Theor Chem Acc (1997) 98:192–196

Theoretical
Chemistry Accounts

Regular Article

Solution of the Schrödinger equation for two different molecular potentials by the Nikiforov-Uvarov method

Fevzi Büyükiliç, Harun Eğrifes, Doğan Demirhan

Department of Physics, Faculty of Science, Ege University, 35100 Bornova, Izmir, Turkey

Received: 20 November 1996 / Accepted: 1 October 1997

Abstract. In this study, the solution of the Schrödinger equation by a method developed by Nikiforov and Uvarov which is not based on the manipulation of formal power series has been schematically presented. The method gives elegant, easy and exact solutions of the Schrödinger equation. In order to demonstrate the applications of the method, solutions of the Schrödinger equation for the well-known pseudo-harmonic oscillator and a new symmetrical potential proposed by the authors are given. The concrete energy spectra and corresponding wave functions are obtained. The superiority and the limitations of the method compared to other methods have also been emphasized.

Key words: Analytically soluble problems – Pöschl-Teller potential – Pseudo-harmonic potential

1 Introduction

The Schrödinger equation (SE) is one of the fundamental equations of quantum mechanics, i.e. atomic, molecular, nuclear, condensed matter and high energy physics. The method is capable of providing solutions for the radial part of effective single-particle SE which can be reduced to an effective one-dimensional equation. The SE is reduced to a hypergeometric equation by an appropriate coordinate transformation where the solutions are orthogonal special functions.

The method has been presented without the traditional use of generalized power series. Hence, elegant, easy and exact solutions of the SE are obtained. In the examples that we have chosen, the determination of the discrete energy spectra and corresponding wave functions are accomplished with the help of classical orthogonal polynomials.

Various methods such as 1/N expansion [1–4], analytic continuation [5–7], group theoretical [8–11], series expansion [12, 13], finite difference methods [14] and the phase integral approach [15] could be enumerated amongst others. One method which has been developed by Nikiforov and Uvarov (NU method) is based on solving the SE by reduction to a generalized hypergeometric equation [16].

2 The method

The radial part of the SE for a particle of mass m moving under the influence of a potential $V(r)$ is given by

$$R'' + \frac{2m}{\hbar^2}\left[E - V(r) - \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]R = 0 \qquad (1)$$

where ℓ is the angular momentum quantum number. This equation enables us to establish the energy levels of the bound states ($E < 0$) of the particle as well as the corresponding wave functions.

In the NU method, for a given $V(r)$, Eq. (1) could be reduced to the generalized equation of a hypergeometric type by an appropriate $r \rightarrow s$ coordinate transformation (Ref. [16], p. 1):

$$\Phi'' + \frac{\tilde{\tau}(s)}{\sigma(s)}\Phi' + \frac{\tilde{\sigma}(s)}{\sigma^2(s)}\Phi = 0 \ , \qquad (2)$$

where $\sigma(s)$ and $\tilde{\sigma}(s)$ are polynomials of a degree at the most two whereas $\tilde{\tau}(s)$ is of a degree at the most one. In general, the solutions of Eq. (2) are special functions.

Using the transformation

$$\Phi(s) = \phi(s)y(s) \qquad (3)$$

together with

$$\lambda = \lambda_n = -n\tau' - \frac{n(n-1)}{2}\sigma'' \quad (n = 0, 1, 2, \ldots) \qquad (4)$$

Eq. (2) could be reduced to the hypergeometric-type equation (for an explanation see Ref. [16], p. 253)

$$\sigma(s)y'' + \tau(s)y' + \lambda y = 0 \ , \qquad (5)$$

whose solutions are given by the Rodrigues formula (Ref. [16], p. 8)

Correspondence to: D. Demirhan,

FAX: 90-232-388 1892 e-mail: tirnakl@fenfak.ege.edu.tr

$$y_n(s) = \frac{B_n}{\rho(s)} \frac{d^n}{ds^n}[\sigma^n(s)\rho(s)] \ , \tag{6}$$

where

$$\frac{\phi'(s)}{\phi(s)} = \frac{\pi(s)}{\sigma(s)} \tag{7}$$

$$\tau(s) = \tilde{\tau}(s) + 2\pi(s) \tag{8}$$

$$\pi(s) = \frac{\sigma' - \tilde{\tau}}{2} \pm \sqrt{\left(\frac{\sigma' - \tilde{\tau}}{2}\right)^2 - \tilde{\sigma} + k\sigma} \tag{9}$$

$$k = \lambda - \pi' \tag{10}$$

and the weight function $\rho(s)$ satisfies the equation (Ref. [16], pp. 2, 3, 7)

$$(\sigma\rho)' = \tau\rho \ . \tag{11}$$

Since $\pi(s)$ must be a polynomial of a degree at most one, in Eq. (9) the expression under the square root must be the square of a polynomial. This is possible only if its discriminant is zero. Hence we obtain an equation, in general quadratic, for k.

In order to demonstrate the solution of Eq. (2) with the NU method, the SE written for two molecular potentials where the solutions are classical orthogonal polynomials, have been selected. The second potential is a rather symmetrical potential resembling Manning-Rosen [19] and Rosen-Morse [20] potentials and has been recently proposed by the present authors.

3 Solution of the SE for the pseudo-harmonic oscillator

An investigation of the pseudo-harmonic oscillator has recently been performed [11]. In this manuscript we re-examine with the purpose of presenting an application of the NU method.

The radial part of the N-dimensional SE for the isotropic-harmonic oscillator has the form

$$R''_{n\ell} + \frac{N-1}{r} R'_{n\ell} + \frac{2m}{\hbar^2}\left[E - \frac{1}{2}m\omega^2 r^2 - \frac{\hbar^2 \ell(\ell + N - 2)}{2mr^2}\right] R_{n\ell} = 0 \ .$$

Writing down

$$R_{n\ell}(r) = r^{(1-N)/2} u(r)$$

one gets:

$$u'' + \frac{2m}{\hbar^2}\left[E - \frac{1}{2}m\omega^2 r^2 - \frac{\hbar^2 (d-1)(d-3)}{8mr^2}\right] u = 0 \ , \tag{12}$$

where $d = N + 2\ell$. The expression

$$V(r) = \frac{1}{2}m\omega^2 r^2 + \frac{\hbar^2(d-1)(d-3)}{8mr^2}$$

appearing in Eq. (12), is called the "pseudo-harmonic" potential [17].

The radial part of the dimensionless SE of the pseudo-harmonic oscillator is given by

$$u'' + \left[2\varepsilon - \frac{(d-1)(d-3)}{4y^2} - y^2\right] u = 0 \ , \tag{13}$$

where

$$r = \alpha y, \quad \alpha = \left(\frac{\hbar}{m\omega}\right)^{1/2}, \quad \varepsilon = \frac{E}{\hbar\omega} \ . \tag{14}$$

By performing a transformation $y^2 = s$ in Eq. (13), the generalized hypergeometric equation

$$\Phi'' + \frac{1}{2s}\Phi' + \frac{1}{4s^2}\left[-s^2 - \beta^2 s - \gamma^2\right]\Phi = 0 \quad (0 \leq s \leq \infty) \tag{15}$$

could be obtained, where

$$\beta^2 = -2\,\varepsilon\,(\varepsilon < 0), \quad \gamma^2 = \frac{(d-1)(d-3)}{4} \ . \tag{16}$$

A comparison of Eq. (15) with the reference generalized hypergeometric equation given by Eq. (2) identifies the following:

$$\tilde{\tau}(s) = 1, \quad \sigma(s) = 2s, \quad \tilde{\sigma}(s) = -s^2 - \beta^2 s - \gamma^2 \ . \tag{17}$$

When these polynomials are substituted in Eq. (9),

$$\pi(s) = \tfrac{1}{2} \pm \sqrt{s^2 + (\beta^2 + 2k)s + \gamma^2 + \tfrac{1}{4}} \tag{18}$$

has been attained. The constant k could be determined by the condition that the expression under the square root should have a double zero which leads to

$$\pi(s) = \frac{1}{2} \pm \begin{cases} s + \frac{(1+4\gamma^2)^{1/2}}{2} & \text{for } k = \frac{-\beta^2 + (1+4\gamma^2)^{1/2}}{2} \qquad 19(\mathrm{a}) \\ s - \frac{(1+4\gamma^2)^{1/2}}{2} & \text{for } k = \frac{-\beta^2 - (1+4\gamma^2)^{1/2}}{2} \ . \qquad 19(\mathrm{b}) \end{cases}$$

From these equations, the $\pi(s)$ expression, which makes the polynomial $\tau(s)$ given by Eq. (8) have a zero and a negative derivative in the interval $(0, \infty)$, has been chosen (Ref. [16], p. 67). This condition is satisfied when

$$\pi(s) = \frac{1}{2} - s + \frac{(1+4\gamma^2)^{1/2}}{2} \ . \tag{20}$$

By substituting $\pi(s)$ in Eq. (8), one ends up with

$$\tau(s) = 2 - 2s + (1 + 4\gamma^2)^{1/2} \ . \tag{21}$$

The polynomials $\sigma(s)$ and $\pi(s)$ given by Eqs. (17) and (20) respectively have been substituted in Eq. (7), which after integration yields

$$\phi(s) = s^{v}\,\mathrm{e}^{-s/2} \ , \tag{22}$$

whereas the substitution of π' and k into Eq. (10) gives

$$\lambda = \frac{-\beta^2 - (1+4\gamma^2)^{1/2}}{2} - 1 \ . \tag{23}$$

On the other hand, the weight function could be obtained from Eq. (11) in the form

$$\rho(s) = s^{\theta}\mathrm{e}^{-s} \ . \tag{24}$$

In Eqs. (22) and (24) v and θ are defined by

$$v = \frac{1+\left(1+4\gamma^2\right)^{1/2}}{4}, \quad \theta = \frac{1+\left(1+4\gamma^2\right)^{1/2}}{2} \quad . \tag{25}$$

The quantized energy eigenvalues of the pseudo-harmonic oscillator are attained by substituting λ given by Eq. (23) together with τ' and σ'' into Eq. (4). The discrete energy eigenvalues in $\hbar\omega$ units are given by

$$\varepsilon_{n\ell} = (2n+1) + \tfrac{1}{2}[1+(d-1)(d-3)]^{1/2} \quad . \tag{26}$$

The corresponding eigenfunctions, however, can be found out from Eq. (6) in the following form:

$$y_n(s) = B_n 2^n e^s s^{-\theta} \frac{d^n}{ds^n}\left(s^{n+\theta} e^{-s}\right) \quad . \tag{27}$$

Keeping in mind the definition of Laguerre polynomials, which are classical orthogonal polynomials [18], one could write

$$y_n(s) \approx L_n^{\theta}(s) \quad . \tag{28}$$

On the other hand, the wave functions could be determined from Eq. (3) giving

$$\Phi_{n\ell} = \phi(s) y_n(s) = C_{n\ell} s^v e^{-s/2} L_n^{\theta}(s) \quad , \tag{29}$$

where $C_{n\ell}$ is a normalization coefficient.

4 Solution of the SE for a new symmetrical potential

Let us consider a particle of mass m moving in a potential field

$$V(x) = C\tanh^2(\alpha x) - \frac{D}{\cosh^2(\alpha x)} \tag{30}$$

which is similar in shape to the Manning-Rosen and Rosen-Morse potentials [19, 20] but rather symmetrical in comparison to the former ones. When the potential function of Eq. (30) is substituted in the one-dimensional SE

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x)$$

and after changing the variable using

$$s = \tanh(\alpha x) \tag{31}$$

the generalized hypergeometric equation

$$\Phi'' + \frac{(-2s)}{1-s^2}\Phi' + \frac{1}{\left(1-s^2\right)^2}\left[-A^2 s^2 + \gamma^2 - \beta^2\right]\Phi = 0 \tag{32}$$

is obtained, where

$$\beta^2 = -\frac{2mE}{\hbar^2\alpha^2}, \quad A^2 = \frac{2m(C+D)}{\hbar^2\alpha^2}, \quad \gamma^2 = \frac{2mD}{\hbar^2\alpha^2} \quad . \tag{33}$$

A comparison of Eq. (32) with the reference generalized hypergeometric equation (Eq. 2) identifies the associated polynomials as

$$\begin{aligned} \tilde{\tau}(s) &= -2s, \\ \sigma(s) &= 1-s^2, \\ \tilde{\sigma}(s) &= -A^2 s^2 + \gamma^2 - \beta^2 \quad . \end{aligned} \tag{34}$$

The substitution of these expressions into Eq. (9) leads to

$$\pi(s) = \pm\left[(A^2-k)s^2 + \beta^2 + k - \gamma^2\right]^{1/2} \quad . \tag{35}$$

The constant k is determined by the condition that the expression inside the brackets should have a double zero. Thus

$$\pi(s) = \pm\begin{cases} u & \text{for } k = A^2 \quad (36a) \\ us & \text{for } k = \gamma^2 - \beta^2 \quad , \quad (36b) \end{cases}$$

where $u = \left(\beta^2 + A^2 - \gamma^2\right)^{1/2}$. Choosing $\pi(s) = -us$, one can obtain from Eq. (8)

$$\tau(s) = -2(1+u)s \quad . \tag{37}$$

Introducing π' and k into Eq. (10), one can find

$$\lambda = \left(\gamma^2 - \beta^2\right) - u \quad . \tag{38}$$

In this case

$$\phi(s) = \left(1-s^2\right)^{u/2}, \quad \rho(s) = \left(1-s^2\right)^u \tag{39}$$

have been obtained from Eqs. (7) and (11), respectively.

The discrete energy eigenvalues of the system under consideration are calculated from Eqs. (4) and (38), giving

$$E_n = -\frac{\hbar^2\alpha^2}{2m}\beta_n^2 \quad , \tag{40}$$

where

$$\begin{aligned} \beta_n^2 = n^2 &+ \left(1-\sqrt{1+4A^2}\right)n + \gamma^2 \\ &+ \tfrac{1}{2}\left(1-\sqrt{1+4A^2}\right) \quad . \end{aligned} \tag{41}$$

Here it is worthwhile to point out that for $C = 0$ in Eq. (30), $A^2 = \gamma^2$ and Eq. (40) leads to

$$E_n = -\frac{\hbar^2\alpha^2}{2m}\left[-\left(n+\frac{1}{2}\right) + \left(A^2 + \frac{1}{4}\right)^{1/2}\right]^2 \quad , \tag{42}$$

which are the energy eigenvalues of the Pöschl-Teller potential [16, 21, 22].

Lastly, the eigenfunctions are determined from the Rodrigues formula given by Eq. (6):

$$y_n(s) = B_n\left(1-s^2\right)^{-u}\frac{d^n}{ds^n}\left[\left(1-s^2\right)^{n+u}\right] \quad . \tag{43}$$

Using the definition of the Jacobi polynomials, which are classical orthogonal polynomials [18], one ends up with

$$y_n(s) \approx P_n^{(u,u)}(s) \quad .$$

Now referring back to Eq. (3), the wave function reads

$$\Phi(s) = C_n\left(1-s^2\right)^{u/2} P_n^{(u,u)}(s) \quad ,$$

where C_n is a normalization coefficient.

5 Application to the ammonia molecule problem

An example of the use of energy eigenvalue (Eq. 40) can be taken from the treatment of the vibrations of the ammonia molecule.

The equilibrium configuration of the ammonia molecule has a pyramidal structure with the three hydrogen atoms located at the vertices of an equilateral triangle for the base, and the nitrogen atom along a perpendicular line through the centre of the base. Due to the symmetry of the molecule there will be two equivalent positions of the equilibrium for the nitrogen, at equal distances above and below the plane of the hydrogens. This equivalence of the two minima makes every vibrational level a doublet, a result which is found experimentally (Ref. [23], p. 301)

Such a potential can be made up by joining two potential fields $V(x)$ of the form given in Eq. (30) in a symmetric manner:

$$V(x) = \begin{cases} C\tanh^2(\alpha x + \alpha_0) - \frac{D}{\cosh^2(\alpha x + \alpha_0)}, & -\infty \le x \le 0 \\ C\tanh^2(\alpha x - \alpha_0) - \frac{D}{\cosh^2(\alpha x - \alpha_0)}, & 0 \le x \le \infty \end{cases} . \tag{44}$$

The value of the potential, which is symmetric about $x = 0$, is C as $x \to \pm\infty$ and has a peak (hill) at $x = 0$, where the potential is

$$V_0 = (C + D)\tanh^2\alpha_0 - D . \tag{45}$$

It has two minima symmetrically placed at $x_m = \pm\alpha_0/\alpha$ and separated by a potential hill where the potential is D. If m_H is the mass of one of the hydrogens and m_N is that of the nitrogen, then the reduced mass for this case is simply $m = \frac{3m_H m_N}{3m_H + m_N} \cong 4.15 \times 10^{-27}$ kg (Ref. [23], p. 305).

The parameters of the potential (Eq. 44) are estimated by comparing them to the experimental data as in [24]: $C = 0.0124\,\text{eV}$, $D = 0.2517\,\text{eV}$, $\alpha = 5.75 \times 10^{10}\,\text{m}^{-1}$, $\alpha_0 = 2.24$. Then $x_m = \pm 0.39$ Å and the corresponding value of the dissociation energy is $V(x_m) = -D = -0.2517\,\text{eV}$. From Eq. (40) the separation between the lower two pairs is $E_1 - E_0 = 0.1177$ eV. The height of the potential peak (hill) is found from Eq. (45), giving 0.2525 eV, and the hill is not higher than the value of $V(x)$ at $x = \pm\infty$. We note that the eigenvalue doublet E_0, E_1 lies below the potential hill and is separated from other energy levels lying above the local maximum of the potential.

6 Conclusions and discussion

By using the NU method including suitable coordinate transformations, a number of important problems in theoretical physics and molecular chemistry could be reduced to a hypergeometric equation (Eq. 2). The equations which could be reduced to this form are: Laplace and Helmholtz equations, the equation for the motion of a single particle in a spherically symmetrical field (for example, the solution of the SE for the Coulomb field, Ref. [16], p. 320), the harmonic-oscillator equation (Ref. [16], p. 71), the solutions of the Dirac and Klein-Gordon equations for the Coulomb field (Ref. [16], pp. 326–341), the equations of motion of a particle in an electric and magnetic field, the SE written for the Natanzon-type molecular potentials (Rosen-Morse, Manning-Rosen, Pöschl-Teller) as well as Morse, Kratzer and Hulthen potentials [25].

The limitations (restrictions) which are imposed on the polynomials in the generalized hypergeometric-type equation given by Eq. (2) make the method unworkable in the solutions for some of the potentials. For example, the SE with double-well potentials [26] and non-polynomial and strongly singular potentials [27] could be mentioned.

In this work to demonstrate the power of the NU method, the well-known pseudo-harmonic potential has been chosen for the illustration of the method and it is observed that the solutions are the same as those using the group theoretical method [11]. The corresponding wave functions have been determined as well. The solution for a new potential proposed by the authors that has been rather symmetrical compared to the Rosen-Morse and Manning-Rosen potentials has also been established. By a suitable choice of one of the parameters of this potential, the energy spectra of the Pöschl-Teller potential are readily obtained from the solution which represent a verification of the results. In the course of the calculations, there has been no reference to the use of generalized power series. Exact solutions for the energy spectra and the wave functions have been established which illustrate the advantage of this method.

A practical application of the proposed potential has been realized for the ammonia molecule (NH_3) and vibrational energy levels as well as the corresponding wave functions have been obtained.

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