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THE STATISTICAL PROPERTIES OF THE VARSHNI POTENTIAL MODEL USING MODIFIED FACTORIZATION METHOD

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ABSTRACT

We have solved the Schrodinger equation with Varshni potential model using the modified factorization method. By employing the Greene Aldrich approximation scheme and an appropriate transformation scheme, analytical expressions of the energy eigenvalues and its corresponding normalized eigenfunctions were obtained in terms of the hypergeometric function in closed form. Numerical results of the energy eigenvalues for different quantum states were computed at varying screening parameters and discussed. The effects of the Varshni potential model parameters on the energy eigenvalues have been evaluated. The analytical expression of the energy eigenvalues obtained have been used to obtain an expression for the ro-vibrational partition function and other thermodynamic functions for the Varshni potential model. The variation of the thermodynamic functions with temperature for different quantum states have been analyzed. Our results obtained promises to be relevant in different areas of studies including molecular and chemical physics.

Keywords: Varshni Potential, Modified factorization method, Energy eigenvalues, Partition function, Thermodynamic properties.

INTRODUCTION

The studies of both nonrelativistic and relativistic systems with various potentials have been a major research interest to most researchers. This is due to the fact that potential energy functions have proven to be useful in explaining atomic and molecular structures theoretically in non-relativistic and relativistic frame- works (Ocak *et al*., 2016). Some of the potential energy functions still under investigation include: Morse potential (Morse, 1929), Eckart potential (Eckart, 1930), Rosen-Morse potential (Rosen and Morse, 1932), Manning-Rosen potential (Manning and Rosen, 1933), Poschl-Teller potential (Poschl and Teller, 1933), Woods-Saxon potential (Woods and Saxon, 1954), Varshni potential (Varshni, 1957), Deng-Fan potential (Deng and fan, 1957), Tietz potential (Tietz, 1963), Schioberg potential (Schioberg, 1986), Hua potential (Hua, 1990), etc. Also, more convenient forms of the above-mentioned potentials have been constructed for diatomic molecules (Jia *et al*., 2014; Zhang *et al*., 2012; Wang *et al*., 2012; Yanar *et al*., 2016). This is possible with the use of different explicit parameters like the equilibrium bond length and the dissociation energy.

Hitherto, some of the above-mentioned potentials have been solved exactly, while others can only be solved using different approximation schemes like Pekeris-type approximation scheme (Pekeris, 1934) and Greene-aldrich-type approximation scheme (Greene and Aldrich, 1976). The solutions of nonrelativistic and relativistic wave equations with any chosen potential function have be obtained using any of the following methods: The factorization method (Dong, 2007), asymptotic iteration method (AIM) (Ciftci *et al*., 2005), Nikiforov-Uvarov (NU) method (Nikiforov and Uvarov, 1988), supersymmetric quantum mechanics (SUSYQM) (Witten, 1981), exact and proper quantization method (Ma and Xu, 2005), modified factorization method (Liu *et al*., 2013), and others.

Recently, several authors have obtained the rotation-vibrational energy spectra for diatomic molecules and dimers. Okorie *et al*. (2018a) solved the Dirac and Schrodinger equation using modified factorization method to obtain the relativistic and non-relativistic ro-vibrational energy spectra with the shifted Tietz-Wei potential model for hydrogen, nitrogen and oxygen dimers. Onate and his collaborators (2017) obtained the eigensolutions and entropic system for Hellmann potential in the presence of the Schrodinger equation. The bound state solutions of the Schrodinger equation for the modified Kratzer plus screened Coulomb potential has been studied using NU method (Collins *et al*., 2019). In higher dimensions, the rotation-vibrational energies for selected diatomic molecules have been obtained with improved Rosen-Morse potential model (Udoh *et al*., 2019).

By employing the rotation-vibrational energies obtained for various potential models, the partition function and other thermodynamic functions of various molecules have been studied by different authors (Ikot *et al*., 2018b; Jia *et al*., 2017; Okorie *et al*., 2018b; Ikot *et al*., 2019). There has also been a recent trend towards obtaining some thermochemical properties of gaseous substances with their rotation-vibrational energy spectra (Deng and Jia, 2018; Peng *et al*., 2018).

Hence, we are motivated to study the Varshni potential model which is defined as (Varshni, 1957)

$$V(r)=a\left(1-\frac{b}{r}e^{-\alpha r}\right) \qquad (1).$$

Here, a and b represents the potential strengths, α is the screening parameter and r denotes the inter-nuclear distance. The Varshni potential is known to be a short range repulsive potential energy function which has received remarkable attention in the areas of chemical and molecular physics. Worth mentioning is the use of this potential to describe multi-body condensed matter using the 2-body Kaxiras-Pandey parameters (Lim, 2009). The relativistic and bound state energies and spinor wave function of the Varshni potential have been obtained by some authors using the Dirac equation (Arda and Sever, 2014). Recently, Oluwadare and Oyewumi (2017) studied the scattering states of the Duffin-Kemmer-Petiau (DKP) equation with the Varshni potential. The authors also obtained the asymptotic wave function, the scattering phase shift and normalization constant for the DKP equation. We are also motivated to obtain the thermodynamic properties of the Varshni potential model, which has not been studied before to the best of our knowledge.

MATERIALS AND METHOD

Bound state solutions of the Schrodinger equation with the Varshni potential

The radial part of the Schrödinger equation is given by (Okorie *et al.*, 2018c)

$$\frac{d^2\psi(r)}{dr^2}+\frac{2\mu}{\hbar^2}\left[E_{n\ell}-V(r)-\frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\right]\psi(r)=0 \qquad (2).$$

Substituting Equation (1) into Equation (2), we obtain

$$\left[\frac{d^2}{dr^2}+\frac{2\mu}{\hbar^2}(E_{n\ell}-a)+\frac{2\mu abe^{-\alpha r}}{\hbar^2 r}-\frac{\ell(\ell+1)}{r^2}\right]\psi_{n\ell}(r)=0 \qquad (3).$$

Equation (3) cannot be solved analytically for $\ell\neq 0$ due to the centrifugal term. Therefore, we employ the Greene-Aldrich approximation scheme of the form (Greene and Aldrich, 1976)

$$\frac{1}{r^2}=\frac{\alpha^2}{\left(1-e^{-\alpha r}\right)^2},\ \frac{1}{r}=\frac{\alpha}{\left(1-e^{-\alpha r}\right)} \qquad (4).$$

Substituting Equation (4) and introducing a coordinate transformation of the form $z=\left(1-e^{-\alpha r}\right)^{-1}$, Equation (3) becomes

$$\left[z(1-z)\frac{d^2}{dz^2}+(1-2z)\frac{d}{dz}-\frac{\varepsilon^2}{z(1-z)}-\frac{G}{z}-\frac{\lambda z}{(1-z)}\right]\psi_{n\ell}(z)=0 \qquad (5).$$

Here, we have adopted the following abbreviations

$$-\varepsilon^2=\frac{2\mu}{\hbar^2\alpha^2}(E_{n\ell}-a),\ G=\frac{2\mu ab}{\hbar^2\alpha},\ \lambda=\ell(\ell+1). \qquad (6).$$

We propose the following ansatz

$$\psi_{n\ell}(z)=z^w(1-z)^v f_{n\ell}(z) \qquad (7),$$

where

$$w=\pm\sqrt{\varepsilon^2+G}\ ,\ v=\pm\sqrt{\varepsilon^2+\lambda}\,. \qquad (8).$$

Substituting Equation (7) into Equation (5), we obtain

$$z(1-z)\frac{d^2 f_{n\ell}(z)}{dz^2}+\left[(1+2w)-(2w+2v+2)z\right]\frac{df_{n\ell}(z)}{dz}-\left[\left(w+v+\frac{1}{2}-\phi\right)\left(w+v+\frac{1}{2}+\phi\right)\right]f_{n\ell}(z)=0$$

(9),

where

$$\phi=\sqrt{\frac{1}{4}+\lambda} \qquad (10).$$

The solution of the hypergeometric Gauss differential equation given in Equation (9) is obtained as

$$\psi_{n\ell}(z)=N_1 z^w (1-z)^v \, {}_2F_1(x,y,t,z) \tag{11),}$$

where

$$x=w+v+\frac{1}{2}-\phi \tag{12),}$$

$$y=w+v+\frac{1}{2}+\phi \tag{13),}$$

$$t=1+2w \tag{14).}$$

The energy eigenvalues can be obtained by equating either Equation (12) or Equation (13) to a negative integer $(-n)$. After doing this and carrying out simple algebra, we have

$$\varepsilon^2=\frac{1}{4}\left[\frac{G-\lambda}{\left(n+\frac{1}{2}+\phi\right)}-\left(n+\frac{1}{2}+\phi\right)\right]^2-\lambda \tag{15).}$$

Substituting Equations (6) into Equation (15), we obtain the nonrelativistic energy eigenvalues of the Varshni potential to be

$$E_{n\ell}=\frac{\hbar^2\alpha^2}{2\mu}\ell(\ell+1)+a-\frac{\hbar^2\alpha^2}{2\mu}\left[\frac{\left(\frac{2\mu ab}{\hbar^2\alpha}-\ell(\ell+1)\right)}{2(n+\ell+1)}-\frac{(n+\ell+1)}{2}\right]^2 \tag{16).}$$

The unnormalized wave function of the Varshni potential given in Equation (11) can also be written in terms of the Jacobi polynormials as

$$\psi_{n\ell}(z)=N_1 z^w (1-z)^v \frac{n!\Gamma(1+2w)}{\Gamma(1+n+2w)} P_n^{(2w,\,2v)}(1-2z) \tag{17),}$$

where we have used the definition (Gradshteyn and Ryzhik, 2007)

$$P_n^{(A,\,B)}(1-2q)=\frac{\Gamma(1+n+A)}{n!\Gamma(1+A)}\,{}_2F_1(-n,\,1+n+A+B;\,1+A;\,z) \tag{18),}$$

and N_1 is the normalization constant which can be calculated by the normalization conditions of the wave function:

$$\int_0^\infty |\psi_{nl}(r)|^2\,dr=1\ . \tag{19).}$$

Substituting equation (17) into Equation (19), we have

$$\left(\frac{n!\Gamma(1+2w)}{\alpha\Gamma(1+n+2w)}\right)^2\int_0^1 N_1^2\, z^{2w-1}(1-z)^{2v-1}\left[P_n^{(2w,\,2v)}(1-2z)\right]^2 dz=1,\quad z=\left(1-e^{-\alpha r}\right)^{-1} \tag{20).}$$

Equation (20) can be transformed into

$$\left(\frac{n!\Gamma(1+2w)}{\alpha\sqrt{2}\,\Gamma(1+n+2w)}\right)^2 \int_{-1}^{1} N_1^{\,2}\left(\frac{1-s}{2}\right)^{2w-1}\left(\frac{1+s}{2}\right)^{2v-1}\left[P_n^{(2w,\,2v)}s\right]^2 ds = 1,\ s = 1-2z \qquad (21).$$

Employing the standard integral (Falaye *et al.*, 2014),

$$\left(\frac{1-f}{2}\right)^h\left(\frac{1+f}{2}\right)^g\left[P_n^{(h+1,\,g+1)}(u)\right]du = \frac{2^{2n+1}\,n!\Gamma(2+n+h)\Gamma(2+n+g)\Gamma(2+n+h+g)}{\left[\Gamma(3+2n+h+g)\right]^2} \qquad (22),$$

we obtain the normalization constant from Equation (21) to be

$$N_1 = \sqrt{\frac{\alpha^2\,\Gamma(1+n+2w)\left[\Gamma(1+2n+2w+2v)\right]^2}{(n!)^3\,2^{2n}\left[\Gamma(1+2w)\right]^2\Gamma(1+n+2v)\Gamma(n+2w+2v)}} \qquad (23).$$

Partition Function and Thermodynamic Properties of Varshni Potential

The bound state contributions to the rotation-vibrational partition function of any system at a given temperature T is defined as (*Jia et al.*, 2017)

$$Z(\beta) = \sum_{n=0}^{\xi} e^{-\beta E_{n\ell}},\ \beta = (k_B T)^{-1} \qquad (24),$$

where k_B is the Boltzmann's constant, ξ is the upper bound quantum number, $E_{n\ell}$ is the ro-vibrational energy eigenvalues of the Varshni potential.
Substituting Equation (16) into Equation (24), we obtain

$$Z(\beta) = \sum_{n=0}^{\xi} e^{-\beta\left[P_2 - \frac{\hbar^2\alpha^2}{2\mu}\left(\frac{P_1}{2(n+\sigma)} - \frac{(n+\sigma)}{2}\right)^2\right]} \qquad (25),$$

where

$$P_1 = \frac{2\mu ab}{\hbar^2\alpha} - \ell(\ell+1),\ P_2 = \frac{\hbar^2\alpha^2}{2\mu}\ell(\ell+1) + a,\ \sigma = \ell+1 \qquad (26).$$

Replacing the sum by an integral in the classical limit, we obtain:

$$Z(\beta) = \int_{\sigma}^{\xi+\sigma} e^{\left[L\beta\rho^2 + \frac{M}{\rho^2}\beta - N\beta\right]} d\rho,\ \rho = n+\sigma \qquad (27),$$

where

$$L = \frac{\hbar^2\alpha^2}{8\mu};\ M = \frac{\hbar^2\alpha^2 P_1^2}{8\mu};\ N = \frac{\hbar^2\alpha^2 P_1}{4\mu} + P_2 \qquad (28).$$

By employing a Maple software to evaluate the integral in Equation (27), we obtain ro-vibrational partition function of the Varshni potential to be

$$Z(\beta) = e^{\left(L\rho^2\beta - N\beta\right)}\left[\sqrt{M\beta}\sqrt{\pi}\left(erfi\left(\frac{\sqrt{M\beta}}{\sigma}\right) - erfi\left(\frac{\sqrt{M\beta}}{(\xi+\sigma)}\right)\right) - \sigma e^{\frac{M\beta}{\sigma^2}} + (\sigma+\xi)e^{\frac{M\beta}{(\xi+\sigma)^2}}\right]$$

(29),
where the imaginary error function is defined as (Jia *et al.*, 2017)

$$erfi(u)=\frac{erf(iu)}{i}=\frac{2}{\sqrt{\pi}}\int_0^u e^{s^2}ds \qquad (30).$$

With the help of the ro-vibrational partition function of Equation (29), other thermodynamic properties of the Varshni potential can be obtained with the following relations:

- Rotational-vibrational internal energy

$$U(\beta)=-\frac{\partial \ln Z(\beta)}{\partial\beta} \qquad (31).$$

- Rotational-vibrational free energy

$$F(\beta)=-\frac{1}{\beta}\ln Z(\beta) \qquad (32).$$

- Rotational-vibrational entropy

$$S(\beta)=k\ln Z(\beta)-k\beta\frac{\partial \ln Z(\beta)}{\partial\beta} \qquad (33).$$

- Rotational-vibrational specific heat capacity

$$C(\beta)=k\beta^2\frac{\partial^2}{\partial\beta^2}\ln Z(\beta) \qquad (34).$$

RESULTS AND DISCUSSION

In our study, we employed the Maple software throughout our computation. The rotational-vibrational energy eigenvalues of the Varshni potential are computed for different states (1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d and 4f) and different screening parameters ranging from 0.01 to 0.1, using Equation (16). These results are given in Tables 1 and 2. In Table 1, we observe complete bound state energies for 1s state. Also, these bound state energies increase as the screening parameter increases. In other states considered, there is a corresponding increase in energy eigenvalues as the screening parameter increases. Table 2 also shows the same trend of energy behavior observed in Table 1 for each state. The variation in the energy eigenvalues with different parameters of the Varshni potential such as α, a and b are shown in Figures 1 – 3. Figure 1 shows a monotonous increase in energy as the screening parameter increases. Also, the increase in energy is much sharper for 4f state. Figures 2 and 3 show a decrease in the energy eigenvalues as the potential parameters a and b increases, respectively. We also observe a sharp decrease for state 4f, as compared with other quantum states considered.

Figures 4 – 8 show the variation of ro-vibrational partition function and other thermodynamic properties of the Varshni potential with various temperatures, for different quantum states. In figure 4, the rotational-vibrational partition function decreases as the temperature increases. In Figure 5, there is a sharp increase in rotational-vibrational free energy for all the quantum states at a particular temperature. Thereafter, the free energies for each state remains constant as the temperature increases. The rotational-vibrational free energy is seen to be highest for state 1s and least for state 4f. We also observe first, a slow decrease in ro-vibrational internal energy and later a constant internal energy as temperature increases as shown in Figure 6. But, there is a sharp decrease in the rotational-vibrational internal energy as exhibited by state 4f, when the temperature begins to increase. In Figure 7, we observe a monotonous decrease in rotational-vibrational entropy as the temperature increases for the quantum states considered. Figure 8 exhibits an "increase-decrease-constant" phenomenon of the rotational-vibrational specific heat capacity as it varies with temperature for different quantum states. In this graph, we see that increase-decrease-constant phenomenon for the different quantum states is unique, and it is much sharper for state 4f. Since this study of thermodynamic properties is not carried out before for Varshni potential, it is therefore, difficult to compare our results with any literature.

Table 1: Rotational-vibrational energy eigenvalues of Varshni potential for states (1s, 2s, 2p, 3s, 3p, 3d).

Screening Parameter	$(E_{n\ell})$					
	$1s$	$2s$	$2p$	$3s$	$3p$	$3d$
0.01	-5.970025000	0.7799000000	0.7651750000	2.029775000	2.023397223	2.010575000
0.02	-5.940100000	0.8096000000	0.7807000000	2.059100000	2.046922222	2.022300000
0.03	-5.910225000	0.8391000000	0.7965750000	2.087975000	2.070575000	2.035175000
0.04	-5.880400000	0.8684000000	0.8128000000	2.116400000	2.094355556	2.049200000
0.05	-5.850625000	0.8975000000	0.8293750000	2.144375000	2.118263889	2.064375000
0.06	-5.820900000	0.9264000000	0.8463000000	2.171900000	2.142300000	2.080700000
0.07	-5.791225000	0.9551000000	0.8635750000	2.198975000	2.166463888	2.098175000
0.08	-5.761600000	0.9836000000	0.8812000000	2.225600000	2.190755556	2.116800000
0.09	-5.732025000	1.011900002	0.8991750020	2.251775000	2.215175000	2.136575000
0.10	-5.702500000	1.040000000	0.9175000000	2.277500000	2.239722223	2.157500000

Table 2: Rotational-vibrational energy eigenvalues of Varshni potential for states (4s, 4p, 4d, 4f).

Screening Parameter	$(E_{n\ell})$			
	$4s$	$4p$	$4d$	$4f$
0.01	2.467100000	2.463643750	2.456693750	2.446175000
0.02	2.495900000	2.489575000	2.476775000	2.457200000
0.03	2.523900000	2.515293750	2.497743750	2.470575000
0.04	2.551100000	2.540800000	2.519600000	2.486300000
0.05	2.577500000	2.566093750	2.542343750	2.504375000
0.06	2.603100000	2.591175000	2.565975000	2.524800000
0.07	2.627900000	2.616043750	2.590493750	2.547575000
0.08	2.651900000	2.640700000	2.615900000	2.572700000
0.09	2.675100000	2.665143750	2.642193750	2.600175000
0.10	2.697500000	2.689375000	2.669375000	2.630000000

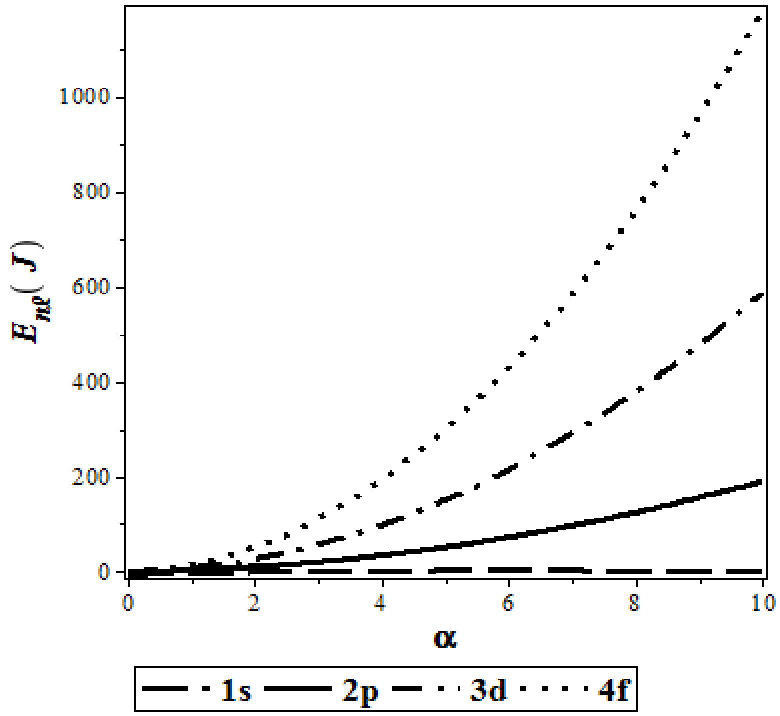

Figure 1: Rotational-vibrational energy eigenvalues variation with α for various quantum states.

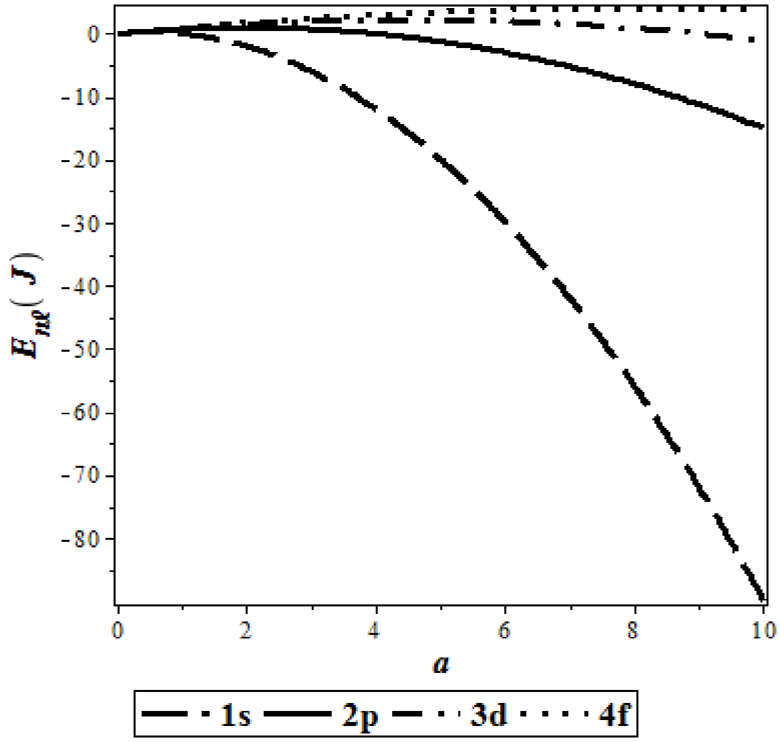

Figure 2: Rotational-vibrational energy eigenvalues variation with a for various quantum states.

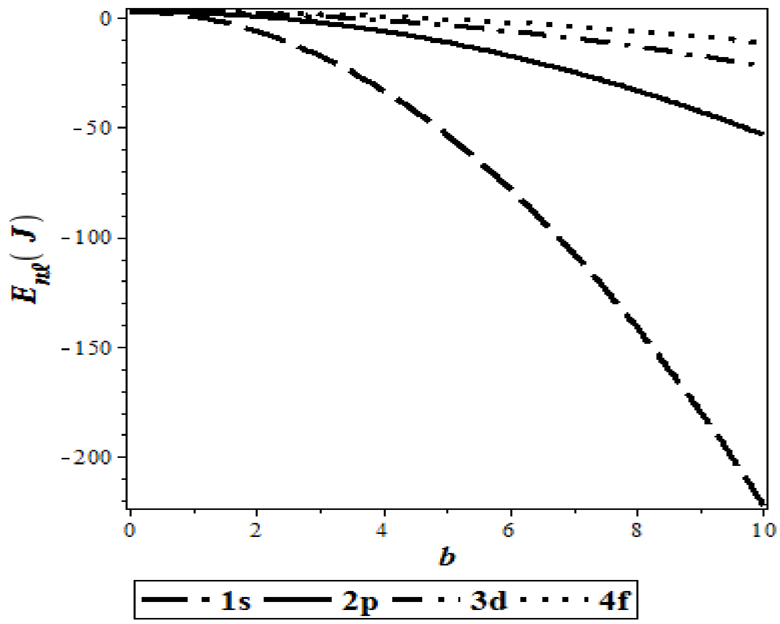

Figure 3: Rotational-vibrational energy eigenvalues variation with b for various quantum states.

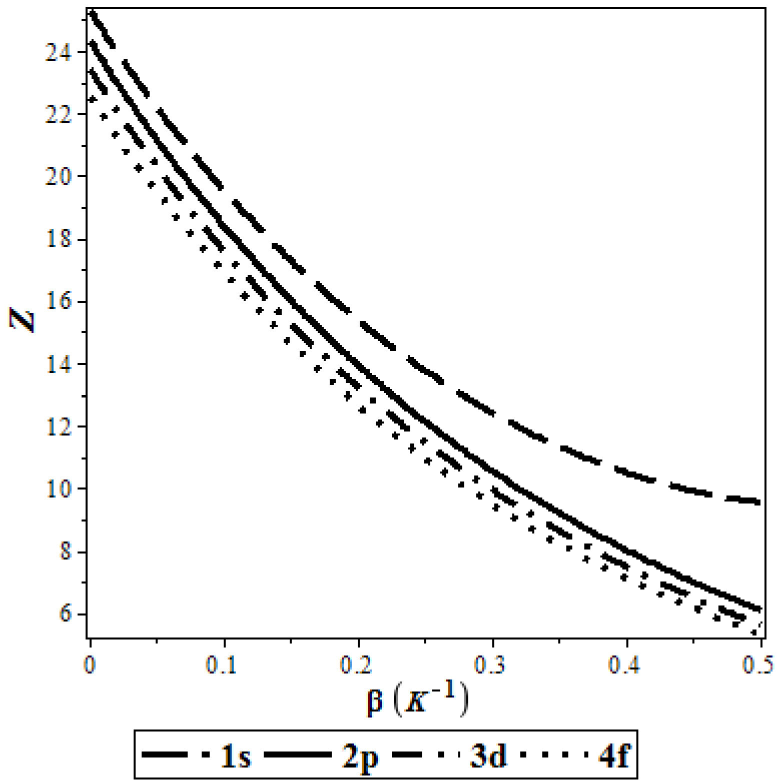

Figure 4: Rotational-vibrational partition function versus β for different quantum states.

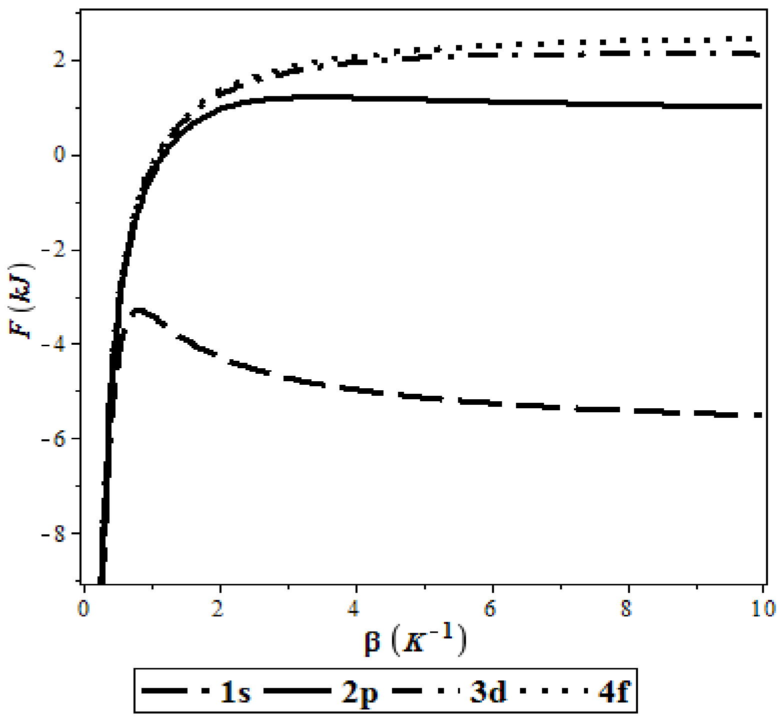

Figure 5: Rotational-vibrational free energy versus β for different quantum states.

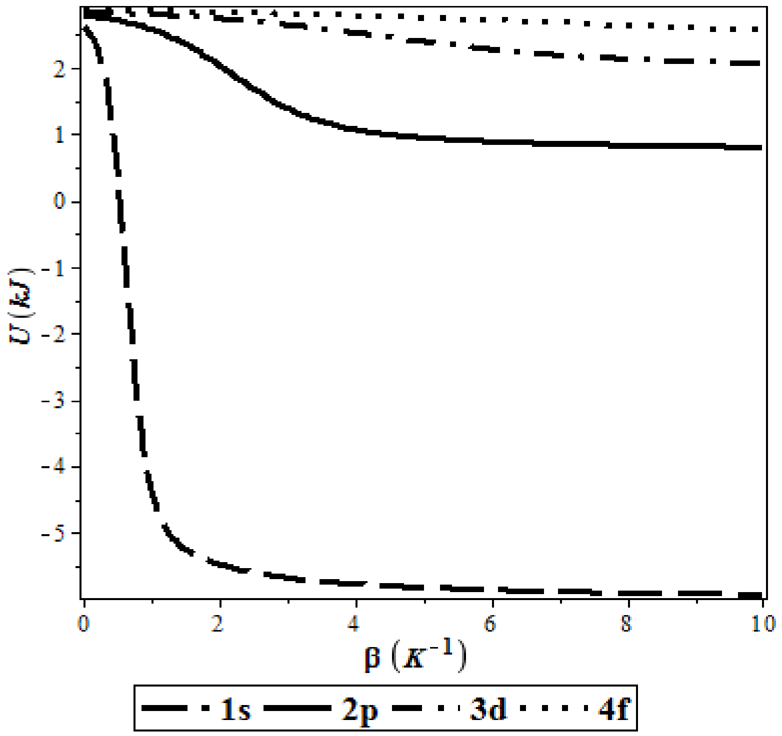

Figure 6: Rotational-vibrational internal energy versus β for different quantum states.

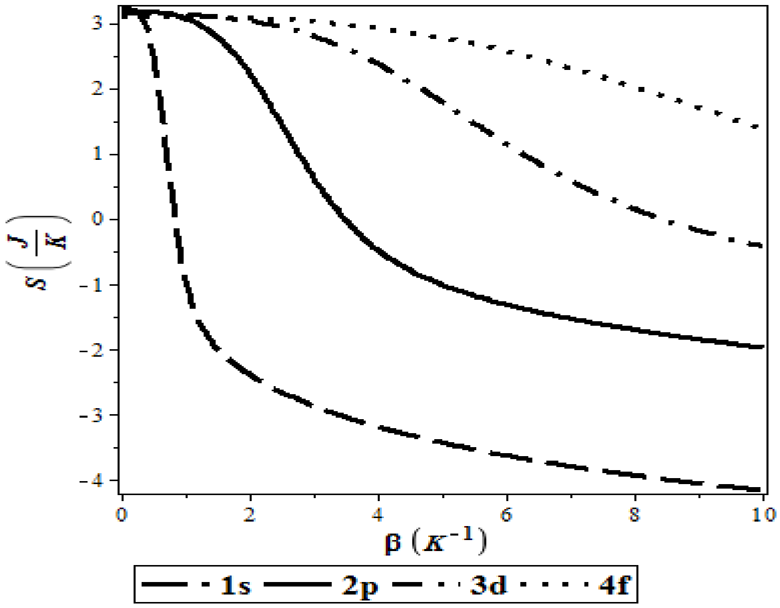

Figure 7: Rotational-vibrational entropy versus β for different quantum states.

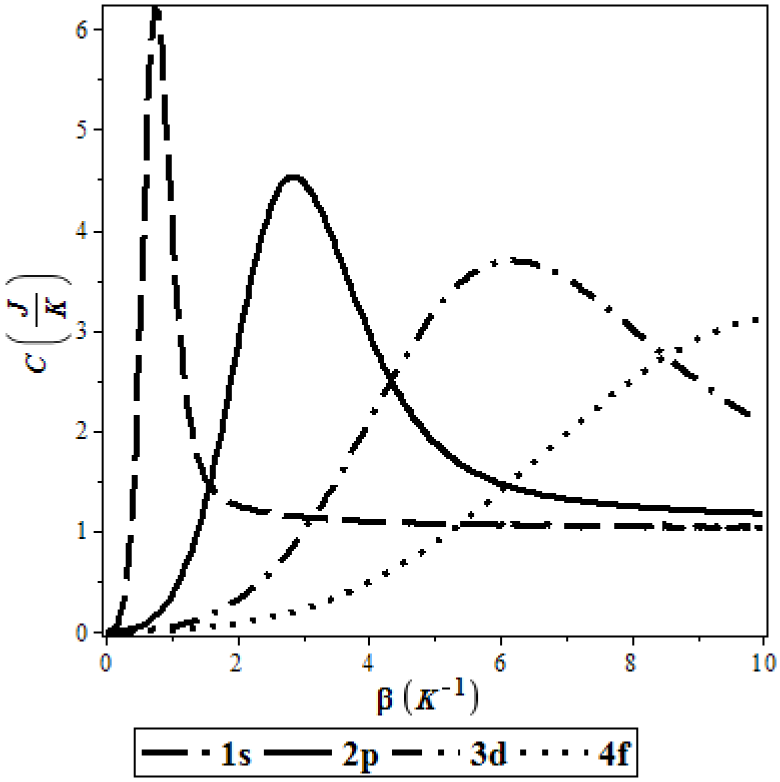

Figure 8: Rotational-vibrational specific heat capacity versus β for different quantum states.

CONCLUSION

In this study, the Schrodinger equation was solved with Varshni potential within the framework of modified factorization method. The energy eigenvalues and its corresponding normalized eigenfunction were obtained in terms of hypergeometric function in closed form. The numerical results of the energy eigenvalues were obtained for different quantum states, at varying screening parameters. Here, we observed that the energy eigenvalues increase as the screening parameter increases for the different quantum states. In addition, we considered the effect of the Varshni potential parameters on the energy eigenvalues for different quantum states considered. As such, we see that the energy eigenvalues increase as the screening parameter increases. But, the reverse is the case when considering the variation of the energy eigenvalues with other potential parameters. We also extended our studies to the consideration of the rotational-vibrational partition function and other thermodynamic properties of the Varshni potential. These include the rotational-vibrational free energy, rotational-vibrational internal energy, rotational-vibrational entropy and rotational-vibrational specific heat capacity. A striking result obtained is the “increase-decrease-constant” phenomenon exhibited by the rotational-vibrational specific heat capacity for various quantum states, as it varies with temperature. As an extension, this studies can be applied to many areas of studies including molecular and chemical physics, thermochemical engineering and high energy physics.

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