Rovibrational Spectroscopy of Diatomic Molecules in Modified-Morse Potential using Nikiforov-Uvarov Functional Analysis

Algebra

The radial time-independent Schrödinger equation (TISE) is given by: $-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}\psi(r) + (V_{\text{eff}} - E)\,\psi(r) = 0$. The effective potential V_{eff} is the sum of the given potential function, $V(r)$, and the centrifugal term, $V_{\text{rot}} = \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}$. In this work, we consider the Modified-Morse potential, $V(r) = D_e\,e^{-2\alpha\frac{(r-r_e)}{r_e}} - 2D_e\,e^{-\alpha\frac{(r-r_e)}{r_e}}$.

We apply the NUFA method as highlighted in *Ikot, A.N., Okorie, U.S., Amadi, P.O. et al. The Nikiforov–Uvarov-Functional Analysis (NUFA) Method: A New Approach for Solving Exponential-Type Potentials. Few-Body Syst 62, 9 (2021). https://doi.org/10.1007/s00601-021-01593-5*.

The objective of NUFA is to convert the TISE into the following *hypergeometric* form:
$$\psi''(z) + \frac{(\alpha_1 - \alpha_2 z)}{z(1-\alpha_3 z)}\psi'(z) + \frac{1}{z^2(1-\alpha_3 z)}\left(-\xi_1^2 z^2 + \xi_2 z - \xi_3\right)\psi(z) = 0.$$

Once this is done, the energy eigenvalues and eigenfunctions can be calculated using the α and ξ parameters (note that the α in the Modified-Morse potential is a molecular parameter and has nothing to do with NUFA, however we stick with these symbols here to be notationally consistent with other works we have cited).

Later, we will find that for our case, it is not exactly possible to reduce the TISE with the Modified-Morse potential to the form given above, as α_3 needs to be 0, and the eigenvalue/eigenfunction equations that follow from the work cited above become unsolvable with $\alpha_3 = 0$. The approach given in *Udoh, M.E., Amadi, P.O., Okorie, U.S. et al. Thermal properties and quantum information theory with the shifted Morse potential. Pramana - J Phys 96, 222 (2022). https://doi.org/10.1007/s12043-022-02463-3* specifically derives the eigenvalue/eigenfunction equations for the case when $\alpha_3 \to 0$, and the TISE is transformed into a *confluent hypergeometric* equation.

```
In[•]:= (*Define subscripted symbols*)
       Notation`AutoLoadNotationPalette = False;
       << Notation`;
       Symbolize /@ { α₁ , α₂ , α₃ , ξ₁ , ξ₂ , ξ₃ , Eₙₗ , ψₙₗ , Dₑ , rₑ , V_eff };
```

I. The Pekeris Approximation

Given the exponential nature of the Modified-Morse potential, it is convenient to introduce a change of variables: $z = e^{-\alpha \frac{(r-r_e)}{r_e}}$. The Modified Morse potential now becomes: $V(z) = D_e z^2 - 2 D_e z$.

The centrifugal term, $\frac{1}{r^2}$, in V_{rot} is the main problem whenever we wish to find analytical solutions for the TISE. We use the Pekeris approximation here, which involves Taylor-expanding $\frac{1}{r^2}$ about the point $r = r_e$. We begin our analysis by approximating the effective potential.

At $r = r_e$, $z = 1$; and by definition, $r = r_e \left(1 - \frac{\ln(z)}{\alpha}\right)$. To expand $\frac{1}{r^2}$ at $r = r_e$ is thus equivalent to expanding $\frac{1}{r_e^2 \left(1 - \frac{\ln(z)}{\alpha}\right)^2}$ about $z = 1$. Up to quadratic terms will suffice. The effective potential is transformed as follows:

$In[\circ]:=$ **ModifiedMorse = D_e z^2 - 2 D_e z;**

(*Normal is used to remove the big-O term*)

pekerisApproximation = Normal $\Big[$ Series $\Big[\dfrac{1}{\left(1 - \frac{\text{Log}[z]}{\alpha}\right)^2}$, {z, 1, 2}$\Big]\Big]$;

(*Rearrange the expansion by powers of

 z. The following is an approximation for $\frac{r_e^2}{r^2}$ *)

pekerisApproximation = Collect[Expand[pekerisApproximation], z]

$Out[\circ]=$

$$1 + z^2 \left(\frac{3}{\alpha^2} - \frac{1}{\alpha}\right) + z \left(-\frac{6}{\alpha^2} + \frac{4}{\alpha}\right) + \frac{3}{\alpha^2} - \frac{3}{\alpha}$$

It is convenient to express V_{eff} in the form $X_1 + X_2 z + X_3 z^2$ as we have expressed the Modified-Morse potential in a similar form:

$$V_{\text{rot}} = \frac{\hbar^2 \, l(l+1)}{2 \mu r_e^2} \left(\left(\frac{3}{\alpha^2} - \frac{1}{\alpha}\right) z^2 + \left(-\frac{6}{\alpha^2} + \frac{4}{\alpha}\right) z + \left(1 + \frac{3}{\alpha^2} - \frac{3}{\alpha}\right)\right);$$

$$V_{\text{eff}} = V(r) + V_{\text{rot}} = \left(D_e + \frac{\hbar^2 \, l(l+1)}{2 \mu r_e^2}\left(\frac{3}{\alpha^2} - \frac{1}{\alpha}\right)\right) z^2 + \left(-2 D_e + \frac{\hbar^2 \, l(l+1)}{2 \mu r_e^2}\left(-\frac{6}{\alpha^2} + \frac{4}{\alpha}\right)\right) z + \left(\frac{\hbar^2 \, l(l+1)}{2 \mu r_e^2}\left(1 + \frac{3}{\alpha^2} - \frac{3}{\alpha}\right)\right);$$

$In[\circ]:=$ **V_{eff} = X_1 z^2 + X_2 z + X_3;**

(*The values of the X-

 coefficients are substituted in Part II: NUFA Calculations. Here,

they are kept as is for simplicity.*)

(*$X_1 = D_e + \frac{\hbar^2 \ell(\ell+1)}{2\mu \, r_e^2} \left(\frac{3}{\alpha^2} - \frac{1}{\alpha}\right)$;

$X_2 = -2D_e + \frac{\hbar^2 \ell(\ell+1)}{2\mu \, r_e^2} \left(-\frac{6}{\alpha^2} + \frac{4}{\alpha}\right)$;

$X_3 = \frac{\hbar^2 \ell(\ell+1)}{2\mu \, r_e^2} \left(1 + \frac{3}{\alpha^2} - \frac{3}{\alpha}\right)$;*)

We have simplified the effective potential and can proceed to transform the TISE.

II. TISE to NUFA Standard Form

Now, we write the TISE in full and perform the same change of variables as before.

In[ ]:= `TISE = `$\psi_{n\ell}$`''[r] + `$\frac{2\,\mu}{\hbar^2}$` (E`$_{n\ell}$` - V`$_{\text{eff}}$`) `$\psi_{n\ell}$`[r] == 0`

Out[ ]=

$$\frac{2\,\mu\,\left(E_{n\ell} - z^2\,X_1 - z\,X_2 - X_3\right)\,\psi_{n\ell}[r]}{\hbar^2} + \psi_{n\ell}{}''[r] == 0$$

In[ ]:= `(*Variable Transformation*)`

`DSolveChangeVariables[`

`    Inactive[DSolve][TISE, `$\psi_{n\ell}$`[r], r], `$\psi_{n\ell}$`[z], z, z == `$e^{-\alpha\,\frac{(r-r_e)}{r_e}}$`] // Simplify;`

`(*The above returns an inaactive DSolve function with the transformed equation`
` as the first argument. The 'First' function is used to extract it.*)`
`reducedSWE = First[%] // Expand`

Out[ ]=

$$\frac{2\,E_{n\ell}\,\mu\,\psi_{n\ell}[z]}{\hbar^2} - \frac{2\,z^2\,\mu\,X_1\,\psi_{n\ell}[z]}{\hbar^2} - \frac{2\,z\,\mu\,X_2\,\psi_{n\ell}[z]}{\hbar^2} - \frac{2\,\mu\,X_3\,\psi_{n\ell}[z]}{\hbar^2} + \frac{z\,\alpha^2\,\psi_{n\ell}{}'[z]}{r_e^2} + \frac{z^2\,\alpha^2\,\psi_{n\ell}{}''[z]}{r_e^2} == 0$$

Now, we further reduce the transformed equation to match the standard NUFA form defined above. First, we make the coefficient of the second derivative equal to 1, then we collect the coefficients of $\psi_{n\ell}$`[z]` and group them by powers of *z*.

In[ ]:= `MultiplySides[reducedSWE, r`$_e$`2 / (z2 `α^2`), Assumptions → r`$_e$`2 / (z2 `α^2`) > 0] // Expand`

`Collect[%, `$\psi_{n\ell}$`[z]]`
`(*To extract the coefficient of `$\psi_{n\ell}$`[z]:*)`
`zeroOrderCoefficient = % // First // First`

Out[ ]=

$$\frac{2\,E_{n\ell}\,r_e^2\,\mu\,\psi_{n\ell}[z]}{z^2\,\alpha^2\,\hbar^2} - \frac{2\,r_e^2\,\mu\,X_1\,\psi_{n\ell}[z]}{\alpha^2\,\hbar^2} - \frac{2\,r_e^2\,\mu\,X_2\,\psi_{n\ell}[z]}{z\,\alpha^2\,\hbar^2} - \frac{2\,r_e^2\,\mu\,X_3\,\psi_{n\ell}[z]}{z^2\,\alpha^2\,\hbar^2} + \frac{\psi_{n\ell}{}'[z]}{z} + \psi_{n\ell}{}''[z] == 0$$

Out[ ]=

$$\left(\frac{2\,E_{n\ell}\,r_e^2\,\mu}{z^2\,\alpha^2\,\hbar^2} - \frac{2\,r_e^2\,\mu\,X_1}{\alpha^2\,\hbar^2} - \frac{2\,r_e^2\,\mu\,X_2}{z\,\alpha^2\,\hbar^2} - \frac{2\,r_e^2\,\mu\,X_3}{z^2\,\alpha^2\,\hbar^2}\right)\,\psi_{n\ell}[z] + \frac{\psi_{n\ell}{}'[z]}{z} + \psi_{n\ell}{}''[z] == 0$$

Out[ ]=

$$\left(\frac{2\,E_{n\ell}\,r_e^2\,\mu}{z^2\,\alpha^2\,\hbar^2} - \frac{2\,r_e^2\,\mu\,X_1}{\alpha^2\,\hbar^2} - \frac{2\,r_e^2\,\mu\,X_2}{z\,\alpha^2\,\hbar^2} - \frac{2\,r_e^2\,\mu\,X_3}{z^2\,\alpha^2\,\hbar^2}\right)\,\psi_{n\ell}[z]$$

Already, we can see by comparing the above with the standard form of NUFA that $\alpha_1 = 1$, $\alpha_2 = \alpha_3 = 0$. Now we convert the coefficient of $\psi_{n\ell}$`[z]` to the proper form. The fraction $\frac{2\,r_e^2\,\mu}{\alpha^2\,\hbar^2}$ appears in all four terms of this coefficient, so for simplicity, we name it a new parameter, β.

In[ ]:= $\beta = \dfrac{2\,r_e{}^2\,\mu}{\alpha^2\,\hbar^2}$;

zeroOrderCoefficient * z^2 / ($\beta\,\psi_{n\ell}$[z]) // Expand

Collect[%, z];

(*β is used in definitions below,

so we clear its value here to preserve simplicity*)

ClearAll[β];

Out[ ]=

$E_{n\ell} - z^2\,X_1 - z\,X_2 - X_3$

Finally, we have reduced to TISE to the form required for for NUFA:

In[ ]:= TISEreducedtoNUFA = ψ'' (z) + $\dfrac{1}{z}$ ψ' (z) + $\dfrac{1}{z^2}$ $\left(-\beta\,X_1\,z^2 + (-\beta\,X_2)\,z - \beta\,(X_3 - E_{n\ell})\right)$ ψ (z) == 0;

Comparing with the standard form defined at the start, we obtain the required parameters for NUFA:

In[ ]:= α_1 = 1;

α_2 = 0;

α_3 = 0;

ξ_1 = $\beta\,X_1$;

ξ_2 = $-\beta\,X_2$;

ξ_3 = $\beta\,(X_3 - E_{n\ell})$;

The *X*-parameters and β are depend only on the molecular constants and are defined as follows (β is used to simplify the definitions of *X*-parameters):

In[ ]:= (*X$_1$=D$_e$+$\dfrac{\ell(\ell+1)}{\alpha^2\beta}$ $\left(\dfrac{3}{\alpha^2}-\dfrac{1}{\alpha}\right)$;

X$_2$=-2D$_e$+$\dfrac{\ell(\ell+1)}{\alpha^2\beta}$ $\left(-\dfrac{6}{\alpha^2}+\dfrac{4}{\alpha}\right)$;

X$_3$=$\dfrac{\ell(\ell+1)}{\alpha^2\beta}$ $\left(1+\dfrac{3}{\alpha^2}-\dfrac{3}{\alpha}\right)$;

β=$\dfrac{2r_e{}^2\mu}{\alpha^2\hbar^2}$;*)

We have refrained from simplifying these parameters (β cancels out with parts of the *X* parameters). This is done to keep the energy term E_{nl} separate as we will be solving for it later.

III. The NUFA Energy Equation

Now that we have obtained the required parameters for NUFA, we can begin writing out the energy equation and simplifying. Solving this equation leads us to analytical solutions of the *l*-state energy eigenvalues of the Modified-Morse potentials.

In[ ]:= **energyEqn = (2 λ ν + α_1 λ + α_2 ν − ξ_2) + n (2 λ + α_2) == 0**
(∗From the definitions given in Udoh et al.,
we see that only ν contains E$_{n\ell}$, so we solve for ν:∗)
νSolution = ν /. Expand[Solve[energyEqn, ν]]〚1〛〚1〛

Out[ ]=

$\lambda + 2\,n\,\lambda + 2\,\lambda\,\nu + \beta\,X_2 == 0$

Out[ ]=

$-\dfrac{1}{2} - n - \dfrac{\beta\,X_2}{2\,\lambda}$

In[ ]:= **(∗Actual definitions of λ and ν∗)**

$\lambda = \dfrac{-\alpha_2 + \sqrt{\alpha_2{}^2 + 4\,\xi_1}}{2}$

$\nu = \dfrac{-(\alpha_1 - 1) + \sqrt{(\alpha_1 - 1)^2 + 4\,\xi_3}}{2}$

Out[ ]=

$\sqrt{\beta\,X_1}$

Out[ ]=

$\sqrt{\beta\,(-E_{n\ell} + X_3)}$

In[ ]:= **ν == νSolution**
Distribute$\left[\%^2,\ \text{Equal}\right]$ // FullSimplify (∗Squaring both sides∗)
energyExpression = E$_{n\ell}$ /. Solve[%, E$_{n\ell}$]〚1〛〚1〛 // Simplify

Out[ ]=

$\sqrt{\beta\,(-E_{n\ell} + X_3)} == -\dfrac{1}{2} - n - \dfrac{\beta\,X_2}{2\,\sqrt{\beta\,X_1}}$

Out[ ]=

$\beta\,(-E_{n\ell} + X_3) == \left(\dfrac{1}{2} + n + \dfrac{\beta\,X_2}{2\,\sqrt{\beta\,X_1}}\right)^2$

Out[ ]=

$-\dfrac{\left(\dfrac{1}{2} + n + \dfrac{\beta\,X_2}{2\,\sqrt{\beta\,X_1}}\right)^2}{\beta} + X_3$

In[ ]:= **(∗Final Expression for Eigenvalues∗)**

$E_{n\ell} := X_3 - \dfrac{1}{\beta}\left(\dfrac{1}{2} + n + \dfrac{X_2}{2}\sqrt{\dfrac{\beta}{X_1}}\right)^2;$

This expression depends solely on molecular constants and quantum numbers (*n*, *l*). We have deduced an equation to find the energy eigenvalues of diatomic molecules for any *n* and *l*-states. In the Results notebook, we will use the parameters defined above the find numerical values of energy eigenvalues and the corresponding eigenfunctions.