Comment on ” The Rotation-Vibration Spectrum of Diatomic Molecules with the Tietz-Hua Rotating Oscillator ”

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Abstract
We present arguments demonstrating that the application of the Nikiforov-Uvarov polynomial method to solve the Schrödinger equation with the Tietz-Hua potential is valid only when \( e^{-b_{r}r_{c}} \leq c_{h} < 1 \) and \( r_{0} < r < +\infty \). In particular, it is pointed out that the numerical results with \( c_{h} \neq 0 \) for the diatomic molecules HF, N\(_{2}\), I\(_{2}\), H\(_{2}\), O\(_{2}\) and O\(_{2}^{+}\) given in Tables 3-5 by Hamzavi and co-workers are wrong. When \( -1 < c_{h} < 0 \) or \( 0 < c_{h} < e^{-b_{r}r_{c}} \), this approach is not suitable. In both cases, it is shown that the solutions of the Schrödinger equation are expressed in terms of the generalized hypergeometric functions \( \,_2F_1(a, b; c; z) \). The determination of the energy levels requires the solution of transcendental equations involving the hypergeometric function by means of the numerical procedure.

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In a recent work \( \text{II} \) published in this journal, Hamzavi and co-workers claimed to have obtained the vibrational energy levels corresponding to \( s \) states of a set of diatomic molecules through the resolution of the radial Schrödinger equation

\[
\left[ \frac{d^2}{dr^2} + \frac{2\mu}{\hbar^2} \left( E - V_{TH}(r) \right) \right] R_{E,0}(r) = 0, \tag{1}
\]

where \( \mu \) is the reduced mass of the rotating oscillator, \( R_{E,0}(r) \) denotes the reduced radial wave function of a \( s \) state and \( V_{TH}(r) \) is the so-called Tietz-Hua potential function \( \text{II} \, \text{III} \, \text{IV} \) defined by
\[ V_{TH}(r) = D \left[ \frac{1 - e^{-b_h(r-r_e)}}{1 - c_h e^{b_h(r-r_e)}} \right]^2; \quad b_h = \beta (1 - c_h). \]  

In equation (2), \( r \) is the internuclear distance, \( D \) and \( r_e \) stand for the potential well depth and the molecular bond length, respectively. \( \beta \) is the Morse constant and for physical reasons the dimensionless constant \( c_h \) is an optimization parameter chosen such that \( |c_h| < 1 \).

To solve (1), the authors of the Ref. [1] introduce the new variable \( s = e^{-\alpha x} \) with \( \alpha = b_h r_e \) and \( x = \frac{r - r_e}{r_e} \) and use the parametric generalization of polynomial Nikiforov-Uvarov (NU) method [5] without considering of the conditions of its application. One can see by simple inspection that the Tietz-Hua potential (2) is not continuous throughout the interval \( R^+ \) whatever \( c_h \in [-1, 1] \). It has a strong singularity at the point \( r = r_0 = r_e + \frac{1}{b_h} \ln c_h \) when \( c_h > 0 \). Moreover, according to the theorem on the orthogonality of hypergeometric-type polynomials (see Ref. [5], Eq. (17), p. 29), we note that the weight function \( \rho(s) \) satisfies the condition

\[ \sigma(s) \rho(s) s^k \left| a \right|_b = 0; \quad (k = 0, 1, 2, \ldots), \]  

only in the case where \( e^{-b_h r_e} \leq c_h < 1 \). Here \( (a, b) = \left( \frac{1}{c_h}, 0 \right) \), and the polynomials \( \sigma(s) \) and \( \rho(s) \) are given by (see Eqs. (A3) and (17) in Ref. [1])

\[ \sigma(s) = s(1 - c_h s), \]  

and

\[ \rho(s) = s \frac{2 \sqrt{s^2(d-\varepsilon)}}{\sqrt{\frac{2}{c_h} + \frac{s^2}{c_h} (c_h - 1)^2 - 1}}, \]  

(note that \( c_h \) is missing in the second factor of equation (17)). As the expression (15) of the energy eigenvalues obtained in [1] is incorrect, it is worthwhile to discuss again the resolution of the equation (1) considering all the possible cases:

(i) \( e^{-b_h r_e} \leq c_h < 1 \) and \( r_0 < r < +\infty \)

By introducing the new variable

\[ \tilde{s} = c_h s, \]  

the radial Schrödinger equation (1) can be reduced to

\[ \left[ \frac{\tilde{s}(1 - \tilde{s})}{d\tilde{s}^2} + \frac{d}{d\tilde{s}} \left( \frac{\tilde{d}}{c_h} - \varepsilon \right) - \frac{\tilde{d} - \varepsilon}{b_h^2 \tilde{s}} - \frac{\tilde{d}}{b_h^2} \left( 1 - \frac{1}{c_h} \right)^2 \right] R_{E,0}(\tilde{s}) = 0, \]  

where \( \varepsilon = \frac{2\mu E}{\hbar^2} \) and \( \tilde{d} = \frac{2\mu D}{\hbar^2} \). Since \( \tilde{s} = 0 \) and \( \tilde{s} = 1 \) are two singularities of (7), we look for a solution in the form

\[ R_{E,0}(\tilde{s}) = \tilde{s}^\lambda (1 - \tilde{s})^\delta u_{E,0}(\tilde{s}). \]
If we impose on \( \lambda \) and \( \nu \) the conditions

\[
\begin{align*}
\lambda^2 &= \frac{d}{b h}, \\
(\delta - \frac{1}{2})^2 &= \frac{1}{4} + \frac{d}{b h} \left( 1 - \frac{1}{c h} \right)^2,
\end{align*}
\]

and on account of the boundary conditions

\[
R_{E,0}(1) = 0,
\]

and

\[
R_{E,0}(0) = 0,
\]

both \( \lambda \) and \( \nu \) have to be positive. Substituting (8) in (7) and taking

\[
\lambda = \frac{1}{b h} \sqrt{d - \varepsilon},
\]

and

\[
\delta = \frac{1}{2} + \sqrt{\frac{1}{4} + \frac{d}{b h} \left( 1 - \frac{1}{c h} \right)^2},
\]

the following differential equation for \( u_{E,0}(\bar{s}) \) is obtained

\[
\left\{ \bar{s}(1 - \bar{s}) \frac{d^2}{d\bar{s}^2} + [2\lambda + 1 - (2\lambda + 2\delta + 1) \bar{s}] \frac{d}{d\bar{s}} \right. - (\lambda + \delta)^2 + \gamma^2 \} u_{E,0}(\bar{s}) = 0,
\]

with

\[
\gamma = \frac{1}{b h} \sqrt{\frac{d}{c h^2} - \varepsilon}.
\]

The solution of this equation, for which (8) fulfills the boundary condition (11), can be written

\[
u_{E,0}(\bar{s}) = N \, _2F_1 (\lambda + \delta - \gamma, \lambda + \delta + \gamma, 2\lambda + 1; \bar{s}) ,
\]

where \( N \) is a constant factor. Thus, the wave function satisfying Eqs. (II), (8) and (11) is given by

\[
R_{E,0}(\bar{s}) = N \bar{s}^\lambda (1 - \bar{s})^\delta \, _2F_1 (\lambda + \delta - \gamma, \lambda + \delta + \gamma, 2\lambda + 1; \bar{s}) .
\]

For the wave function to remain finite as \( \bar{s} \to 0 \), i.e. \( r \to +\infty \), one has to have

\[
\lambda + \delta - \gamma = -n_r,
\]

where \( n_r = 0, 1, 2, ..., \) (the hypergeometric function reduces to a Jacobi polynomial). The energy eigenvalues are then given by

\[
E_{n_r,0} = D - \frac{\hbar^2 b^2}{8 \mu} \left[ n_r + \delta - \frac{2\mu D}{2\mu b^2} \left( \frac{1}{n_r + \delta} - 1 \right) \right]^2 .
\]
and the corresponding eigenfunctions by
\begin{equation}
R_{n_r,0}(r) = N_{n_r} \left[ c_h e^{-b_h(r-r_e)} \right]^\lambda \left[ 1 - c_h e^{-b_h(r-r_e)} \right]^\delta P_{n_r}^{(2\lambda,2\delta-1)} \left( 1 - 2c_h e^{-b_h(r-r_e)} \right).
\end{equation}

The $P_{n_r}^{(\alpha,\beta)}$ are Jacobi polynomials. In Eq. (19), the normalization constant $N_{n_r}$ reads
\begin{equation}
N_{n_r} = \left[ \frac{2b_h}{n_r + \delta} \frac{\lambda(n_r + \lambda + \delta)}{\Gamma(n_r + 2\lambda + 1) \Gamma(n_r + 2\delta)} \right]^\frac{1}{2}.
\end{equation}

The number of bound states $n_{r_{\text{max}}}$ is set by
\begin{equation}
n_{r_{\text{max}}} = \left\{ k \right\} \frac{1}{\lambda} \sqrt{2\mu D \left( \frac{1}{c_h^2} - 1 \right) - \delta},
\end{equation}
and $\left\{ k \right\}$ denotes the largest integer inferior to $k$. Note that the numerical results of the energy levels for some molecules can be calculated from expression (19) when the values of the parameter $c_h$ are greater than or equal to those contained in Table 1.

### Table 1: minimal values of the parameter $c_h$ for obtaining the energy levels from Eq. (19)

| molecule | $b_h \left( A^{-1} \right)$ | $r_e \left( \AA \right)$ | $c_h$ |
|----------|-----------------|-----------------|-------|
| HF       | 1.94207         | 0.917           | 0.168490115 |
| N$_2$    | 2.78585         | 1.097           | 0.047071975 |
| I$_2$    | 2.12343         | 2.666           | 0.003478812 |
| H$_2$    | 1.61890         | 0.741           | 0.301313237 |
| O$_2$    | 2.59103         | 1.207           | 0.043832785 |
| O$_2^+$  | 2.86987         | 1.116           | 0.040649248 |

(ii) $e^{-b_hr_e} \leq c_h < 1$ and $0 < r < r_0$

The solution of Eq. (1) can not be obtained analytically and has no physical interest.

(iii) $0 < c_h < e^{-b_hr_e}$ and $r \in \mathbb{R}^+$

The analysis presented above holds. But in this case, by using the boundary condition $R_{E,0}(r) \to 0$ as $r \to +\infty$, we show that the solution of the radial Schrödinger equation (1) can be written as
\begin{equation}
R_{E,0}(r) = \left[ c_h e^{-b_h(r-r_e)} \right]^\lambda \left[ \varphi^+(r) + \varphi^-(r) \right],
\end{equation}
with
\begin{align}
\varphi^\pm(r) & = C^\pm \left[ 1 - c_h e^{-b_h(r-r_e)} \right]^\delta \times_2 F_1 \left( \lambda + \delta \pm \gamma, \lambda + \delta \pm \gamma, 2\lambda + 1; c_h e^{-b_h(r-r_e)} \right),
\end{align}
where $C^\pm$ are two constant factors and
\begin{equation}
\delta = \frac{1}{2} \pm \frac{1}{4} + \frac{x}{b_h^2} \left( 1 - \frac{1}{c_h} \right)^2.
\end{equation}
Now, taking into account the formula (see Ref. [6], Eq. (9.131), p. 1043)

\[ 2F_1(a, b, c; z) = (1 - z)^{-a-b} \quad 2F_1(c - a, c - b, c; z), \]  

and since \( \delta_- = 1 - \delta_+ \), we can rewrite the obtained bound state wave functions \[22\] as

\[ R_{E,0}(r) = C \left[ c_{ch} e^{-b_{h}(r-r_e)} \right]^\lambda \left[ 1 - c_{ch} e^{-b_{h}(r-r_e)} \right]^\delta_+ \times 2F_1 \left( \lambda + \delta_+ - \gamma, \lambda + \delta_+ + \gamma, 2\lambda + 1; c_{ch} e^{-b_{h}(r-r_e)} \right), \]  

where \( C \) is a constant factor. This solution fulfills the boundary condition \( R_{E,0}(0) = 0 \), when

\[ 2F_1 \left( \lambda + \delta_+ - \gamma, \lambda + \delta_+ + \gamma, 2\lambda + 1; c_{ch} e^{-b_{h}(r-r_e)} \right) = 0. \]  

It follows that the energy eigenvalues of the bound states can be found by numerically solving the transcendental equation \[27\].

(iv) \(-1 < c_{ch} < 0\) and \(r \in \mathbb{R}^+\)

In this case too, instead of \(r\), let us introduce a new variable \(s\) defined by

\[ s = \frac{|c_{ch}| e^{b_{h}r_e}}{e^{b_{h}r} + |c_{ch}| e^{b_{h}r_e}}. \]  

By making the substitution

\[ R_{E,0}(r) = s^\lambda (1 - s)^\gamma u_{E,0}(s), \]

and, with arguments similar to those used in the preceding case, we show that the solution of Eq. \[11\] has the form

\[ R_{E,0}(r) = C \left[ \frac{|c_{ch}|}{e^{b_{h}(r-r_e)} + |c_{ch}|} \right]^\lambda \left[ \frac{1}{1 + |c_{ch}| e^{-b_{h}(r-r_e)}} \right]^{\overline{\delta}_+} \times 2F_1 \left( 1 + \lambda + \overline{\gamma}_+ - \overline{\delta}_+, \lambda + \overline{\gamma}_+ + \overline{\delta}_+, 2\lambda + 1; \frac{|c_{ch}|}{e^{b_{h}(r-r_e)} + |c_{ch}|} \right), \]  

where

\[ \overline{\delta}_+ = \frac{1}{2} + \sqrt{\frac{1}{4} + \frac{d}{2e_{ch}} \left( 1 + \frac{|c_{ch}|}{|c_{ch}|} \right)^2}, \]

\[ \overline{\gamma}_+ = \frac{1}{b_{ch}} \sqrt{\frac{d}{c_{ch}} - \varepsilon}, \]  

and \( C \) is a constant factor. As we see, the wave functions \[30\] satisfy the boundary condition \( R_{E,0}(0) = 0 \), when

\[ 2F_1 \left( 1 + \lambda + \overline{\gamma}_+ - \overline{\delta}_+, \lambda + \overline{\gamma}_+ + \overline{\delta}_+, 2\lambda + 1; \frac{|c_{ch}|}{e^{-b_{h}r_e} + |c_{ch}|} \right) = 0. \]  

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Thus, the levels of energy bound states are determined by the solutions of the transcendental equation (32), which can be solved numerically.

(v) $c_h \to 0$ and $r \in \mathbb{R}^+$

If we let $c_h \to 0$, the expression (2) reduces to the radial Morse potential

$$V_M(r) = D \left[1 - e^{-\beta(r-r_e)}\right]^2.$$  \hspace{1cm} (33)

In this case, we can see from (12), (15) and (24) that

$$\begin{cases} 
\lambda & \approx \frac{1}{\hbar} \sqrt{2\mu(D-E)}, \\
\gamma & \approx \frac{\sqrt{2\mu D}}{\hbar c_h} \to +\infty \\
\delta_+ & \approx \frac{1}{2} + \frac{\sqrt{2\mu D}}{\hbar} \left(\frac{1}{c_h} - 1\right) \to +\infty.
\end{cases}$$  \hspace{1cm} (34)

On the other hand, using the relation of the confluent hypergeometric function to the hypergeometric series [7]

$$1F_1(\alpha, \gamma; z) = \lim_{\beta \to \infty} 2F_1\left(\alpha, \beta, \gamma; \frac{z}{\beta}\right),$$  \hspace{1cm} (35)

we can show without difficulty that, as $c_h \to 0$, the wave functions (26) can be expressed as:

$$R_{E,0}(r) \approx \frac{N e^{-\sqrt{2\mu(D-E)}(r-r_e)} \exp \left[-\frac{\sqrt{2\mu D}}{\hbar \beta} e^{-\beta(r-r_e)}\right]}{\sqrt{2\mu(D-E) - \sqrt{2\mu D}} \frac{2\sqrt{2\mu (D-E)}}{\hbar \beta} + 1 + \frac{2\sqrt{2\mu D}}{\hbar \beta} e^{-\beta(r-r_e)}},$$ \hspace{1cm} (36)

where $N$ is a normalization constant. This solution vanishes at infinity only if

$$\frac{1}{2} + \frac{1}{\beta \hbar} \left[\sqrt{2\mu(D-E)} - \sqrt{2\mu D}\right] = -n_r.$$  \hspace{1cm} (37)

Finally, from this condition we find the energy levels to be given by

$$E_{n_r} = D - \frac{\hbar^2 \beta^2}{2\mu} \left(n_r + \frac{1}{2} - \frac{\sqrt{2\mu D}}{\hbar \beta}\right)^2, \quad n_r = 0, 1, 2, \ldots, \left\{\frac{\sqrt{2\mu D}}{\hbar \beta} - \frac{1}{2}\right\}.$$  \hspace{1cm} (38)

Note that, by starting from the wave functions (30) and proceeding to the limit $|c_h| \to 0$, we recover the wave functions (36) and the energy spectrum (38) of diatomic molecules in the radial Morse potential.

In conclusion, the analytical and numerical results obtained by the authors of Ref. [1] are inconsistent because the NU polynomial method is used without taking into account the conditions for its application. The radial Schrödinger equation [12] can only solved by this method when $e^{-b_0 r_e} \leq c_h < 1$ and $r_0 < r <
It is quite evident that the potential \( \Pi \) in these two cases corresponds to eigenfunctions which are represented by Jacobi polynomials and confluent hypergeometric functions or Laguerre polynomials respectively. Unfortunately, for \(-1 < c_h < 0\) or \(0 < c_h < e^{-b_h r_e}\), the NU method cannot be applied. This is a conceptual drawback of this technique to treat wave equations admitting only orthogonal polynomials as solutions. In the latter two cases, the exact solutions of Eq. (1) are expressed in terms of hypergeometric series. From these, we have shown by applying the boundary conditions that the energy levels can be found from numerical solution of transcendental equations involving the hypergeometric function.

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