Exact Solutions of the Schrödinger Equation via Laplace Transform Approach: Pseudoharmonic potential and Mie-type potentials

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Abstract

Exact bound state solutions and corresponding normalized eigenfunctions of the radial Schrödinger equation are studied for the pseudoharmonic and Mie-type potentials by using the Laplace transform approach. The analytical results are obtained and seen that they are the same with the ones obtained before. The energy eigenvalues of the inverse square plus square potential and three-dimensional harmonic oscillator are given as special cases. It is shown the variation of the first six normalized wavefunctions of the above potentials. It is also given numerical results for the bound states of two diatomic molecular potentials, and compared the results with the ones obtained in literature.

Keywords: Exact Solution, Bound states, Laplace transform, Pseudoharmonic potential, Mie-type potential, Schrödinger equation

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I. INTRODUCTION

Molecular vibrational and rotational spectroscopy is one of the important parts of molecular physics and one of the main tools for other scientific areas such as biology [1] and environmental sciences [2]. The harmonic oscillator could be useful ground to explain the molecular vibrations but this model is restricted for only lowest states [3]. To improve the theory of molecular vibrations the anharmonic oscillators such as Morse and Mie-type potentials (Kratzer potential and its generalization) can be used to solve exactly the Schrödinger equation (SE) and provide more reliable model for diatomic molecules [4]. Mie-type potentials being considered as an example in the present work have important advantages such as having eigenfunctions behaving correctly at $r \to 0$ and $r \to \infty$ and providing exact solutions to the SE [5]. So, these potentials have been used to determine molecular structures and received much attention in literature [6]. In the present work, we deal with also another diatomic potential called pseudoharmonic potential proposed by Davidson [7]. This potential is used to describe the roto-vibrational states of diatomic molecules and nuclear rotations and vibrations [8].

In the light of the above considerations, it could be interesting to solve exactly the SE for the pseudoharmonic potential and Mie-type potentials and find any $\ell$-state solutions in the view of molecular physics phenomenon. Moreover, obtaining the exact solutions of the SE for the molecular potentials is one of the main problems in quantum physics [6]. One of the methods giving exact solutions of the SE is used in Ref. [9] where the wave equation is solved for the non-central potential within the framework of the supersymmetric quantum mechanics. In Ref. [10], the energy eigenvalues of the radial SE are obtained for the Coulomb potential by using path integral formalism and the author also stated how can be obtained the wave functions. In Ref. [11], energy spectrum of the Coulomb, Morse and harmonic oscillator potentials have been studied by using point canonical transformation where the formalism has been extended to the case of position-dependent mass.

We list some methods used in literature to solve the wave equations for the
pseudoharmonic potential and Mie-type potentials: Nikiforov-Uvarov method [12, 13], algebraic approach [14], polynomial solution [15], exact quantization rule [16], hypervirial theorem with perturbation theory [17], shape-invariance procedure [18], solutions in terms of hypergeometric functions [19], etc. In this work, we find exact bound state solutions of pseudoharmonic potential and Mie-type potentials by reducing the SE to a first-order differential equation via Laplace transform approach (LTA) and therefore we make use of integral to obtain energy eigenvalues and the corresponding eigenfunctions. Actually, the LTA is an integral transform which has been used by many authors to solve the SE for different potentials [20, 21, 22, 23]. The LTA could be a nearly new formalism in the literature and serve as a powerful algebraic treatment for solving the second-order differential equations. As a result, the LT methods describe a simple way for solving of radial and one-dimensional differential equations. The other advantage of this approach is that a second-order equation can be converted into more simpler form whose solutions may be obtained easily [22].

II. ENERGY EIGENVALUE SOLUTIONS

Time-independent Schrödinger equation is written as

\[ \left\{ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right\} \psi(r, \theta, \varphi) = E_{\ell n} \psi(r, \theta, \varphi), \tag{1} \]

and defining the wave function \( \psi(r, \theta, \varphi) = \frac{1}{r} R(r) Y(\theta, \varphi) \), we obtain the radial SE as [6]

\[ \left\{ \frac{d^2}{dr^2} - \frac{\ell(\ell + 1)}{r^2} + \frac{2m}{\hbar^2} \left[ E_{\ell n} - V(r) \right]\right\} R(r) = 0. \tag{2} \]

where \( \ell \) is the angular momentum quantum number, \( m \) is the particle mass moving in the potential field \( V(r) \) and \( E_{\ell n} \) is the nonrelativistic energy of particle.
A. Pseudoharmonic Potential

The pseudoharmonic potential is given [8]

$$V(r) = a_1 r^2 + \frac{a_2}{r^2} + a_3,$$

(3)

where $a_i (i = 1, 2, 3)$ are real parameters. Inserting Eq. (3) into Eq. (2), we obtain

$$\left\{ \frac{d^2}{dr^2} - \mu^2 r^2 - \frac{\nu(\nu + 1)}{r^2} + \varepsilon^2 \right\} R(r) = 0,$$

(4)

where

$$\mu^2 = \frac{2ma_1}{\hbar^2}; \nu(\nu + 1) = \frac{2ma_2}{\hbar^2} + \ell(\ell + 1); \varepsilon^2 = \frac{2m}{\hbar^2} \left( E_{n\ell} - a_3 \right).$$

(5)

Defining the new variable $y = r^2$ and rewriting the radial wave function as $R(y) = y^{-\nu/2} \phi(y)$, Eq. (4) turns into

$$\left\{ y \frac{d^2}{dy^2} - \left( \nu - \frac{1}{2} \right) \frac{d}{dy} - \frac{1}{4} \left( \mu^2 y - \varepsilon^2 \right) \right\} \phi(y) = 0,$$

(6)

By using the Laplace transform defined as [24]

$$\mathcal{L} \{ \phi(y) \} = f(t) = \int_0^\infty dy e^{-ty} \phi(y),$$

(7)

Eq. (6) reads

$$\left( t^2 - \frac{\mu^2}{4} \right) \frac{df(t)}{dt} + \left\{ \left( \nu + \frac{3}{2} \right) t - \frac{\varepsilon^2}{4} \right\} f(t) = 0,$$

(8)

which is a first-order ordinary differential equation and its solution is simply given

$$f(t) = N \left( t + \frac{\mu}{2} \right)^{-\frac{\varepsilon^2}{4\mu} - \frac{1}{4}(\nu + \frac{3}{2})} \left( t - \frac{\mu}{2} \right)^{\frac{\varepsilon^2}{4\mu} - \frac{1}{4}(\nu + \frac{3}{2})},$$

(9)

where $N$ is a integral constant. In order to obtain finite wave functions, it should be

$$\frac{\varepsilon^2}{4\mu} - \frac{1}{2} \left( \nu + \frac{3}{2} \right) = n, \quad (n = 0, 1, 2, 3, \ldots)$$

(10)
which gives single-valued wave functions. By using this requirement and expanding Eq. (9) into series, we get
\[
f(t) = N' \sum_{k=0}^{n} \frac{(-1)^k n! (t + \frac{\mu}{2})^{-(\nu + \frac{3}{2} + k)}}{(n - k)!k!},
\]
where \(N'\) is a constant. By using the inverse Laplace transformation \([24]\) we immediately obtain the solution of Eq. (6)
\[
\phi(y) = N'' \sum_{k=0}^{n} \frac{(-1)^k n!}{(n - k)!k!} \frac{\Gamma(\nu + \frac{3}{2})}{\Gamma(\nu + \frac{3}{2} + k)} y^{\nu+\frac{3}{2}+k} e^{-\mu y/2},
\]
where \(N''\) is a constant. On the other hand, the confluent hypergeometric functions is defined as a series expansion \([25]\)
\[
_{1}F_{1}(-n, \sigma, z) = \sum_{m=0}^{n} \frac{(-1)^m n!}{(n - m)!m!} \frac{\Gamma(\sigma)}{\Gamma(\sigma + m)} y^m,
\]
So, comparing Eq. (12) with Eq. (13) we deduce that
\[
\phi(y) = N''' e^{-\mu y/2} y^{\nu+\frac{3}{2}} _{1}F_{1}(-n, \nu + \frac{3}{2}, y),
\]
We obtain finally the radial wave functions
\[
R(y) = \mathcal{N} e^{-\mu y/2} y^{(\nu+1)/2} _{1}F_{1}(-n, \nu + \frac{3}{2}, y),
\]
where \(\mathcal{N}\) is normalization constant. Using the normalization condition given as \(\int_{0}^{\infty} [R(r)]^2 dr = 1\) and the relation between the Laguerre polynomials and confluent hypergeometric functions as \(L_{n}^{p}(x) = \frac{\Gamma(n+p+1)}{n!} _{1}F_{1}(-n, p + 1, x)\) \([25]\), the normalization constant in Eq. (15) is written
\[
\mathcal{N} = \mu^{(\nu+3/2)/2} \sqrt{\frac{2\Gamma(n + \nu + \frac{3}{2})}{n!}} \left[\Gamma\left(\nu + \frac{3}{2}\right)\right]^{-1},
\]
where we have used \([25]\)
\[
\int_{0}^{\infty} x^q e^{-x} L_{n}^{q}(x) L_{n'}^{q}(x)dx = \frac{\Gamma(q + n + 1)}{n!} \delta_{nn'}.
\]
In Fig. (1) we show the variation of the normalized wave functions of the pseudoharmonic potential on the coordinate \(r\). We give first six wave
functions according to the quantum number pairs \((n, \ell)\). Inserting the parameters in Eq. (5) into Eq. (10), the energy spectrum of the pseudo-harmonic potential is obtained

\[
E_{n\ell} = a_3 + \sqrt{\frac{8\hbar^2 a_1}{m}} \left( n + \frac{1}{2} + \frac{1}{4} \sqrt{1 + 4\ell(\ell + 1) + \frac{8ma_2}{\hbar^2}} \right). \tag{18}
\]

We give our numerical energy eigenvalues for two different diatomic potentials in Table I. We compare our results with the ones given in Ref. [12] by setting the potential parameters as

\[
a_1 = \frac{D_0}{r_0^2}, \quad a_2 = D_0 r_0^2 \quad \text{and} \quad a_3 = -2D_0.
\]

Let us study the results of some special cases. Firstly, if we put \(a_3 = 0\) we obtain from Eq. (18)

\[
E_{n\ell} = \sqrt{\frac{8\hbar^2 a_1}{m}} \left( n + \frac{1}{2} + \frac{1}{4} \sqrt{1 + 4\ell(\ell + 1) + \frac{8ma_2}{\hbar^2}} \right), \tag{19}
\]

which is the same result given in Ref. [26] for the potential of the form \(\frac{4}{r^2} + Br^2\). Secondly, if we choose the parameters as \(a_2 = a_3 = 0\) and \(a_1 = \frac{1}{2}m\omega^2\) in Eq. (18) we get

\[
E_{n\ell} = \hbar \omega \left( 2n + \ell + \frac{3}{2} \right), \tag{20}
\]

where if we define \(n' = 2n + \ell\) as 'principal quantum number' we obtain

\[
E_{n'\ell} = \hbar \omega \left( n' + \frac{3}{2} \right). \tag{21}
\]

which is exactly the spectrum of three-dimensional harmonic oscillator [26].

**B. Mie-type Potentials**

The Morse potential is an example of this type of potentials or Kratzer potential and its generalization having the forms, respectively,

\[
V(r) = -D \left( \frac{2r_0}{r} - \frac{r_0^2}{r^2} \right), \tag{22}
\]

and

\[
V(r) = D \left( \frac{r - r_0}{r} \right)^2. \tag{23}
\]
where $D$ is the dissociation energy and $r_0$ is the equilibrium distance [15].

So, the Mie-type potentials can be simply given as

$$V(r) = \frac{a}{r^2} + \frac{b}{r} + c,$$

(24)

where $a, b, c$ are real potential parameters. Inserting Eq. (24) into Eq. (2), redefining the wave function as $R(r) = \sqrt{r} \varphi(r)$ and using the following abbreviations

$$\gamma^2 = \frac{2ma}{\hbar^2} + \ell(\ell + 1) + \frac{1}{4}; \delta^2 = \frac{2mb}{\hbar^2}; \varepsilon^2 = \frac{2m}{\hbar^2}(c - E_n),$$

(25)

gives

$$\left\{ r^2 \frac{d^2}{dr^2} + r \frac{d}{dr} - \left[ \frac{\gamma^2}{r^2} + \frac{\delta^2}{r} + \varepsilon^2 \right] r^2 \right\} \varphi(r) = 0.$$

(26)

Setting $\varphi(r) = r^\alpha \phi(r)$ with $\alpha$ is a constant and then inserting into Eq. (26) leads

$$\left\{ r^2 \frac{d^2}{dr^2} + (2\alpha + 1) r \frac{d}{dr} - \varepsilon^2 r^2 - \delta^2 r + \alpha^2 - \gamma^2 \right\} \phi(r) = 0,$$

(27)

In order to obtain a finite wave function when $r \to \infty$, we must take $\alpha = -\gamma$ in Eq. (27) and then we get

$$\left\{ r \frac{d^2}{dr^2} - (2\gamma - 1) \frac{d}{dr} - \delta^2 - \varepsilon^2 r \right\} \phi(r) = 0.$$

(28)

Applying the Laplace transform to Eq. (28) we obtain a first-order differential equation

$$(t^2 - \varepsilon^2) \frac{df(t)}{dt} + [(2\gamma + 1) t + \delta^2] f(t) = 0,$$

(29)

whose solution is

$$f(t) = N (t + \varepsilon)^{-(2\gamma+1)} \left( \frac{t - \varepsilon}{t + \varepsilon} \right)^{-\frac{\delta^2}{2\varepsilon} - \frac{2\gamma+1}{2}}.$$

(30)

The wave functions must be single-valued which requiring that

$$-\frac{\delta^2}{2\varepsilon} - \frac{2\gamma + 1}{2} = n, \quad (n = 0, 1, 2, 3, \ldots)$$

(31)
Taking into account this requirement and applying a simple series expansion to Eq. (30) gives

\[
f(t) = N' \sum_{k=0}^{n} \frac{(-1)^k n!}{(n-k)! k!} (2\varepsilon)^k (t + \varepsilon)^{-(2\gamma+1)-k},
\]  

(32)

where \( N' \) is a constant. Using the inverse Laplace transformation [24] in Eq. (32) we deduce that

\[
\phi(r) = N'' r^{2\gamma} e^{-\varepsilon r} \sum_{k=0}^{n} \frac{(-1)^k n!}{(n-k)! k!} \frac{\Gamma(2\gamma + 1)}{\Gamma(2\gamma + 1 + k)} (2\varepsilon r)^k,
\]  

(33)

Finally, we obtain

\[
\psi(r) = N''' r^{\gamma+\frac{1}{2}} e^{-\varepsilon r} \sum_{k=0}^{n} \frac{(-1)^k n!}{(n-k)! k!} \frac{\Gamma(2\gamma + 1)}{\Gamma(2\gamma + 1 + k)} (2\varepsilon r)^k,
\]  

(34)

Comparing last equation with Eq. (13) we write the radial wave function as

\[
R(r) = N r^{\gamma+\frac{1}{2}} e^{-\varepsilon r} _1F_1(-n, 2\gamma + 1, 2\varepsilon r).
\]  

(35)

where the normalization constant is given by following the same procedure in previous section as

\[
\mathcal{N} = \Gamma(2\gamma + 1) \sqrt{\frac{n!(2n + 2\gamma + 1)}{\Gamma(n + 2\gamma + 1)}}.
\]  

(36)

We give the dependence of the wave functions of the Kratzer potential on spatially coordinate \( r \) in Fig. (2) where the wave functions are plotted for the same quantum number values as in pseudoharmonic potential. Using Eqs. (25) and (31) we obtain the energy eigenvalues of the Mie-type potentials

\[
E_{n\ell} = c - \frac{\hbar^2}{8m} \left[ \frac{2mb/\hbar^2}{n + \frac{1}{2} \left( 1 + 2\sqrt{\frac{2ma}{\hbar^2}} + \ell(\ell + 1) + \frac{1}{4} \right)} \right]^2.
\]  

(37)

which is the same result with the ones obtained in Ref. [27]. We summarize our numerical results for different quantum number pairs \((n, \ell)\) in Table II. To compare our results we chose the potential parameters as \( a = D_e \tau_e^2, \) \( b = -2D_e \tau_e, \) \( c = D_e \) used in Ref. [13].
III. RESULTS

Our numerical energy eigenvalues of two diatomic molecules interacting in short-range [28] given in Tables I and II have a good accuracy with the ones obtained in Refs. [15] and [13]. Figs. 1 and 2 show the variation of the wave functions versus $r$ for the pseudoharmonic and Kratzer potentials. The wave functions of the pseudoharmonic (Kratzer potential) go to zero as $r \to 0$ and as $r \sim 8$ ($r \sim 35$). The eigenfunctions corresponding to $n = 1$ for each potential go to zero from lower part of the vertical axes while the remaining functions go to zero from upper part of the zero axes.

IV. CONCLUSIONS

We have exactly solved the radial Schrödinger equation for the pseudo-harmonic and Mie-type potentials by using Laplace transform approach. We have found the energy eigenvalues and the corresponding normalized eigenfunctions of the diatomic potentials. We discussed briefly some special cases of the potentials. We observed that our analytical results and also the results for the special cases are the same with the ones obtained in literature. We also summarized our numerical energy eigenvalues for two different diatomic molecules. It seems that the Laplace transform approach is very economical method about solving the wave equations for some potentials.

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TABLE I: Energy eigenvalues of the pseudoharmonic potential for different values of \( n \) and \( \ell \) in eV (the parameter values are used in Ref. [12]:

\( D_0 = 96288.03528 \text{ cm}^{-1}, r_0 = 1.0940 \text{ Å}, m = 7.00335 \text{ amu for } N_2; \)

\( D_0 = 87471.42567 \text{ cm}^{-1}, r_0 = 1.1282 \text{ Å}, m = 6.860586 \text{ amu for } CO). \)

| \( n \) | \( \ell \) | \( N_2 \) | \( \text{Our Results} \) | \( \text{Ref. [15]} \) | \( CO \) | \( \text{Our Results} \) | \( \text{Ref. [15]} \) |
|-------|-------|----------|----------------|----------------|----------|----------------|----------------|
| 0     | 0     | 0.109180 | 0.1091559      | 0.101953       | 0.1019306 |
| 1     | 0     | 0.327414 | 0.3273430      | 0.305738       | 0.3056722 |
|       | 1     | 0.327913 | 0.3278417      | 0.306217       | 0.3061508 |
| 2     | 0     | 0.545648 | 0.5455302      | 0.509524       | 0.5094137 |
|       | 1     | 0.546147 | 0.5460288      | 0.510003       | 0.5098923 |
|       | 2     | 0.547145 | 0.5470260      | 0.510961       | 0.5108495 |
| 3     | 0     | 0.763883 | 0.763510       | 0.713310       |           |
|       | 1     | 0.764382 | 0.713789       |               |
|       | 2     | 0.765380 | 0.714747       |               |
|       | 3     | 0.766877 |               |               |
| 4     | 0     | 0.982117 | 0.9819045      | 0.917095       | 0.9168969 |
|       | 1     | 0.982616 | 0.9824031      | 0.917574       | 0.9173755 |
|       | 2     | 0.983614 | 0.9834003      | 0.918532       | 0.9183327 |
|       | 3     | 0.985111 | 0.9848961      | 0.919969       | 0.9197684 |
|       | 4     | 0.987107 | 0.9868903      | 0.921885       | 0.9216825 |
TABLE II: Energy eigenvalues of the Kratzer potential for different values of $n$ and $\ell$ in eV.

| $n$ | $\ell$ | $N_2$    |            | $CO$      |            |
|-----|--------|----------|------------|----------|------------|
|     |        | Our Results | Ref. [13]  | Our Results | Ref. [13]  |
| 0   | 0      | 0.054434  | 0.054430   | 0.050827  | 0.050823   |
| 0   | 0      | 0.162068  | 0.162057   | 0.151296  | 0.151287   |
| 1   | 0      | 0.162557  | 0.162546   | 0.151765  | 0.151755   |
| 1   | 0      | 0.268245  | 0.268229   | 0.250369  | 0.250354   |
| 2   | 0      | 0.268728  | 0.268711   | 0.250831  | 0.250816   |
| 1   | 0      | 0.269692  | 0.269675   | 0.251756  | 0.251744   |
| 2   | 0      | 0.372992  | 0.372972   | 0.348070  | 0.348051   |
| 3   | 0      | 0.375846  | 0.375823   | 0.350806  | 0.350785   |
| 3   | 1      | 0.373468  | 0.373447   | 0.348526  | 0.348507   |
| 2   | 1      | 0.374419  | 0.374398   | 0.349438  | 0.349418   |
| 3   | 1      | 0.476334  | 0.476313   | 0.444425  | 0.444403   |
| 4   | 0      | 0.476803  | 0.476779   | 0.444871  | 0.444852   |
| 1   | 0      | 0.477742  | 0.477717   | 0.445774  | 0.445751   |
| 2   | 0      | 0.479150  | 0.479124   | 0.447123  | 0.447099   |
| 3   | 0      | 0.481026  | 0.480999   | 0.448921  | 0.448895   |

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FIG. 1: Variation of the first six normalized eigenfunctions of the pseudoharmonic potential (in $m = \hbar = 1$ unit).
FIG. 2: Dependence of the first six normalized eigenfunctions of the Kratzer potential on spatially coordinate $r$ (in $m = \hbar = 1$ unit).