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ORIGINAL PAPER

Exact solution of the Schrödinger equation with a new expansion of anharmonic potential with the use of the supersymmetric quantum mechanics and factorization method

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Abstract The study involves finding exact eigenvalues of the radial Schrödinger equation for new expansion of the anharmonic potential energy function. All analytical calculations employ the mathematical formalism of the supersymmetric quantum mechanics. The novelty of this study is underlined by the fact that for the first time the recurrence formulas for rovibrational bound energy levels have been derived employing factorization method and algebraic approach. The ground state and the excited states have been determined by means of the hierarchy of the isospectral Hamiltonians. The Riccati nonlinear differential equation with superpotentials has been solved analytically. It has been shown that exact solutions exist when the potential and superpotential parameters satisfy certain supersymmetric constraints. The results obtained can be utilized both in computations of quantum chemistry and theoretical spectroscopy of diatomic molecules.

Keywords Factorization method · Riccati equation · Supersymmetric quantum mechanics · Isospectral Hamiltonians · Anharmonic potentials

1 Introduction

One of the most important issues in non-relativistic quantum mechanics is to solve the Schrödinger equation analytically for various singular potentials. In the recent

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years authors have analytically derived exact solutions for diverse potentials, i.a. the fourth-order inverse power potential [1–3]:

$$V(r) = \frac{A_1}{r} + \frac{A_2}{r^2} + \frac{A_3}{r^3} + \frac{A_4}{r^4}. \tag{1}$$

Supersymmetric quantum mechanics (SUSYQM) is a theoretical concept which has been employed in many fields of physics and theoretical chemistry. This method is widely used to solve the Schrödinger equation with various exactly solvable potential energy functions. Kostelecky and Nieto [4] have computed low Z-alkali-metal-atom transition probabilities between low-n states with the use of supersymmetric wave function. Arai [5] demonstrated a class of supersymmetric quantum mechanics whose eigenvalues problem has a solvable spectrum. Similarly, in a review paper, Bougie et al. [6] presented solvable models within the SUSYQM framework. The authors prove that shape of invariance conditions allows to solve analytically many quantum systems. The factorization method that is strongly connected with the SUSYQM has been profoundly explored in recent years, for example by Mielnik. In one of his papers [7] he considers the general solution of the Riccati type differential equation associated with the Infeld–Hull factorization method [8]. In particular, Mielnik was the one to introduce into theoretical physics a modified factorization method that enabled to construct a one-parameter family of new exactly solvable potentials. It should be noted that Fernández [9] applied this important method to investigate hydrogen-like radial differential equation. He also constructed a new family of exactly solvable potentials. Bagrov et al. [10] have established an interesting insight into connection between this method and the Darboux transformation. The study presented in this paper is strictly related to the SUSYQM and operators' techniques connected with the SUSYQM formalism. Therefore, the SUSYQM can be utilized with the integral Darboux transformation to solve second-order differential equations. Moreover, Nieto and Simmons [11] connected the SUSYQM, the factorization method and the Darboux transformation with the use of the algebraic approach.

In the present study we are solving analytically the Schrödinger equation with new anharmonic oscillator which is expanded into convergent series of the modified Kratzer-Fues variable. The crucial purpose of this paper is to determine a recurrence formula for the ground vibrational state and the excited rovibrational states using algebraic approach within supersymmetric quantum mechanics. Satisfactory convergence of this series permits the eigenvalues constructed to be used in theoretical spectroscopy to reproduce IR and MW spectra.

2 Factorization method for the Schrödinger equation and background information related to the SUSYQM

For a given potential energy function $V(x)$ the Schrödinger equation is governed by the following Hamiltonian operator ($\hbar = 1$, $m = 1$):

$$\hat{H} = -\frac{1}{2}\frac{d^2}{dx^2} + V(x) \tag{2}$$

This Hermitian operator can be factorized in the following way:

$$\hat{H} = \hat{A}^\dagger \hat{A} + \varepsilon$$
$$\hat{A}^\dagger = \frac{1}{\sqrt{2}}\left[-\frac{d}{dx} + W(x)\right]$$
$$\hat{A} = \frac{1}{\sqrt{2}}\left[\frac{d}{dx} + W(x)\right], \tag{3}$$

where ε is an undetermined constant, whereas $W(x)$ stands for superpotential, which satisfies the following nonlinear Riccati equation:

$$\frac{dW(x)}{dx} + W^2(x) = 2(V - \varepsilon) \tag{4}$$

It is worth to emphasise that the SUSYQM superpotential $W(x)$ permits construction of the supersymmetric Schrödinger equation with an exact solution that can be obtained straightforward from the equation.

For the ground state we can write $W(x)$ as:

$$W_0(x) = \frac{d}{dx}\ln\Psi_0(x), \tag{5}$$

where $\Psi_0(x)$ is a solution of the Schrödinger equation with energy equal to $E_0 = \varepsilon$:

$$\hat{H}\Psi_0(x) = E_0\Psi_0(x) \tag{6}$$

It can be proved that the general solution of the Eq. (4) is given by a one-parameter family of solutions:

$$W(x, \lambda) = \frac{d}{dx}\ln\Psi(x) + \frac{1}{\Psi^2(x, \varepsilon)\left[\lambda + \frac{\int^x dy}{\Psi^2(y,\varepsilon)}\right]}, \tag{7}$$

where λ is an arbitrary parameter. It should be pointed out that a proper choice of ε and the corresponding wave function leads to the factorization of Hamiltonian operator $\hat{H} = \hat{A}^\dagger(\varepsilon)\hat{A}(\varepsilon) + \varepsilon$. $\hat{A}$ is an operator and $\hat{A}^\dagger$ is its adjoint operator. Applying the supersymmetric approach we can consider the following partner Hamiltonian:

$$\hat{\tilde{H}} = E_0 + \hat{A}\hat{A}^\dagger = \hat{H} + \left[\hat{A}, \hat{A}^\dagger\right] \tag{8}$$

corresponding to the potential energy function:

$$\tilde{V} = V(x) - \frac{d^2}{dx^2}\Psi_0(x). \tag{9}$$

Moreover, it is well known that $\hat{A}^\dagger \hat{A}$ has an energy spectrum with a_1 ground state which satisfies the relation $\hat{A}\Psi_0^{(a_1)} = 0$. It should be stressed that the $\hat{\hat{H}}$ operator has no eigenstate corresponding to the ground state of the $\hat{H}$ operator and all the excited energy levels of this operator are degenerate, with the eigenstates of $\hat{\hat{H}}$. The SUSY procedure can be used to the process of finding a supersymmetric partner Hamiltonians hierarchy. The process is iterated and generates the hierarchy of Hamiltonians in the following way:

$$\hat{H}_n = -\frac{1}{2}\frac{d^2}{dx^2} + V_n(x) = \hat{A}_n^\dagger \hat{A}_n + E_n^{(0)} = \hat{A}_{n-1}\hat{A}_{n-1}^\dagger + E_{n-1}^{(0)}, \qquad (10)$$

where $n = 2, 3, \ldots,$

$$\hat{A}_n^\dagger = \frac{1}{\sqrt{2}}\left[-\frac{d}{dx} + \frac{d}{dx}\ln\Psi_n^{(0)}(x)\right],$$

$$\hat{A}_n = \frac{1}{\sqrt{2}}\left[\frac{d}{dx} + \frac{d}{dx}\ln\Psi_n^{(0)}(x)\right],$$

$$V_n(x) = V_{n-1}(x) - \frac{d^2}{dx^2}\ln\Psi_{n-1}^{(0)}(x), \qquad (11)$$

$E_n^{(m)}$ and $\Psi_n^{(m)}$ are the eigenvalues and eigenfunction of $\hat{H}_n$ with the following properties [13]:

$$E_n^{(m)} = E_{n-1}^{(m+1)} = \cdots = E^{m+n-1},$$

$$\Psi_n^{(m)} = \left[E_n^{(m)} - E_{n-1}^{(0)}\right]\hat{A}_{n-1}\Psi_{n-1}^{(m+1)},$$

$$\Psi_{n-1}^{(m+1)} = \left[E_n^{(m)} - E_{n-1}^{(0)}\right]\hat{A}_{n-1}^\dagger \Psi_n^{(m)}, \quad m = 0, 1, 2, \ldots \qquad (12)$$

This procedure allows to construct the excited energy levels of Hamiltonian operator $\hat{H}$ from the ground state of the hierarchy of the V_n potential energy functions.

As the operators $\hat{A}$ and $\hat{A}^\dagger$ are Hermitian we can define the following operators:

$$\hat{H}_- = \hat{A}^\dagger \hat{A} = -\frac{\hbar}{\sqrt{2\mu}r_e}\frac{d^2}{dx^2} + V_-(x),$$

$$\hat{H}_+ = \hat{A}\hat{A}^\dagger = -\frac{\hbar}{\sqrt{2\mu}r_e}\frac{d^2}{dx^2} + V_+(x) \qquad (13)$$

These Hamiltonians are featured by isospectrality—they have the same spectra, except for the ground state eigenvalue. In SUSYQM $\hat{H}_+$ and $\hat{H}_-$ are known as partner Hamiltonians and are explicitly given by:

$$\hat{H}_+ = -\frac{\hbar}{\sqrt{2\mu}r_e}\frac{d^2}{dx^2} + W_0^2(x) + \frac{dW_0(x)}{dx} = -\frac{\hbar}{\sqrt{2\mu}r_e}\frac{d^2}{dx^2} + V_+(x) \qquad (14)$$

$$\hat{H}_- = -\frac{\hbar}{\sqrt{2\mu r_e}}\frac{d^2}{dx^2} + W_0^2(x) - \frac{dW_0(x)}{dx} = -\frac{\hbar}{\sqrt{2\mu r_e}}\frac{d^2}{dx^2} + V_-(x) \quad (15)$$

where the potentials $V_-(x)$ and $V_+(x)$ can be defined by the superpotential:

$$V_\pm(x) = W_0^2(x) \pm \frac{dW_0(x)}{dx} \quad (16)$$

These facts indicate that a Hamiltonian operator for the supersymmetric quantum mechanics can be written as $\hat{H} = \hat{H}_+ \oplus \hat{H}_-$. Let us define $|\Psi_n\rangle_\pm$ as an eigenvector of $\hat{H}_\pm$ that corresponds to $E_n^\pm$, $n = 1, 2, \ldots$ to prove the iso-spectrality of $\hat{H}_+$ and $\hat{H}_-$

$$\hat{H}_+\left(\hat{A}\,|\Psi_n\rangle_-\right) = \hat{A}\hat{A}^\dagger\left(\hat{A}\,|\Psi_n\rangle_-\right) = \hat{A}\left(\hat{A}^\dagger\hat{A}\,|\Psi_n\rangle_-\right)$$
$$= \hat{A}\hat{H}_-\,|\Psi_n\rangle_- = E_n^-\,\hat{A}\,|\Psi_n\rangle_- \quad (17)$$

This calculation proves that $\hat{A}\,|\Psi_n\rangle^-$ is an eigenstate of $\hat{H}_+$ (the corresponding eigenvalue is E_n^-). Moreover, we can conclude from the relation $\hat{A}\,|\Psi_0\rangle_- = 0$ (for ground state of $\hat{H}_-$) that $|\Psi_{n-1}\rangle^+ = N \cdot \hat{A}\,|\Psi_n\rangle^-$ and $E_{n-1}^+ = E_n^-$. The normalization constant N can be easily calculated as follows:

$$1 = \langle\Psi_n^+|\Psi_n^+\rangle = |N|^2\left\langle\Psi_{n-1}^-\hat{A}^\dagger|\hat{A}\Psi_{n+1}^-\right\rangle$$
$$= |N|^2\left\langle\Psi_{n-1}^-\right|\hat{H}_+\left|\Psi_{n+1}^-\right\rangle = |N|^2\,E_{n+1}^- = |N|^2\,E_n^+ \quad (18)$$

Hence, we can write $|\Psi_n\rangle^+$ and $|\Psi_n\rangle^-$ in the following way:

$$|\Psi_n\rangle^+ = \frac{1}{\sqrt{E_{n+1}^-}}\hat{A}\,|\Psi_{n+1}^-\rangle$$
$$|\Psi_n\rangle^- = \frac{1}{\sqrt{E_{n-1}^+}}\hat{A}^\dagger\,|\Psi_{n-1}\rangle^+ \quad (19)$$

The Hamiltonians $\hat{H}_+$ and $\hat{H}_-$ are known as the 'bosonic' and 'fermionic' super-symmetric partners. Introducing charge operators $\hat{Q}$ and $\hat{Q}^\dagger$, the Lie algebra that governs this supersymmetric system is characterized by Cooper et al. [13]:

$$\begin{pmatrix}\hat{H}_+ & 0 \\ 0 & \hat{H}_-\end{pmatrix} = \hat{H} = \{\hat{Q}, \hat{Q}^\dagger\}, \quad \hat{Q}^2 = \hat{0}, \quad \left(\hat{Q}^\dagger\right)^2 = \hat{0} \quad (20)$$

From this, we can construct the following commutation and anticommutation relations:

$$\left[\hat{Q}, \hat{H}\right] = \hat{0}, \quad \left[\hat{Q}^\dagger, \hat{H}\right] = \hat{0}, \quad \{\hat{Q}, \hat{Q}\} = \hat{0}, \quad \{\hat{Q}^\dagger, \hat{Q}^\dagger\} = \hat{0} \quad (21)$$

To realize the algebra defined in Eq. (20) we consider $\hat{Q}$ and $\hat{Q}^\dagger$ as:

$$\hat{Q} = \begin{pmatrix} 0 & 0 \\ \hat{A} & 0 \end{pmatrix}, \quad \hat{Q}^\dagger = \begin{pmatrix} 0 & \hat{A}^\dagger \\ 0 & 0 \end{pmatrix} \tag{22}$$

It should be underlined that $\left\{ \hat{H}, \hat{Q}, \hat{Q}^\dagger \right\}$ form a closed superalgebra (the Witten superalgebra). The operators $\hat{Q}$ and $\hat{Q}^\dagger$ induce unitary transformation between 'bosonic' and 'fermionic' vector in the Hilbert space.

$$\hat{H} = \begin{pmatrix} \hat{A}^\dagger \hat{A} & 0 \\ 0 & \hat{A}\hat{A}^\dagger \end{pmatrix} \tag{23}$$

The above results indicate that given the eigenvalues and eigenfunction of either of two partner isospectral potentials, the spectrum of the other one can be determined. In the next section we will demonstrate an exemplary usage of this efficient quantum method for a new potential energy expansion which might be of some importance in molecular spectroscopy.

3 The energy spectrum for a modified Simons–Parr–Finlan expansion

Recently, Molski [12] introduced a generalized version of the Kratzer–Fues potential:

$$V(r) = D_e \left[1 - \frac{r_e(s+1)}{r} \right]^2, \tag{24}$$

in which D_e is the dissociation energy of a diatomic molecule. Considering the fact that $1 \leq 1 - \frac{r_e(s+1)}{r} \leq 1$ the convergence radius for the new potential energy function is $R \in \left[r_e \frac{s+1}{2}, \infty \right)$. In comparison to the original version of the Kratzer–Fues potential we obtain $R \in \left(\frac{r_e}{2}, \infty \right)$ for $s \in (-1, 0)$. These facts permit construction of the expansion of the potential energy function as follows [12]:

$$V(r) = C_0 \left[\frac{r - r_e(s+1)}{r} \right]^2 \left\{ 1 + \sum_{n=1}^{N} C_n \left[\frac{r - r_e(s+1)}{r} \right]^n \right\} \tag{25}$$

Here r is a distance between nuclei of atoms in diatomic systems, while r_e denotes the equilibrium distance between nuclei. The convergence radius of this expansion provides a much more accurate reproduction of the Rydberg–Klein–Rees curve than the one obtained from the Simons–Perr–Finlan expansions. Additionally, the set of parameters $(r_e, s, C_0, C_1, \ldots)$ can be computed from the IR and MW spectra of diatomic molecules with the use of the fitting procedure.

By introducing the Eq. (25) into the radial Schrödinger equation, we obtain the following rovibrational equation:

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V(r) + \frac{J(J+1)\hbar^2}{2\mu r^2} \right] \Psi_{nJ}(r) = E_{nJ}\Psi_{nJ}(r), \qquad (26)$$

in which μ denotes reduced mass of a diatomic system and J is the rotational quantum number ($J = 0, 1, 2, \ldots$), whereas n stands for the vibrational quantum number. After changing the variable $\frac{r_e}{r} = \frac{1}{x}$ we can rewrite Eq. (26) in the following way:

$$\left[-\frac{\hbar^2}{2\mu r_e^2}\frac{d^2}{dx^2} + V(x) + \frac{J(J+1)\hbar^2}{2\mu r_e^2 x^2} \right] \Psi_{nJ}(x) = E_{nJ}\Psi_{nJ}(x), \qquad (27)$$

in which $V(x)$ can be specified in the below simplified form:

$$V(x) = C_0 + \frac{a_1}{x} + \frac{a_2}{x^2} + \frac{a_3}{x^3} + \cdots + \frac{a_{N+2}}{x^{N+2}} \qquad (28)$$

The coefficients $a_1, a_2, \ldots, a_{N+2}$ are functions of $C_1, C_2, \ldots, C_N$ and s. From this it can be seen that all of the a_i coefficients have an energy dimension. Crucial for the approach proposed is an assumption that the potential energy can be presented in the following way:

$$V(x) = \sum_{i=1}^{k} \frac{a_i}{x^i}, \quad k = 2n, \ n = 1, 2, \ldots \qquad (29)$$

with the following form of the superpotential:

$$W_0(x) = \alpha_0 + \sum_{i=1}^{\frac{k}{2}} \frac{\alpha_i}{x^i} = \sum_{i=0}^{\frac{k}{2}} \frac{\alpha_i}{x^i} \qquad (30)$$

We can construct the following nonlinear Riccati equation:

$$\frac{\hbar^2}{2mr_e^2}\left[W_0^2(x) + \frac{dW_0}{dx} \right] + E_{0J} = V(x) \qquad (31)$$

The superpotential $W_0(x)$ has a zero energy solution and its corresponding eigenfunction is given by:

$$\Psi_0(x) = \exp\left[-\int^x W_0(x)dx \right] \qquad (32)$$

The form of $W_0(x)$ depends on the potential energy function type. Therefore, the explicit expression for $W_0(x)$ can only be constructed for a given form of anharmonic oscillator. If we compare the two sides of Eq. 31, we shall obtain relations between the

potential and superpotential parameters. By choosing the supersymmetric constraint relations we get the following exact formula for vibrational ground state eigenvalues:

$$E_{0J}^{(k)} = -B_e \left(\frac{a_1 \sqrt{-\frac{a_k}{B_e}}}{a_{\frac{k}{2}+1} - \frac{k}{2} B_e \sqrt{-\frac{a_k}{B_e}} + f(a_i)} \right)^2 \tag{33}$$

in which $B_e = \frac{\hbar^2}{2\mu r_e^2}$ is the rotational constant, whereas $f(a_i)$ is the function whose mathematical structure depends on the form of the energy potential function.

By adopting the SUSY approach and hierarchy of Hamiltonians for the calculations we obtain the following relation for all the bound rovibrational states:

$$E_{\upsilon J}^{(k)} = -B_e \left[\frac{-a_1 \sqrt{-\frac{a_k}{B_e}}}{-a_{\frac{k}{2}+1} + f(a_i) + \left(k\upsilon + \frac{k}{2}\right) B_e \sqrt{-\frac{a_k}{B_e}}} \right]^2. \tag{34}$$

To show how this method works we will calculate the ground states energy and all the exited states solving systems which generate the relations between potential and superpotential $W_0(x)$ coefficients . First we take:

$$V(x) = \sum_{i=1}^{8} \frac{a_i}{x^i}. \tag{35}$$

For this potential function the superpotential $W_0(x)$ adopts the following form:

$$W_0(x) = \sum_{i=0}^{4} \frac{\alpha_i}{x^i}. \tag{36}$$

Hence, using Eqs. 35 and 36 the coefficients a_i and α_i are related by the following nonlinear algebraic system:

$$\begin{cases} B\alpha_4^2 = -a_8 \\ 2B\alpha_3\alpha_4 = -a_7 \\ B\alpha_3^2 + 2B\alpha_2\alpha_4 = -a_6 \\ 2B\alpha_2\alpha_3 + 2B\alpha_1\alpha_4 - 4B\alpha_4 = -a_5 \\ B\alpha_2^2 + 2B\alpha_1\alpha_3 + 2B\alpha_0\alpha_4 - 3B\alpha_3 = -a_4 (*) \\ 2B\alpha_0\alpha_3 + 2B\alpha_1\alpha_2 - 2B\alpha_2 = -a_3 (**) \\ -B\alpha_1 + 2B\alpha_0\alpha_2 + B\alpha_1^2 = -A - a_2 (***) \\ 2BC_0C_1 = -a_1 \\ BC_0^2 = E_0 \end{cases} \tag{37}$$

Solving this system and assuming that equations $(*)$, $(**)$ and $(***)$ are supersymmetric constraints the ground state eigenvalue takes the following form:

$$E_{0J}^{(8)} = -B_e \left[\frac{a_1 \sqrt{-\frac{a_8}{B_e}}}{a_5 - \frac{a_6 a_7 a_8 + a_7^3}{8a_8^2} - 4B_e \sqrt{-\frac{a_8}{B_e}}} \right]^2 \tag{38}$$

Applying the same approach for the anharmonic potentials:

$$V(x) = \sum_{i=1}^{4} \frac{a_i}{x^i} \text{ and } V(x) = \sum_{i=1}^{6} \frac{a_i}{x^i} \tag{39}$$

the formula for ground state energies can be written as follows:

$$E_{0J}^{(4)} = -B_e \left(\frac{a_1 \sqrt{-\frac{a_4}{B_e}}}{a_3 - 2B_e \sqrt{-\frac{a_4}{B_e}}} \right)^2,$$

$$E_{0J}^{(6)} = -B_e \left(\frac{a_1 \sqrt{-\frac{a_6}{B_e}}}{a_4 - \frac{a_5^2}{4a_6} - 3B_e \sqrt{-\frac{a_6}{B_e}}} \right)^2. \tag{40}$$

It is easy to show that iterated procedure of generation of partner Hamiltonians leads to first excited rovibrational level for the following potential energy function:

$$V(x) = \sum_{i=1}^{4} \frac{a_i}{x^i} \tag{41}$$

Hence, the rovibrational energy level corresponds to the following formula:

$$E_{1J}^{(4)} = -B_e \left(\frac{-a_1 \sqrt{-\frac{a_4}{B_e}}}{4B \sqrt{-\frac{a_4}{B_e}} - a_3 + 2B \sqrt{-\frac{a_4}{B_e}}} \right)^2. \tag{42}$$

4 Conclusions

In this article the Schrödinger equation with new potential energy function was solved analytically within the framework of the SUSYQM. The factorization method has been adopted to determine the exact solutions of this equation. The algebraic method has been applied to construct isospectral and hermitian Hamiltonians as well as super-potentials. The exact formulas for the eigenvalues of the ground state and the excited states have been determined by comparing appropriate potential and superpotential parameters. The method presented allows to compute all rovibrational eigenvalues.

The above approach will be useful in practical quantum computations of theoretical spectroscopy and quantum chemistry of diatomic molecules.

Compliance with Ethical Standards

Conflict of interest   We declare that all authors of this article have no financial disclosures and conflict of interest.

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