\right) \tag{54}$$

Hulthén Potential

The Hulthén potential is given by (Hulthén, 1942; Bayrak & Boztosun, 2007).

$$V(r) = -V_0 \frac{e^{-\alpha r}}{1-e^{-\alpha r}} \tag{55}$$

Due to complexity of performing analytical integration for excited quantum states, we will solve the problem for the ground state or s-wave case where $l = 0$. The ground state wave function satisfies the boundary conditions $R_{00}(r)|_{r=0} = R_{00}(r)|_{r=\infty} = 0$ and may be written as

$$R_{00}\left(r, \lambda, \nu\right) = G_{00}^2 \left(e^{-\alpha r}\right)^\lambda \left(1-e^{-\alpha r}\right)^\nu \tag{56}$$

where, the terms λ and ν are variational parameters that would be determined from energy minimization. The normalization condition requires that

$$I_{s0} = G_{00}^2 \int_0^\infty \left(e^{-\alpha r}\right)^{2\lambda} \left(1-e^{-\alpha r}\right)^{2\nu} dr = 1 \tag{57}$$

In (57) we let $z = e^{-\alpha r} \in (0,1)$ so that the integral transforms as

$$I_{s0} = \frac{G_{nl}^2}{\alpha} \int_0^1 (z)^{2\lambda-1} (1-z)^{2\nu} dz = 1 \tag{58}$$

Using the standard integral form of the Beta function $B(p,q)$

$$B(p,q) = \int_0^1 (t)^{p-1}(1-t)^{q-1} dt = \frac{\Gamma(p)\Gamma(q)}{\Gamma(p+q)}, \tag{59}$$

the normalization constant is obtained as

$$G_{nl} = \sqrt{\frac{\alpha\Gamma(2\lambda+2\nu+1)}{\Gamma(2\lambda)\Gamma(2\nu+1)}} \tag{60}$$

The average kinetic energy of the system can be derived from Eq. (5). For the ground state, the mean kinetic energy may be obtained as

$$\langle T_{00}(\lambda,\nu)\rangle = \frac{\hbar^2}{2\mu}\left(\left\langle \nabla^2 R_{00}^2(r)\right\rangle\right) = \frac{\hbar^2}{2\mu}\int_0^\infty \left(\frac{dR_{00}(r)}{dr}\right)^2 = \frac{\hbar^2 G_{00}^2}{2\mu}(I_{01}+I_{02}+I_{03}) \tag{61}$$

Where

$$I_{01} = \alpha^2(\lambda+\nu)^2 \int_0^\infty (e^{-\alpha r})^{2\lambda+2}(1-e^{-\alpha r})^{2\nu-2} dr = \alpha(\lambda+\nu)^2 B(2\lambda+2, 2\nu-1) \tag{62}$$

$$I_{02} = -2\alpha^2\lambda(\lambda+\nu)\int_0^\infty (e^{-\alpha r})^{2\lambda+1}(1-e^{-\alpha r})^{2\nu-2} dr = -2\alpha\lambda(\lambda+\nu)B(2\lambda+1, 2\nu-1) \tag{63}$$

$$I_{03} = \alpha^2\lambda^2 \int_0^\infty (e^{-\alpha r})^{2\lambda}(1-e^{-\alpha r})^{2\nu-2} dr = \alpha\lambda^2 B(2\lambda, 2\nu-1) \tag{64}$$

Inserting Eq. (62 - 64) with the standard formula in Eq.(59) into Eq. (61), we obtained a closed form solution of the ground state kinetic energy

$$\langle T_{00}(\lambda,\nu)\rangle = \frac{\alpha^2\hbar^2}{2\mu}\left(\frac{\lambda(\lambda+\nu)}{2\nu-1}\right) \tag{65}$$

The average potential energy is given by

$$\langle V(r,\lambda,\nu)\rangle_{00} = -G_{00}^2 V_0 \int_0^\infty \left(e^{-\alpha r}\right)^{2\lambda+1}\left(1-e^{-\alpha r}\right)^{2\nu-1} dr = \frac{G_{00}^2}{\alpha} B(2\lambda+1, 2\nu) = -\frac{\lambda V_0}{\nu} \tag{66}$$

The total energy is obtained as

$$E_{00}(\lambda,\nu) = \frac{\alpha^2\hbar^2}{2\mu}\left(\frac{\lambda(\lambda+\nu)}{2\nu-1}\right) - \frac{\lambda V_0}{\nu} \tag{67}$$

Applying the energy minimization approach $\frac{\partial E(\lambda,\nu)}{\partial\lambda} = 0$ and solving for λ gives

$$\lambda = \frac{\mu V_0(2\nu-1)}{\alpha^2\hbar^2\nu} - \frac{\nu}{2} \tag{68}$$

Substituting Eq.(68) into Eq. (67) allows us to minimize the energy ($\frac{\partial E(\lambda,\nu)}{\partial\nu} = 0$) and obtained numerical value $\nu = 1$.

Using the values of ν and λ, the total ground state energy for the s-wave case is given by

$$E_{00} = -\frac{\alpha^2\hbar^2}{8\mu}\left(1-\frac{2\mu V_0}{\alpha^2\hbar^2}\right)^2 \tag{69}$$

Hyperbolic Potential

The potential is given as

$$V(x) = V_0\left(1+\tanh^2(\alpha x)\right), \qquad -\infty \text{ p } x \text{ p } \infty \tag{70}$$

The potential has a minimum of V_0 at $= 0$. There is no exact analytical solution of the Schrödinger equation with the potential for any orbital momentum quantum (l). For the one-dimensional Schrödinger equation for a rotationless particle case where, the exact eigenfunction solution may be obtain as the associated Legendre functions of the first kind ($P_n^m(\tanh(\alpha x))$ and second kind ($Y_n^m(\tanh(\alpha x))$). Due to boundary conditions, the function $Y_n^m(\tanh(\alpha x))$ becomes singular and must be discarded. The zeroes of the Legendre functions are obtained from the difference between the degree (n) and order (m) parameters. The energy spectrum may be obtained from the zeroes. However, in using the variational approach care must be taken in choosing the wave function as the Legendre function with non-integer degree and order parameters are difficult to utilize. In what follows, we attempt to obtain the exact ground state energy spectra. We guess the wave function that obeys the boundary conditions for a well-behave function:

$$\psi_0(x) = N_0\left(1-\tanh^2(\alpha x)\right)^{k/2}, \qquad \psi_0(x)\big|_{x=-\infty} = \psi_0(x)\big|_{x=\infty} = 0 \tag{71}$$

The parameter k is a variational constant that would be determined from the energy minimization. The normalization condition requires that

$$\int_{-\infty}^{\infty} \psi_0(x)\psi_0^*(x)dx = 1 \tag{72}$$

Using the wave function in (71), we have

$$N_0^2 \int_{-\infty}^{\infty} \left(1-\tanh^2(\alpha x)\right)^k dx = 1 \tag{73}$$

By letting $y = \tanh(\alpha x) \in (-1,1)$, the integral reduces to

$$\frac{N_0^2}{\alpha}\int_{-1}^{1}\left(1-y^2\right)^{k-1} dy = 1 \tag{74}$$

Evaluating the integral gives the normalization constant as

$$N_0 = \sqrt{\frac{\alpha\Gamma\left(k+\frac{1}{2}\right)}{\Gamma(k)\sqrt{\pi}}} \tag{75}$$

The expectation value for the potential function is given by

$$\langle V(k)\rangle = \frac{V_0\alpha\Gamma\left(k+\frac{1}{2}\right)}{\Gamma(k)\sqrt{\pi}}\int_{-\infty}^{\infty}\left(1+\tanh^2(\alpha x)\right)\left(1-\tanh^2(\alpha x)\right)^k dx \quad (76)$$

Using the change of variable $y=\tanh(\alpha x)\in(-1,1)$ gives

$$\langle V(k)\rangle = \frac{V_0\Gamma\left(k+\frac{1}{2}\right)}{\Gamma(k)\sqrt{\pi}}\int_{-1}^{1}\left(1+y^2\right)\left(1-y^2\right)^{k-1}dy = \frac{2V_0(k+1)}{2k+1} \quad (77)$$

Using similar process in previous sections, the kinetic energy expectation value may be expressed as

$$\langle T_0(k)\rangle = \frac{\hbar^2}{2\mu}\frac{\alpha^2k^2\Gamma\left(k+\frac{1}{2}\right)}{\Gamma(k)\sqrt{\pi}}\int_{-1}^{1}y^2\left(1-y^2\right)^{k-1}dy = \frac{\hbar^2}{2\mu}\frac{k^2\alpha^2}{(2k+1)} \quad (78)$$

The total energy for the ground state is obtained from the sum of (77) and (78) as

$$E_0(k) = \langle T_0(k)\rangle + \langle V(k)\rangle = \frac{2V_0(k+1)}{2k+1} + \frac{\hbar^2}{2\mu}\frac{k^2\alpha^2}{(2k+1)} \quad (79)$$

The parameter k is obtained from the energy minimization

$$\frac{dE_0}{dk} = \frac{1}{(2k+1)^2}\left(\frac{\alpha^2\hbar^2}{\mu}k(k+1) - 2V_0\right) = 0 \quad (80)$$

$$k = -\frac{1}{2} \pm \sqrt{\frac{1}{4} + \frac{2\mu V_0}{\alpha^2\hbar^2}} \quad (81)$$

Inserting k in (81) into (79) gives the exact energy spectrum for the ground state. The solution of this potential is not common so we have obtained the solution by numerically solving the Schrödinger equation using the Matrix Numerov approach (Pillai et al., 2012) as a means for confirming our analytical approach (see Table 1).

$$E_0^{Exact} = 2V_0 - \frac{\alpha^2\hbar^2}{2\mu}\left(\frac{1}{2} - \sqrt{\frac{2\mu V_0}{\alpha^2\hbar^2} + \frac{1}{4}}\right) \quad (82)$$

Exponential Step Potential

We examined the attractive potential given by

$$V(x) = -V_0 e^{-\alpha x} \quad V_0 \text{ f } 0,\ \alpha \text{ f } 0 \quad (83)$$

The potential may find applications in the spectra analysis of the hydrogen-like atoms. The exact analytical energy spectra solutions are not known. However, the exact bound state solutions may be determined numerically using the method of Lucha & Schöberl (1999) or the Matrix Numerov approach (Pillai et al., 2012). These methods solve the Schrödinger equation where analytical solutions are difficult to obtain. We may also apply approximation methods to the problem such as the Wentzel-Kramer-Brillouin (WKB) approximation (Krynytskyi & Rovenchak, 2021). In what follows we will attempt to use the variational method to obtain approximate ground state solutions. Our motivation to study this potential is to demonstrate that the choice of the wave functions highly determine the accuracy in the variational method. The other potentials treated here, allows for the exact analytical solutions. We note that the exact eigenfunction of the exponential potential is the Bessel function of the first kind. However, using this eigenfunction, poses a challenge in obtaining the variational parameters owing to transcendental equations which arises from the minimization of the total energy. We also note that the exact eigenvalues may be obtained from the zeroes of the oscillating Bessel function and are beyond the scope of this present work. We proposed the following trial wave functions

$$\psi_1(x) = N_1 x^{\lambda_0} e^{-\alpha\lambda_1 x/2} \quad (84)$$

$$\psi_2(x) = N_2 x^{\lambda_2} e^{-\alpha\lambda_3 x^2/2} \quad (85)$$

The wave functions obey the boundary conditions $\psi_i(x)\big|_{x=0} = \psi_i(x)\big|_{x=\infty} = 0, \quad i = 1,2.$

The notations N_i and λ_i are real quantities representing the respective normalization constant and variational parameters. By adopting the procedure in the previous sections with the trial wave function in Eq. (86), we obtained the ground state normalization constant, expectation values and the total energy as

$$N_1 = \frac{(\alpha\lambda_1)^{2\lambda_0+1}}{\Gamma(2\lambda_0+1)} \quad (86)$$

$$\langle V(\lambda_0,\lambda_1)\rangle = -V_0\left(\frac{\lambda_1}{1+\lambda_1}\right)^{2\lambda_0+1} \quad (87)$$

$$\langle T(\lambda_0,\lambda_1)\rangle = \frac{\alpha^2\hbar^2\lambda_1^2}{8\mu(2\lambda_0-1)} \quad (88)$$

$$E_0(\lambda_0,\lambda_1) = \frac{\alpha^2\hbar^2\lambda_1^2}{8\mu(2\lambda_0-1)} - V_0\left(\frac{\lambda_1}{1+\lambda_1}\right)^{2\lambda_0+1} \quad (89)$$

Using the Gaussian trial wave function, we obtained the solutions for the normalization factor, expectation values and total energy for the ground state

$$N_2 = \frac{2(\alpha\lambda_3)^{\lambda_2+\frac{1}{2}}}{\Gamma\left(\lambda_2+\frac{1}{2}\right)} \quad (90)$$

$$\langle V(\lambda_2,\lambda_3)\rangle = -V_0\left({}_1F_1\left(\lambda_2+\frac{1}{2},\frac{1}{2},\frac{\alpha}{4\lambda_3}\right) - \frac{\alpha\Gamma(\lambda_2+1)\,{}_1F_1\left(\lambda_2+1,\frac{3}{2},\frac{\alpha}{4\lambda_3}\right)}{\sqrt{\alpha\lambda_3}\,\Gamma\left(\lambda_2+\frac{1}{2}\right)}\right) \quad (91)$$

$$\langle T(\lambda_2,\lambda_3)\rangle = \frac{\alpha\hbar^2\lambda_3(4\lambda_2-1)}{4\mu(2\lambda_2-1)} \quad (92)$$

$$E_0(\lambda_2,\lambda_3) = \frac{\alpha\hbar^2\lambda_3(4\lambda_2-1)}{4\mu(2\lambda_2-1)} - V_0\left({}_1F_1\left(\lambda_2+\frac{1}{2},\frac{1}{2},\frac{\alpha}{4\lambda_3}\right) - \frac{\alpha\Gamma(\lambda_2+1)\,{}_1F_1\left(\lambda_2+1,\frac{3}{2},\frac{\alpha}{4\lambda_3}\right)}{\sqrt{\alpha\lambda_3}\,\Gamma\left(\lambda_2+\frac{1}{2}\right)}\right) \quad (93)$$

By minimizing the total energy equations in Eq. (89) and Eq. (93), we obtained the variational parameters (see Table 2) numerically with the help of Maple program and the corresponding energy eigenvalues in atomic units for increasing α and fixed potential depth V_0 in Table 3 within the appendix.

Discussion

We used the variational approach to obtain the bound-state solutions for solvable potential functions. The variational parameters were determined through minimization of the total energy. The results for the Coulomb, Pseudo-harmonic and the Hulthén potentials show perfect agreement with existing literature, where solutions were obtained using other methods (Rani, Bhardwaj & Chand, 2008; Amani & Ghorbanpour, 2012; Ikhdair & Sever, 2008; Omugbe et al., 2024 ; Bayrak & Boztosun, 2007; Tezcan & Sever, 2009). Also, for the hyperbolic potential, the variational approach reproduced the exact ground state eigenvalues given in Table **1** of the appendix compared with the numerical solutions obtained from the Numerov matrix method. In Table **3**, the results for the exponential potential indicate that the energy eigenvalues obtained with the Gaussian trial wave function gives an absolute percentage average deviation (APAD) $\left(100\Big/5\sum_{i}^{5}\left|\left(1-E_0^{Var}/E_0^{Exact}\right)\right|\right)$ of 0.14%. The errors were larger with the exponential trial wave function and the WKB approximation **(**Krynytskyi & Rovenchak, 2021**)** where we found APAD values of 0.55% and 0.31% respectively. The error in the WKB approach arises for two reasons: the method is accurate as the quantum number increases and also the absence of the Langer correction. This correction which ensures the correct behaviour of the wave function near the origin also contributes to the quantum fluctuation of eigenvalues and maps the centrifugal barrier term from $l(l+1) \rightarrow (l+1/2)^2$ making the WKB approach with the exponential potential non-trivial even for $l = 0$. The accuracy of the variational method fundamentally depends on choosing an appropriate trial wave function. Since the wave functions of exactly solvable quantum systems often share a similar form, it is possible to attempt excited-state solutions for other potentials having orthogonal Jacobi or hypergeometric-type polynomials embedded in their wave functions. However, such attempts are often complicated by the difficulty of obtaining analytical expressions for the variational parameters, owing to the complexity of the integrals involved. In addition, the average effective potential includes an inverse-square term, which leads to divergent integrals for any angular momentum quantum state solutions. These difficulties might be mitigated for the potentials if the energies are evaluated in a piecewise manner across different quantum states. Otherwise, obtaining a closed-form solution in a single step remains a problem with th variational approach.

CONCLUSION

In this paper, we have applied the variational approach to some quantum mechanical potentials using orthogonal trial wave functions. These trial wave functions reproduced the exact analytical energy spectra equations for the Coulomb and Pseudo-harmonic potential functions. The hyperbolic and Hulthén potentials admit the exact ground state energy spectral in comparison with existing literature and the Numerov Matrix approach. We studied the respective exponential potential whose solutions are the Bessel functions of mathematical physics. The analytical solutions involving the trial functions of Bessel functions within the variational method are difficult to obtain due to the solution of the variational parameters. However, we obtained an approximate analytical ground state energy using a two parameter Gaussian trial wave function. The results are in good agreement with numerical solutions and WKB approximation approach.

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Data Availability Statement

All data generated or analyzed during this study are included in this published article.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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APPENDIX

Table 1: Exact Ground State Energy Spectra of the Potential $V(x)=V_0\left(1+\tanh^2(\alpha x)\right)$ · $\mu=\hbar=1, V_0=5$

α	**(Eq. (84))**	E_0^{Exact} **(Pillai et al. 2012)**
0.1	5.155633645	5.155633646
0.2	5.306385840	5.306385840
0.3	5.452374985	5.452374984
0.4	5.593719182	5.593719181
0.5	5.730536098	5.730536096

Table 2: Calculated Variational Parameters $\mu=\hbar=1, V_0=15$

α	λ_0	λ_1	λ_2	λ_3
0.1	1.471828072	34.16459864	0.939605619	9.475033841
0.2	1.454628321	20.70947105	0.935572479	7.092342987
0.3	1.439796891	15.28063338	0.932043268	5.885694634
0.4	1.426225012	12.22577482	0.928770242	5.098586907
0.5	1.413456203	10.22670782	0.925651374	4.522671881

Table 3. Comparison of Variational Ground State Energy with the Exact Values for the Potential $V(x)=-V_0e^{-\alpha x}$ · $\mu=\hbar=1, V_0=15$

α	$E_0(\lambda_0,\lambda_1)$	$E_0(\lambda_2,\lambda_3)$	E_0^{WKB} **Krynytskyi, & Rovenchak,(2021)**	E_0^{Exact} **(Pillai et al. 2012)**
0.1	-12.63623467	-12.6674227	-12.68988967	-12.67287188
0.2	-11.35149591	-11.39305666	-11.42830113	-11.40267084
0.3	-10.33212044	-10.37822149	-10.42403314	-10.39192311
0.4	-9.466521018	-9.513689082	-9.568862952	-9.531519162
0.5	-8.707366086	-8.753197599	-8.816948228	-8.775236085
APAD%	0.55	0.14	0.31	