Applied Journal of Physical Science
Volume 5(1), pages 1-16, February 2023
Article Number: 5B0D79471
ISSN: 2756-6684
https://doi.org/10.31248/AJPS2022.081
https://integrityresjournals.org/journal/AJPS

Full Length Research

Thermal and atomic properties of hydrogen atom and diatomic molecules in Wilson-Racah Quantum System

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Received 4th October 2022; Accepted 25th November 2022

ABSTRACT: In this study, a conventional quantum mechanics in which the potential function is not specified but replaced by specifying four parameters Wilson-Racah orthogonal polynomials in the energy and physical parameter space was presented. The wave function is written as a bounded sum of elements of a complete basis with these polynomials as expansion coefficients. By finding the asymptotic of these Wilson – Racah polynomials, the physical properties of the corresponding system (wave function, bound state energy spectrum and/or scattering phase shift) was obtained. Wilson – Racah quantum system was applied to determine the thermodynamics and atomic properties of Hydrogen atom and diatomic molecules. All properties of associated physical systems are obtained directly and simply from the asymptotic of the associated orthogonal polynomials. This new model, gives good an approximate prediction of the Hydrogen atom energy with an estimated average error of 0.125%. The proposed procedure merely relies on experimental values of five molecular constants. The average relative percentage deviations of the thermodynamic properties' functions Q, U, C, S and F which are 2.42, 0.45, 0.30, 1.23 and 1.50% satisfied the experimental finding as ascertained. These represent satisfactory compromise between accuracy and rapid computations.

Keywords: Energy spectrum, Hydrogen like–atoms, orthogonal polynomial, Wilson–Racah quantum system, Thermodynamics functions.

INTRODUCTION

Wilson-Racah Quantum system (WRQs), Hydrogen atom and diatomic molecules constitute most fundamental and intriguing phenomena in nature. A simple one-dimensional model of a diatomic molecule that can explain all the essential features of a real two particle quantum mechanical system and gives quantitative results in fair agreement with those of a hydrogen molecule was introduced by Nielsen (1978). Recently, electron transport through a diatomic molecular tunnel junction shows wave like interference phenomenon by using Keldysh non-equilibrium Green's function (NEGF) theory (Imran, 2012), current and differential conductance calculation for a diatomic molecular and two isolated atoms (two atoms having zero hybridization between their energy orbitals) tunnel junctions were presented. The vibrational matrix elements and expectation values for a diatomic molecule, including the rotational dependence, are calculated for powers of the reduced displacement in terms of the parameters of the Dunham potential-energy function (Bouanich and Ogilvie, 1986). O'Esquivel *et al*. (2011) investigated quantum entanglement-related aspects of the dissociation process of some selected, representative homo- and hetero- nuclear diatomic molecules and the study was based upon high-quality ab initio calculations of the (correlated) molecular wavefunctions involved in the dissociation processes.

Using a recent formulation of quantum mechanics without a potential function, Alhaidari and Taiwo (2017) presented a four-parameter system associated with the Wilson and Racah polynomials. The continuum scattering states are written in terms of the Wilson polynomials whose asymptotics give the scattering amplitude and phase shift. On the other hand, the finite number of discrete bound states are associated with the Racah polynomials. As the second stage of the project multi-indexed orthogonal polynomials, Odake and Sasaki (2012) presented in the framework of 'discrete quantum mechanics' with real shifts in one dimension, the multi-indexed (q-) Racah polynomials which are obtained from the (q-) Racah polynomials by the multiple application of the discrete analogue of the Darboux transformations or the Crum-Krein-Adler deletion of 'virtual state' vectors, in a similar way to the multi-indexed Laguerre and Jacobi polynomials reported earlier. The virtual state vectors are the 'solutions' of the matrix Schrodinger equation with negative 'eigenvalues', except for one of the two boundary points. Technically, Mironov and Morozov (2016) developed together the universality and the "eigenvalue conjecture", which expresses the Racah and mixing matrices through the eigenvalues of the quantum Racah-matrix, and for dealing with the adjoint polynomials that has to extended to the previously unknown 6 Ã— 6 case. Next step was reported in the program of Racah matrices extraction from the differential expansion of HOMFLY polynomials for twist knots (Morozov, 2018): from the double-column rectangular representations R = (rr) to a triple-column and triple-hook R = (333). A formulation of quantum mechanics based on orthogonal polynomials was presented by Alhaidari (2020). The wavefunction is expanded over a complete set of square integrable basis in configuration space where the expansion coefficients are orthogonal polynomials in the energy. Information about the corresponding physical systems (both structural and dynamical) are derived from the properties of these polynomials. In order to establish a correspondence between the reformulation of quantum mechanics without potential function and the convention quantum mechanics, Taiwo (2020) obtained the potential function of the New (WRQs) in Alhaidari and Taiwo (2017) using any of the proposed formula in Morozov (2018). To achieve this, he used the matrix elements of the potential function and the basis element of the configuration space.

In this present work, a model of the four-parameter Wilson orthogonal polynomialwas solved base on Alhaidari (2017) and then incorporate it into the new WRQs that enable the bound states energies from the energy spectrum formula given by Alhaidari and Taiwo (2017) to be obtained. The objective of this study is twofold: to test the validity of the energy spectrum of the WRQs, by using the experimental values of the hydrogen parameters in the energy spectrum of the WRQs and see its predictions; and to apply the energy spectrum of the WRQs to find the thermodynamic properties of diatomic molecules – Lithium (Koekoek and Swarttouw, 1998). Moreover, the new energy spectrum of this study was used in place of the vibrational energy level belonging to the improved Manning – Rosen potential and thus determine the thermodynamic properties function using vibrational energy levels available to the system. Further, the two sets of energy spectrum of the WRQs with the energy spectrum in Taiwo (2020) and the thermodynamics experimental values in Peng et al. (2018) were compared to validate the results in this study.

THEORETICAL FRAMEWORK

This section considered the orthogonality of energy spectrum in WRQs that represents the potential wave function in quantum mechanical system. It answered the question how the deformation of the obtained potential function of the New WRQs affects the energy spectrum of the particle by presenting Alhaidari and Taiwo (2017) using any of the proposed formula in Alhaidari (2017) to the consideration of the energy spectrum of Hydrogen atom and the thermodynamic properties of diatomic molecules – Lithium.

Wilson – Racah orthogonal polynomial

The four parameters Wilson orthogonal polynomial $\tilde{W}_n^{\mu}\left(y^2;v;a,b\right)$ as defined by Koekoek and Swarttouw (1998) is given as;

$$\tilde{W}_n^{\mu}\left(y^2;v;a,b\right)=\frac{(\mu+a)_n\,(\mu+b)_n}{(a+b)_n\,n!}\;{}_4F_3\left(\left.\begin{matrix}-n,n+\mu+v+a+b-1,\mu+iy,\mu-iy\\ \mu+v,\mu+a,\mu+b\end{matrix}\right|1\right) \tag{1}$$

where $_4F_3\left(\begin{matrix}a,b,c,d\\ e,f,g\end{matrix}\middle|z\right)=\sum_{n=0}^{\infty}\frac{(a)_n(b)_n(c)_n(d)_n}{(e)_n(f)_n(g)_n}\frac{z^n}{n!}$ is the Hypergeometric function and $(a)_n=a(a+1)(a+2)...(a+n-1)=\frac{\Gamma(n+a)}{\Gamma(a)}$.

The generating function of these polynomials is

$$\sum_{n=0}^{\infty}\tilde{W}_n^{\mu}\left(y^2;v;a,b\right)t^n={}_2F_1\left(\begin{matrix}\mu+iy,v+iy\\ \mu+v\end{matrix}\middle|t\right){}_2F_1\left(\begin{matrix}a-iy,b-iy\\ a+b\end{matrix}\middle|t\right) \tag{2}$$

Their three-term recursion relation $(n=1,2,3...,)$ give rise to (A1), and the initial seeds $(n=0)$ for this recursion at $\tilde{W}_0^{\mu}=1$ and the result of $\tilde{W}_1^{\mu}$ is shown by (A2).

The orthogonality relation of the polynomial is

$$\frac{1}{2\pi}\int_0^{\infty}\frac{\Gamma(\mu+v+a+b)\left|\Gamma(\mu+iy)\Gamma(v+iy)\Gamma(a+iy)\Gamma(b+iy)\right|^2}{\Gamma(\mu+v)\Gamma(a+b)\Gamma(\mu+a)\Gamma(\mu+b)\Gamma(v+a)\Gamma(v+b)\left|\Gamma(2iy)\right|^2}\tilde{W}_n^{\mu}\left(y^2;v;a,b\right)\tilde{W}_m^{\mu}\left(y^2;v;a,b\right)dy$$

$$=\left(\frac{n+\mu+v+a+b-1}{2n+\mu+v+a+b-1}\right)\frac{(\mu+a)_n(\mu+b)_n(v+a)_n(v+b)_n}{(\mu+v)_n(a+b)_n(\mu+v+a+b)_n\,n!}\delta_{nm} \tag{3}$$

The normalized weight function is

$$\rho^{\mu}(y;v;a,b)=\frac{1}{2\pi}\frac{\Gamma(\mu+v+a+b)\left|\Gamma(\mu+iy)\Gamma(v+iy)\Gamma(a+iy)\Gamma(b+iy)/\Gamma(2iy)\right|^2}{\Gamma(\mu+v)\Gamma(a+b)\Gamma(\mu+a)\Gamma(\mu+b)\Gamma(v+a)\Gamma(v+b)} \tag{4}$$

In this study, it was observed that if all parameters are positive, there will be no bound states. However, if $\mu<0$ and $\mu+v$, $\mu+a$, $\mu+b$ are positive or pair of complex conjugates with positive real parts, then the polynomial will have a continuum spectrum as well as a finite size discrete spectrum and the polynomial satisfies the following generalized orthogonality relation (Koekoek and Swarttouw, 1998) in (A3) where $W_n^{\mu}(m;v,a,b)\equiv W_n^{\mu}\left(-(m+\mu)^2;v,a,b\right)$ and *N* is the largest integer less than or equal to $-\mu$. The orthonormal version of this polynomial in (A4) gives results of the three – term recursion relation for the orthonormal version in (A5).

In order to derive the asymptotic formula for the Wilson polynomial, Darboux's method was used to its generating function eq. (2) as prescribed by Oliver (1974). With all parameters real and $y\geq 0$, the contiguous relation was employed.

$$(a+b-c)\,{}_2F_1\left(\begin{matrix}a,b\\ c\end{matrix}\middle|z\right)=a(1-z)\,{}_2F_1\left(\begin{matrix}a+1,b\\ c\end{matrix}\middle|z\right)-(c-b)\,{}_2F_1\left(\begin{matrix}a,b-1\\ c\end{matrix}\middle|z\right) \tag{5}$$

the Euler transformation

$${}_2F_1\left(\begin{matrix}a,b\\ c\end{matrix}\middle|z\right)=(1-z)^{c-a-b}\,{}_2F_1\left(\begin{matrix}c-a,c-b\\ c\end{matrix}\middle|z\right) \tag{6}$$

and finally, the Gauss sum

$${}_2F_1\left(\begin{matrix}a,b\\ c\end{matrix}\middle|1\right)=\frac{\Gamma(c)\Gamma(c-a-b)}{\Gamma(c-a)\Gamma(c-b)}\quad \operatorname{Re}(c-a-b)>0 \tag{7}$$

Now using eq. (7) and the first term on (R.H.S) in eq. (2), we have

$$\frac{1}{2iy}\left[(\mu+iy)(1-t)\,{}_2F_1\left(\begin{matrix}\mu+1+iy,v+iy\\ \mu+v\end{matrix}\middle|t\right)-(\mu-iy)\,{}_2F_1\left(\begin{matrix}\mu+iy,v-1+iy\\ \mu+v\end{matrix}\middle|t\right)\right] \tag{8}$$

Applying the Euler transformation eq. (6) to write the first term inside the square bracket in eq. (8), gives

$$(u+iy)(1-t)^{-2iy}\,{}_2F_1\left(\begin{matrix}v-1-iy,\mu-iy\\ \mu+v\end{matrix}\middle|t\right).$$

This shows that the dominant term in a comparison function for this factor is

$$\frac{(1-t)^{-iy}}{2iy}\left[(\mu+iy)(1-t)^{-iy}\,{}_2F_1\left(\begin{matrix}\mu-iy,v-1-iy\\ \mu+v\end{matrix}\middle|t\right)-complexconjugate\right] \tag{9}$$

We now use the Gauss Sum eq. (7), to evaluate the hypergeometric function ${}_2F_1$ at $t=1$ in eq. (9), as

$\dfrac{\Gamma(\mu+v)\Gamma(1+2iy)}{\Gamma(\mu+1+iy)\Gamma(v+iy)}=\dfrac{2iy}{\mu+iy}\dfrac{\Gamma(\mu+v)\Gamma(2iy)}{\Gamma(\mu+iy)\Gamma(v+iy)}$, then eq. (9) becomes (A6)

where $\alpha=\arg\left[\Gamma(2iy)/\Gamma(\mu+iy)\Gamma(v+iy)\right]$. Repeating the same procedure on the second ${}_2F_1$ on the right side of the generating function in eq. (2), we have same result as (A6) but we now use parameter replacement $y\rightarrow -y$, $\mu\rightarrow a$ and $v\rightarrow b$ giving

$$(1-t)^{-iy}\left[(1-t)^{-iy}\frac{\Gamma(a+b)\Gamma(-2iy)}{\Gamma(a-iy)\Gamma(b-iy)}+complexconjugate\right]$$

$$=(1-t)^{-iy}\frac{\Gamma(a+b)\left|\Gamma(2iy)\right|}{\left|\Gamma(a+iy)\Gamma(b+iy)\right|}\left[(1-t)^{-iy}e^{i\beta}+c.c\right] \tag{10}$$

where $\beta=\arg\left[\Gamma(2iy)/\Gamma(a+iy)\Gamma(b+iy)\right]$.

Multiplying (A6) by eq. (10), we have

$$\frac{\Gamma(a+b)\left|\Gamma(2iy)\right|^2}{\left|\Gamma(u+iy)\Gamma(v+iy)\Gamma(a+iy)\Gamma(b+iy)\right|}\left[(1-t)^{-2iy}e^{i(\alpha+\beta)}+e^{i(\alpha-\beta)}+c.c\right] \tag{11}$$

From eq. (11), the comparison function near $t=1$ is $(1-t)^{-2iy}$. Using the expansion of this term

$(1-t)^{-2iy}=\sum_{n=0}^{\infty}\frac{(2iy)_n}{\Gamma(n+1)}t^n$ in (11), hence we have

$$\tilde{W}_n^{\mu}\left(y^2;v;a,b\right)\approx\frac{\Gamma(\mu+v)\Gamma(a+b)\left|\Gamma(2iy)\right|}{\left|\Gamma(u+iy)\Gamma(v+iy)\Gamma(a+iy)\Gamma(b+iy)\right|}\left[n^{2iy-1}e^{-i\gamma}e^{i(\alpha+\beta)}+c.c\right] \tag{12}$$

where $\gamma=\arg\left[\Gamma(2iy)\right]$ and we have used $(z)_n=\frac{\Gamma(n+z)}{\Gamma(z)}$ and $\frac{\Gamma(n+a)}{\Gamma(n+b)}\approx n^{a-b}$. With the following rules $\arg(a)+\arg(b)=\arg(ab)$, $\arg(a)-\arg(b)=\arg(a/b)$ and $a^{ib}=e^{ib\ln a}$.

Using the results of Wilson's work in Wilson (1991) and those in Taiwo (2020), we obtain the following asymptotic $(n\to\infty)$

$$\tilde{W}_n^{\mu}\left(y^2;v;a,b\right)\approx\frac{2}{n}\Gamma(\mu+v)\Gamma(a+b)\left|A(iy)\right|\cos\left\{2y\ln(n)+\arg\left[A(iy)\right]\right\}+O\left(n^{-1}\right) \tag{13}$$

where $A(iy)=\Gamma(2iy)/\Gamma(\mu+iy)\Gamma(v+iy)\Gamma(a+iy)\Gamma(b+iy)$ is the scattering amplitude. Hence the asymptotic of the orthonormal version of the polynomial will be

$$\tilde{W}_n^{\mu}\left(y^2;v;a,b\right)\approx B(\mu,v,a,b)\sqrt{\frac{2}{n}}\Gamma(\mu+v)\Gamma(a+b)\left\{2\left|A(iy)\right|\cos\left[2y\ln(n)+\arg A(iy)\right]\right\}+O\left(n^{-1}\right) \tag{14}$$

where $B(\mu,v,a,b)=\sqrt{\frac{\Gamma(\mu+v)\Gamma(a+b)\Gamma(\mu+a)\Gamma(\mu+b)\Gamma(v+a)\Gamma(v+b)}{\Gamma(\mu+v+a+b)}}$, this is same as eq. (13).

Remember, in this reformulation, the existence of bound states dictates that the scattering amplitude $\left|A(iy)\right|$ vanishes i.e. $\mu+iy=-m$, as $m=0,1,2,\ldots,N$. Hence this implies that $\mu<0$ and $0<N\leq-\mu$. Then $\breve{W}_N^{\mu}(Y^2;v;a,b)$, becomes the Racah polynomial. Using this in the Wilson polynomial changes it to become the discrete Racah Polynomial defined by Koekoek and Swarttouw (1998) in (A7), where $\alpha=\mu+a-1(\alpha>-1)$, $\gamma=\mu+b-1(\gamma>-1)$, $\beta=v+b-1(\beta>N-1)$, and $\delta=-(N+\beta+1)=\mu-b$. However, using the inverse parameter map $\mu=\frac{1}{2}(\gamma+\delta+1)$, $v=\beta+\frac{1}{2}(\delta-\gamma+1)$, $a=\alpha-\frac{1}{2}(\gamma+\delta-1)$ and $b=\frac{1}{2}(\gamma-\delta+1)$ takes the Racah polynomial back to the Wilson Polynomial. Also, the generating function of the Racah polynomial as obtained from eq. (2) using the parameter map giving

$$\sum_{n=0}^{N}\tilde{R}_n^{\mu}(m;\alpha;\beta,\gamma)t^n={}_2F_1\left(\left.\begin{matrix}-m,-m+\beta-\gamma\\-N\end{matrix}\right|t\right){}_2F_1\left(\left.\begin{matrix}m+\alpha+1,m+\gamma+1\\\alpha+\beta+N+2\end{matrix}\right|t\right) \tag{15}$$

Which is the formula in Koekoek and Swarttouw (1998), and the three - term recursion relation is

$$\frac{1}{4}(N+\beta-\gamma-2m)^2\,\tilde{R}_n^N=$$

$$\left[\frac{1}{4}\left(N+\beta-\gamma\right)^2-\frac{\left(n-N\right)\left(n+\alpha+1\right)\left(n+\gamma+1\right)\left(n+\alpha+\beta+1\right)}{\left(2n+\alpha+\beta+1\right)\left(2n+\alpha+\beta+2\right)}-\frac{n\left(n+\beta\right)\left(n+\alpha+\beta-\gamma\right)\left(n+N+\alpha+\beta+1\right)}{\left(2n+\alpha+\beta\right)\left(2n+\alpha+\beta+1\right)}\right]\tilde{R}_n^N$$
$$+\frac{\left(n+\alpha\right)\left(n+\beta\right)\left(n+\gamma\right)\left(n+\alpha+\beta-\gamma\right)}{\left(2n+\alpha+\beta\right)\left(2n+\alpha+\beta+1\right)}\tilde{R}_{n-1}^N+\frac{\left(n+1\right)\left(n-N\right)\left(n+\alpha+\beta+1\right)\left(n+N+\alpha+\beta+2\right)}{\left(2n+\alpha+\beta+1\right)\left(2n+\alpha+\beta+2\right)}\tilde{R}_{n+1}^N \tag{16}$$

The discrete orthogonality relation for the Racah polynomial is

$$\sum_{m=0}^{N}\frac{2m+\gamma-\beta-N}{m+\gamma-\beta-N}\frac{(-N)_m(\alpha+1)_m(\gamma+1)_m(\gamma-\beta-N+1)_m}{(-\beta-N)_m(\gamma-\beta+1)_m(\gamma-\alpha-\beta-N)_m\,m!}\bar{R}_n^N(m;\alpha,\beta,\gamma)\bar{R}_{n'}^N(m;\alpha,\beta,\gamma)$$
$$=\frac{n+\alpha+\beta+1}{2n+\alpha+\beta+1}\frac{(-\alpha-\beta-N-1)_N(\gamma-\beta-N+1)_N}{(-\beta-N)_N(\gamma-\alpha-\beta-N)_N}\frac{(\beta+1)_n(\alpha+\beta-\gamma+1)_n(\alpha+\beta+N+2)_n\,n!}{(-N)_n(\alpha+1)_n(\gamma+1)_n(\alpha+\beta+2)_n}\delta_{n,n'} \tag{17}$$

where $\bar{R}_n^N(m;\alpha,\beta,\gamma)={}_4F_3\left(\left.\begin{matrix}-n,-m,n+\alpha+\beta+1,m-\beta+\gamma-N\\ \alpha+1,\gamma+1,-N\end{matrix}\right|1\right)$ and

$$\rho^N(m;\alpha,\beta,\gamma)=\frac{2m+\gamma-\beta-N}{m+\gamma-\beta-N}\frac{(-N)_m(\alpha+1)_m(\gamma+1)_m(\gamma-\beta-N+1)_m}{(-\beta-N)_m(\gamma-\beta+1)_m(\gamma-\alpha-\beta-N)_m\,m!}\times\frac{(-\beta-N)_N(\gamma-\alpha-\beta-N)_N}{(-\alpha-\beta-N-1)_N(\gamma-\beta-N+1)_N}$$

Similarly like the Wilson polynomial, the discrete Racah polynomial has an orthonormal version defined as (A8) and (A9).

Wilson – Racah Quantum System

The equation $\Psi(t,x)=e^{iEt/\hbar}\Psi(E,x)$ is a total wave function of a system and the associate Hamiltonian is $H\Psi=i\hbar\frac{\partial}{\partial t}\Psi=\mathrm{E}\Psi$. However, since a potential is unknown, H cannot be written in quantum mechanical convention as the sum of kinetic energy operator and a potential function. We will still observe all postulates, physical information about quantum mechanical system that are contained in the wavefunction. The energy polynomials $\{P_n^u(\varepsilon)\}$ are specified and the basis set $\{\phi_n(x)\}$ is chosen. The basis elements will be chosen as we go on, but now we select the four-parameter Wilson polynomial whose normalized version is shown in the Appendix as formula (A4). The corresponding normalized weight function is given by eq. (4). Comparing the asymptotic formula (A9) with Eq. (14) and noting that $\ln n\approx o\left(n^{\xi}\right)$ for any $\xi>0$, the scattering phase shift is

$$\delta(\varepsilon)=\arg\left[\Gamma(2iy)/\Gamma(\mu+iy)\Gamma(v+iy)\Gamma(a+iy)\Gamma(b+iy)\right] \tag{18}$$

where $y=\varepsilon(E)$ such that $y\geq 0$. As earlier stated, if $\mu<0$ and $\mu+v$, $\mu+a$, $\mu+b$ are positive or pair of complex conjugates with positive real parts, then the polynomial will have a continuum spectrum as well as a finite size discrete spectrum. Therefore, the bound states occur $\left\{\varepsilon_m\right\}_{m=0}^{N}$ such that $iy=-(m+\mu)$ which makes the scattering amplitude $A(\varepsilon)$ vanish due to argument of the gamma function $\Gamma(\mu+iy)$ in the denominator of $\left|A(iy)\right|$. Therefore, the bound states energies are obtained from the energy spectrum formula $y^2=-(m+\mu)^2$ giving

$$E_m=-\frac{\lambda^2}{2}(m+\mu)^2 \tag{19}$$

So the continuous orthogonality relation of the Wilson polynomial will now become (A3). The total wavefunction corresponding to the continuous energy ε and discrete energy ε_m will be

$$\psi_m(E,x)=\sqrt{\rho^{\mu}(\varepsilon)}\sum_{n=0}^{\infty}W_n^{\mu}\left(\varepsilon^2;\nu;a,b\right)\phi_n(x)+\sqrt{\rho_m^N}\sum_{n=0}^{N}W_n^{\mu}\left(-(m+\mu)^2;\nu;a,b\right)\phi_n(x) \tag{20}$$

where $\rho^{\mu}(\varepsilon)$ and ρ_m^N are the continuous and discrete normalized wave functions as defined in (A3) and for this physical system, the basis elements are defined as $\phi_n(x)=\left[\sqrt{\pi}\,2^n n!\right]^{-1/2}e^{-\lambda^2x^2/2}H_n(\lambda x)$, where $-\infty<x<\infty$ in the one dimensional coordinate. $H_n(\lambda x)$ is the Hermite polynomial of degree *n*. Now, if the values of the physical parameters (in the Wilson Orthogonal Polynomial), are such that it is totally confined ($\mu<0$, $1>\nu\geq 0$, $\mu+a>0$ and $\mu+b>0$), then only bound states will exist and the mth wavefunction will wholly be written in terms of the discrete Racah polynomial as

$$\psi_m(E,x)=\sqrt{\rho^N(m;\alpha,\beta,\gamma)}\sum_{n=0}^{N}R_n^N(m;\alpha,\beta,\gamma)\phi_n(x) \tag{21}$$

where $\rho^N(m;\alpha,\beta,\gamma)$ and $R_n^N(m;\alpha,\beta,\gamma)$ are given as

$$\rho^N(m;\alpha,\beta,\gamma)=\frac{2m+\gamma-\beta-N}{m+\gamma-\beta-N}\frac{(-N)_m(\alpha+1)_m(\gamma+1)_m(\gamma-\beta-N+1)_m}{(-\beta-N)_m(\gamma-\beta+1)_m(\gamma-\alpha-\beta-N)_m\,m!}\times\frac{(-\beta-N)_N(\gamma-\alpha-\beta-N)_N}{(-\alpha-\beta-N-1)_N(\gamma-\beta-N+1)_N}$$

And consequently (A8) is obtained.

ATOMIC PROPERTIES OF HYDROGEN ATOM IN WILSON-RACAH QUANTUM SYSTEM

A hydrogen atom is an atom of the chemical element hydrogen. This electrically neutral atom contains a single positively charged proton and a single negatively bound to the nucleus by the Coulomb potential force. By atomic spectroscopy, there exist discrete infinite set of states in which hydrogen (or any atom) can exist. As a result of this, the energy spectrum of Hydrogen atom is known. To test the validity of the energy spectrum of the Wilson Racah quantum system, we use the experimental values of the hydrogen parameters in the energy spectrum of the Wilson – Racah quantum system and see its predictions.

In 3D the Schrodinger equation is

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V\right]\psi=E\psi$$

And

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right]+V\psi=E\psi \tag{22}$$

with $x=r\sin\theta\cos\phi$, $y=r\sin\theta\sin\phi$, and $z=r\cos\theta$, all derivatives in terms of (r,θ,ϕ), makes eq. 22

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial r}\left(\sin\theta\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi+V(r)\psi=E\psi \tag{23}$$

where $\psi(r,\theta,\phi)$. Using separation of variable, we write $\psi(r,\theta,\phi)=R(r)Y(\theta,\phi)$ in eq. (23), then we have

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r)Y(\theta,\phi)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)R(r)Y(\theta,\phi)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}R(r)Y(\theta,\phi) \tag{24}$$
$$-\frac{2m}{\hbar^2}\left[V(r)-E\right]R(r)Y(\theta,\phi)=0$$

Implies

$$Y(\theta,\phi)\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r)+R(r)\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)Y(\theta,\phi)+R(r)\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\theta^2}Y(\theta,\phi) \tag{25}$$
$$-\frac{2m}{\hbar^2}\left[V(r)-E\right]R(r)Y(\theta,\phi)=0$$

dividing through by $R(r)Y(\theta,\phi)$, multiplying by r^2 and rearranging terms

$$\left[\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r)-\frac{2m}{\hbar^2}\left[V(r)-E\right]\right]+\left[\frac{1}{Y(\theta,\phi)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right]Y(\theta,\phi) \tag{26}$$
$$+\frac{1}{Y(\theta,\phi)\sin^2\theta}\frac{\partial^2}{\partial\theta^2}Y(\theta,\phi)=0$$

Introducing the separation constant $\lambda=\ell(\ell+1)$, where ℓ is angular momentum, then we have

$$\left[\frac{1}{R(r)}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r)-\frac{2m}{\hbar^2}\left[V(r)-E\right]\right]=\lambda \tag{27}$$

and

$$\left[\frac{1}{Y(\theta,\phi)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right]Y(\theta,\phi)+\frac{1}{Y(\theta,\phi)\sin^2\theta}\frac{\partial^2}{\partial\theta^2}Y(\theta,\phi)=-\lambda \tag{28}$$

changing variables in (27) as $Y(\theta,\phi)=\Phi(\phi)\Theta(\theta)$, then we have

$$-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=\frac{1}{\Theta}\left(\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Theta}{\partial\theta}+\lambda\sin^2\theta\Theta\right)=m^2 \tag{29}$$

where m is an arbitrary constant. Rearranging eq. (29) and writing eq. (27) again, we have the following equations:

Azimuthal equation

$$\frac{\partial^2\Phi(\phi)}{\partial\phi^2}+m^2\Phi(\phi)=0 \tag{30}$$

Angular Momentum Equation

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Theta}{\partial\theta}+\left(\lambda-\frac{m^2}{\sin^2}\right)\Theta=0 \tag{31}$$

$\lambda_\ell=\ell(\ell+1)$ with $\ell=0,1,2,\ldots$ and $m=-\ell,-\ell+1,\ldots,\ell-1,\ell$

Radial wave equation

$$\frac{1}{R}\left[\frac{d}{dr}r^2\frac{dR}{dr}+\frac{2mr^2}{\hbar^2}\left(E-V(r)\right)R\right]=\ell(\ell+1) \tag{32}$$

Now working with eq. (32) in order to get the energy spectrum for the Hydrogen atom, we use Coulomb potential function for hydrogen atom in eq. (32)

$$V(r)=-\frac{Ze^2}{4\pi\varepsilon_0 r} \tag{33}$$

when $\ell=0$ we have

$$-\frac{\hbar^2}{2m}\left(R''+\frac{2}{r}R'\right)-\frac{Ze^2}{4\pi\varepsilon_0 r}=ER \tag{34}$$

Using $R(r)=Ae^{-r/a}$ implies $R'=-\frac{A}{a}e^{-r/a}=-\frac{R}{a}$ and $R''=\frac{A}{a^2}e^{-r/a}=\frac{R}{a^2}$, then eq. (34) becomes

$$-\frac{\hbar^2}{2m}\left(\frac{1}{a_0}-\frac{2}{ar}\right)-\frac{Ze^2}{4\pi\varepsilon_0 r}=E \tag{35}$$

Equation eq. (35) result to

$$E_n=-\frac{\hbar^2}{2ma}=-Z\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{m_e}{2\hbar^2}=\frac{m_e e^4}{8\varepsilon_0^2\hbar^2}\left(\frac{Z^2}{n^2}\right)=\frac{-13.6}{n^2}ev \tag{36}$$

where $a_0=\frac{4\pi\varepsilon_0\hbar^2}{Ze^2m}$ is Bohr radius. To test the validity of the Wilson Racah energy spectrum, we use the parameters of the hydrogen atom in eq. (19) by taking

$$\mu=\frac{1}{n}\left(\sqrt{\frac{me^4}{4\varepsilon_0^2\hbar^2\lambda^2}}-n^2\right) \tag{37}$$

then we have

$$E_n=-\frac{\lambda^2}{2}\left(n+\left[\frac{1}{n}\left(\sqrt{\frac{me^4}{4\varepsilon_0^2\hbar^2\lambda^2}}-n^2\right)\right]\right)^2 \tag{38}$$

This same phenomenon was observed for hydrogen like atoms (Helium He^{+}, Lithium Li^{2+}, Beryllum Be^{+3} and Boron B^{4+}) such the energy spectrum will be given

$$E_n=-\frac{\lambda^2}{2}\left(n+\left[\frac{1}{n}\left(\sqrt{\frac{Z^2me^4}{4\varepsilon_0^2\hbar^2\lambda^2}}-n^2\right)\right]\right)^2 \tag{39}$$

THERMODYNAMICS PROPERTIES OF DIATOMIC MOLECULES –LITHIUM

In this section, we apply the energy spectrum of the Wilson – Racah quantum system to find the thermodynamic properties of diatomic molecules – Lithium. With reference to Peng *et al.* (2018), we used the new energy spectrum of this study in place of the vibrational energy level belonging to the improved Manning – Rosen potential. Therefore, the parameters are denoted by

$$\chi = \frac{2^{1/2}}{\lambda}\left[D_e - \frac{h^2\alpha^2}{2\mu}\left(\frac{m}{s_v} - \frac{s_v}{4}\right)^2 \right]^{1/2} + v \tag{40}$$

and our energy spectrum becomes

$$E_v = -\frac{\lambda^2}{2}\left(2v + \frac{2^{1/2}}{\lambda}\left[D_e - \frac{h^2\alpha^2}{2\mu}\left(\frac{m}{s_v} - \frac{s_v}{4}\right)^2 \right]^{1/2} \right)^2 \tag{41}$$

Where:

$$s_v = 2v + 1 + \sqrt{1 + \frac{8\mu D_e\left(e^{\alpha r_e} - 1\right)^2}{h^2\alpha^2}}, \quad m = \frac{2\mu}{h^2\alpha^2} D_e\left(e^{2\alpha r_e} - 1\right)$$

$$\alpha = \pi c\omega_e\sqrt{\frac{2\mu}{D_e}} + \frac{1}{r_e} W\left(-\pi c\omega_e r_e\sqrt{\frac{2\mu}{D_e}} e^{-\pi c\omega_e r_e\sqrt{\frac{2\mu}{D_e}}} \right),$$

D_e is the dissociation energy, r_e is the equilibrium bond length, α is the adjustable parameter for range of interaction, *c* is the speed of light, *h* is Planck constant, *v* is the iterative number $v = 0, 1, 2, 3, \ldots, v_{\max}$) , $v_{\max}$ is the maximum upper bound vibration quantum number, μ is the reduced mass of lithium diatomic molecule. The vibrational partition function, a direct summation over all possible vibrational energy levels available to the system, for our model is

$$Q = \sum_{v=0}^{v_{\max}} e^{-\beta E_n} = \sum_{v=0}^{v_{\max}} e^{\frac{\beta\lambda^2}{2}(v+\chi)^2} = \sum_{v=0}^{v_{\max}} e^{\frac{\beta\lambda^2}{2}\left(2v + \frac{2^{1/2}}{\lambda}\left[D_e - \frac{h^2\alpha^2}{2\mu}\left(\frac{m}{s_v} - \frac{s_v}{4}\right)^2 \right]^{1/2} \right)^2} \tag{42}$$

Where $\beta = \frac{1}{kT}$, where *k* is the Boltzmann's constant. Using Vibrational partition function (42) the thermodynamics properties function can be calculated as follows:

Vibrational Mean Energy, $U = -\frac{\partial \ln Q}{\partial \beta}$, (43)

Vibrational Heat Capacity, $C = -k\beta\frac{\partial U}{\partial \beta}$, (44)

Vibrational Free Energy, $F = -\frac{1}{\beta}\ln Q$, (45)

Vibrational Entropy, $S = k\ln Q - k\beta\frac{\partial \ln Q}{\partial \beta}$. (46)

Table 1. Experimental values of H_2 and Li molecules.

Molecule	λ(m)	e(C)	m(kg)	h (kgm^2s^{-1})	ε_0 (kgs^{-2})	D_e (m^{-1})	M (μkg)	r_e (Å)	ω_e (m^{-1})	n	Ref.
H_2	0.2	1.602×10^{-19}	9.109×10^{-31}	6.626×10^{-34}	8.854×10^{-12}	-	-	-	-	1,2…	Alhaidari (2020)
Li	-	-	-	6.626×10^{-34}	-	8.854×10^{-12}	3..626	4.173	65.130×10^2	1,2…	Koekoek (1998)

RESULTS AND DISCUSSION

This section considers hydrogen and lithium molecules and present sets of results of energy spectrum of Hydrogen atom, thermodynamic functions with respect to temperature all for Wilson-Racah quantum system obtained within the framework of two approaches. The corresponding input experimental parameters used are summarized in Table 1.

It can be seen from Figure 1 that eq. (38), the new model, gives good approximate prediction of the Hydrogen atom energy spectrum with an estimated average error of 0.125% and we are able to ascertain that the new physical model gives a good prediction of the hydrogen model with Figure 2. Moreover, the comparison of the first set of the energy spectrum with the energy spectrum of hydrogen atom obtained by the numerical solution of the Schrödinger eq. (38), enables us to determine the region of validity of the expression eq. (19) derived for the energy spectrum in the WRQs, as well as to reveal the efficiency of the direct WRQs method in its presented realization.

Without using any experimental spectroscopy data except the one shown in Table 1, the total thermodynamics properties function was calculated using vibrational partition function of Lithium molecule for a wide range of temperatures varying for -5 to 500k at 1 bar pressure. Figures 3 to 7 show the variation of thermodynamic properties function with respect to temperature for Q, U, C, S and F respectively. The calculated theoretically predicted values of thermodynamic function in WRQs are represented by red dotted line while the blue dotted line represent the experimental data extracted from Peng *et al*. (2018). The Figures 3 to 7 show good agreement between the values of thermodynamic functions obtained from the proposed model and experimental values over a wide range of temperature (0-500k).

It can be seen that all thermodynamic functions increase as temperature, T increases. It can further be observed in Figures 3 to 4, that the vibrational partition function Q, mass energy U increase monotonically as temperature T increases. However, it is known from Eq. (42) that the vibrational partition function, a direct summation over all possible vibrational energy levels available to the system may increase with increasing temperature; therefore, we have fixed the value of T at a reasonably moderate value $0 - 500℃$ (Peng *et al*., 2018). The Q and U are increasing almost linearly with increasing temperature.

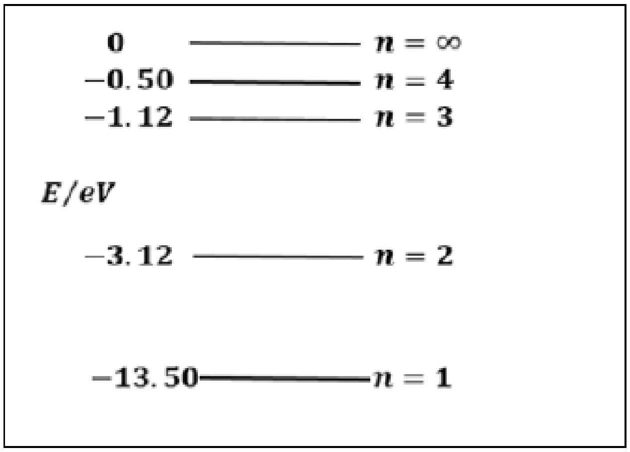

Figure 1. Energy spectrum of the hydrogen atom using experimental values in WRQs.

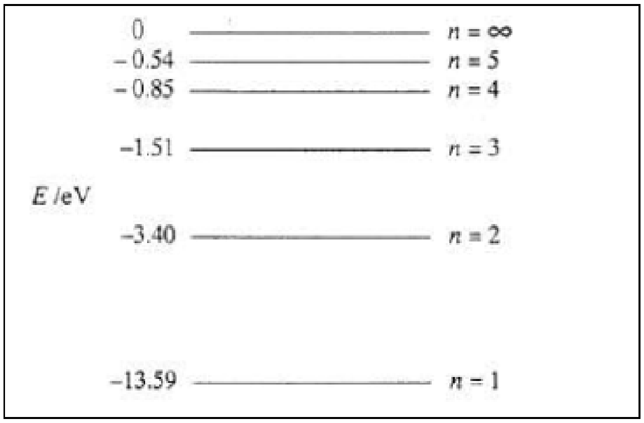

Figure 2. Energy spectrum of the hydrogen atom from Bohr model.

The analogous dependencies have been received in Peng *et* al. (2018). Note that, increasing the temperature, the tilt angle of the curve is increasing.

Figure 5 shows the dependence of vibrational heat capacity C on temperature, T. the vibrational specific heat *C* increases as T increases to a maximum value and decreases thereafter. It may also be observed that the vibrational specific heat *C* become more or less equal as

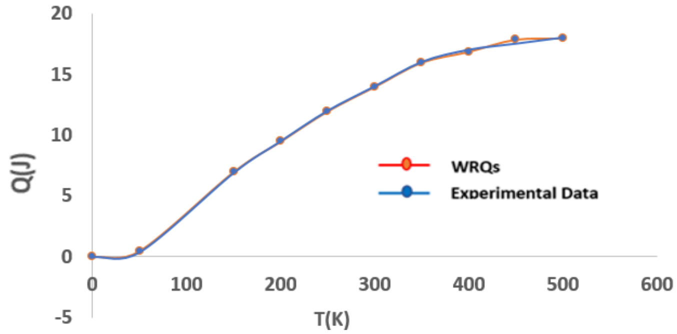

Figure 3. Vibrational partition function Q as a function of temperature T.

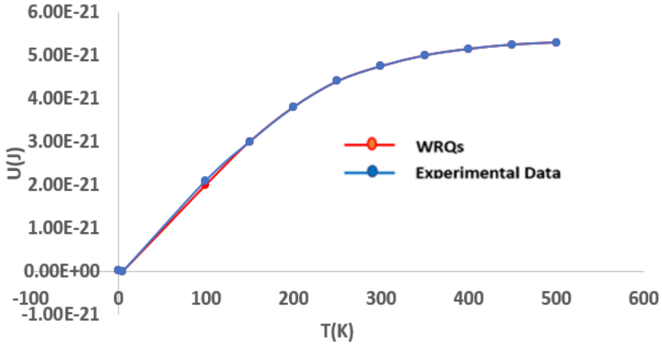

Figure 4. Vibrational mean energy U as a function of temperature T.

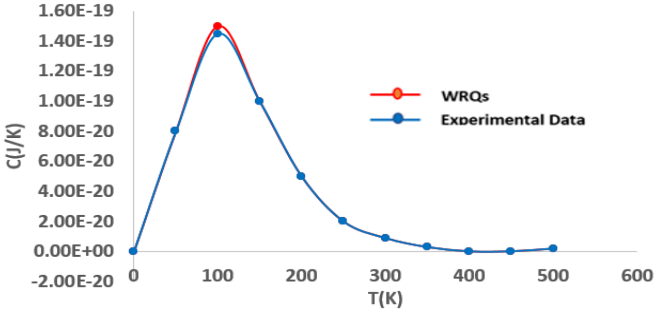

Figure 5. Vibrational heat capacity, C as a function of temperature T.

T increases to about $100^{\circ}\mathrm{C}$, T is therefore set equal to $500^{\circ}\mathrm{C}$ (Peng *et al*., 2018). Figure 6 shows the Vibrational entropy S for the diatomic molecule as a function of temperature T. The entropy S increases as T increases but reaches a constant value at $300-500^{\circ}\mathrm{C}$ subsequently, as expected. In Figure 7**,** the Vibrational free energy F for the diatomic molecule as a function of temperature T is presented. The free energy F increases to the maximum value and then decreases with increasing temperature.

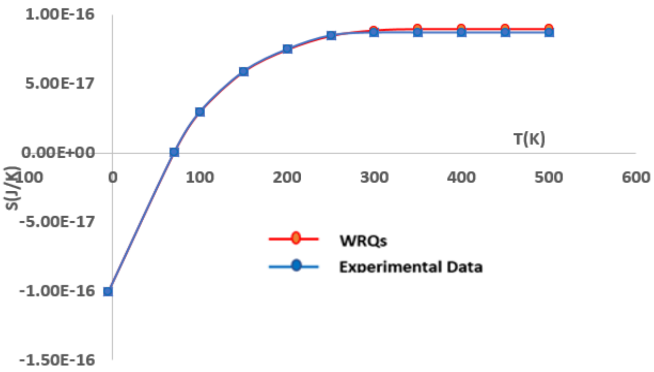

Figure 6. Vibrational entropy S for the diatomic molecule as a function of temperature T.

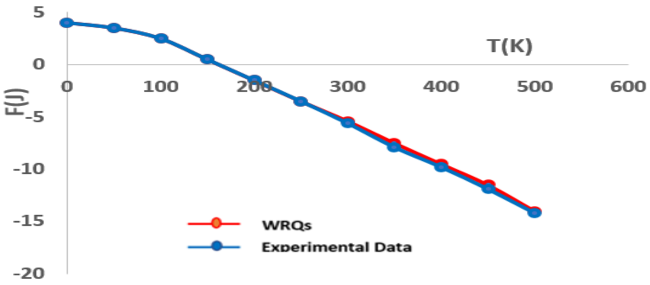

Figure 7. Vibrational free energy F for the diatomic molecule as a function of temperature T.

As it can be seen from the figures the curves have extremum. Increasing the temperature, the curve of the Vibrational specific heat dependence on the temperature is changing its slope. For higher temperatures the curve is firstly increasing than decreasing having the minimum point. For lower temperatures the curve firstly increases and after reaching maximum point decreases.

The relative percentage of the predicted values was calculated from Peng *et al*. (2018). The results are shown in Table 2. The corresponding average relative deviations $d_{avg}(\%)$ are 2.42% , 0.45% , 0.30%, 1.23%, and 1.50% for Q, U, C, S and F thermodynamic functions respectively. This proves the efficiency of model to calculate the thermodynamic properties of any atomic or diatomic molecular substances. The excellent agreement with the experiment will deteriorate with increasing temperature. The reason is that the calculated thermodynamic functions in the present work contains only contributions of the ground states of molecules to the vibrational energy level and does not include the contributions of the excited states of molecules. In the Peng *et al.* (2018) data, the contributions of all states are included. At low temperature ($T < 300$ K), the discrepancy between the predicted values and Peng *et al*. (2018) data increases because the

Table 2. Comparison between experimental and predicted thermodynamic functions for Q, U, C, S and F.

T(K)	Q(J)		U(J)		C(J/K)		S(J/K)		F(J)	
	R_{Th}	R_{Exp}	R_{Th}	R_{Exp}	R_{Th}	R_{Exp}	R_{Th}	R_{Exp}	R_{Th}	R_{Exp}
-5	-	-	-	-	-	-	-1.00E-16	-1.00E-16	-	-
0	0.000	0.000	1.00E-23	1.00E-23	0.00E+00	0.00E+00	-	-	4.000	4.000
5	-	-	2.50E-48	2.50E-48	-	-	-	-	-	-
50	0.500	0.400	-	-	8.00E-20	8.00E-20	2.50E-19	2.50E-19	3.500	3.500
70	-	-	-	-	-	-	3.00E-17	3.00E-17	-	-
100	-	-	2.00E-21	2.00E-21	1.50E-19	1.45E-19	5.90E-17	5.90E-17	2.500	2.500
150	7.000	6.900	3.00E-21	3.00E-21	1.00E-19	1.00E-19	7.50E-17	7.50E-17	0.500	0.500
200	9.500	9.500	3.80E-21	3.80E-21	5.00E-20	5.00E-20	8.50E-17	8.50E-17	-1.500	-1.500
250	12.000	12.000	4.40E-21	4.40E-21	2.00E-20	2.00E-20	8.90E-17	8.90E-17	-3.500	-3.500
300	14.000	14.000	4.75E-21	4.75E-21	9.00E-20	9.00E-20	9.00E-17	8.70E-17	-5.400	-5.400
350	16.000	16.000	5.00E-21	5.00E-21	3.00E-21	3.00E-21	9.00E-17	8.70E-17	-7.500	-7.500
400	16.900	17.000	5.15E-21	5.15E-21	1.60E-21	1.60E-21	9.00E-17	8.70E-17	-9.500	-9.800
450	17.900	17.500	5.25E-21	5.25E-21	1.80E-22	1.80E-22	9.00E-17	8.70E-17	-11.500	-11.900
500	18.000	18.000	5.30E-21	5.30E-21	2.00E-21	2.00E-21	9.00E-17	8.70E-17	-14.000	-14.200
$d_{avg}(\%)$	2.42		0.45		0.30		1.30		1.50	

vibrational partition function obtained by employing the improved Manning – Rosen potential formula only contains the lowest order approximation contributions (Koekoek and Swarttouw, 1998).

To check the sensitivity of the predicted results to the molecular constant used, the average relative deviation for *C* was calculated when changing the value of each parameter by 1%, while the four other parameters are fixed. When the value of D_e increased by 1%, the average relative deviation varies from 2.42 to 1.48%. If the value of r_e is increased by 1% and values of D_e and ω_e remain unchanged, the average relative deviation varies from 2.42 to 1.48%. When the value of ω_e increased by 1% and keep the original values of D_e and r_e, the average relative deviation turns to 2.45% from 2.42%. It is obvious that the sensitivity of predicted results most depends on the value of the equilibrium bond length.

Conclusion

This work theoretically studied the thermodynamic properties of diatomic molecules as a function of temperature as well as the atomic properties of Hydrogen atom, using WRQs. The energy spectrum of WRQs has been obtained and applied to these two physical models to test its validity as it shows good approximation of the Hydrogen atom energy with an estimated average error of 0.125%. The vibrational partition function has been calculated and using it, the thermodynamically properties of the diatomic molecules have been calculated. The proposed procedure merely relies on experimental values of five molecular constants. The average relative percentage deviations of the thermodynamic properties' functions Q, U, C, S, and F are 2.42% , 0.45% , 0.30%, 1.23%, and 1.50% respectively. The mean energy increases monotonically with temperature increase. The entropy increases monotonically for all values at low temperature, whereas it depends on the energy spectrum at high temperatures. The heat capacity shows a peak structure. Vibrational free energy has a positive sign and decreases with the temperature value increase. These represent satisfactory compromise between accuracy and rapid computations.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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APPENDIX A

The three-term recursion relation of the four parameters Wilson orthogonal polynomial at $(n=1,2,3...,)$ is

$$y^2\tilde{W}_n^{\mu}=\left[\frac{(n+\mu+v)(n+\mu+a)(n+\mu+b)(n+\mu+v+a+b-1)}{(2n+\mu+v+a+b)(2n+\mu+v+a+b-1)}+\frac{n(n+v+a-1)(n+v+b-1)(n+a+b-1)}{(2n+\mu+v+a+b-1)(2n+\mu+v+a+b-2)}-\mu^2\right]\tilde{W}_n^{\mu}$$
$$-\frac{(n+\mu+a-1)(n+\mu+b-1)(n+v+a-1)(n+v+b-1)}{(2n+\mu+v+a+b-1)(2n+\mu+v+a+b-2)}\tilde{W}_{n-1}^{\mu}-\frac{(n+1)(n+\mu+v)(n+a+b)(n+\mu+v+a+b-1)}{(2n+\mu+v+a+b)(2n+\mu+v+a+b-1)}\tilde{W}_{n+1}^{\mu} \quad \text{(A1)}$$

The initial seeds $(n=0)$ for this recursion at $\tilde{W}_0^{\mu}=1$ and

$$\tilde{W}_1^{\mu}=\frac{(\mu+a)(\mu+b)}{(a+b)}-\frac{\mu+v+a+b}{(\mu+v)(a+b)}\left(y^2+\mu^2\right) \quad \text{(A2)}$$

The generalized orthogonality relation is

$$\int_0^{\infty}\rho^{\mu}(y;v,a,b)W_n^{\mu}\left(y^2;v,a,b\right)W_m^{\mu}\left(y^2;v,a,b\right)dy-2\frac{\Gamma(\mu+v+a+b)\Gamma(v-\mu)\Gamma(a-\mu)\Gamma(b-\mu)}{\Gamma(-2\mu+1)\Gamma(a+b)\Gamma(a+v)\Gamma(v+b)}\times \quad \text{(A3)}$$

The orthonormal version of this polynomial in is

$$W_n^{\mu}\left(y^2;v;a,b\right)=\sqrt{\left(\frac{2n+\mu+v+a+b-1}{n+\mu+v+a+b-1}\right)\frac{(\mu+v)_n(a+b)_n(\mu+v+a+b)_n\,n!}{(\mu+a)_n(\mu+b)_n(v+a)_n(v+b)_n}}\tilde{W}_n^{\mu}\left(y^2;v;a,b\right)$$

$$=\sqrt{\left(\frac{2n+\mu+v+a+b-1}{n+\mu+v+a+b-1}\right)\frac{(\mu+v)_n(\mu+a)_n(\mu+b)_n(\mu+v+a+b)_n}{(a+b)_n(v+a)_n(v+b)_n\,n!}}\;{}_4F_3\left(\left.\begin{matrix}-n,n+\mu+v+a+b-1,\mu+iy,\mu-iy\\ \mu+v,\mu+a,\mu+b\end{matrix}\right|1\right) \quad \text{(A4)}$$

And the three – term recursion relation for the orthonormal version is

$$y^2W_n^{\mu}=\left[\frac{(n+\mu+v)(n+\mu+a)(n+\mu+b)(n+\mu+v+a+b-1)}{(2n+\mu+v+a+b)(2n+\mu+v+a+b-1)}+\frac{n(n+v+a-1)(n+v+b-1)(n+a+b-1)}{(2n+\mu+v+a+b-1)(2n+\mu+v+a+b-2)}-\mu^2\right]W_n^{\mu}$$
$$-\frac{1}{2n+\mu+v+a+b-2}\sqrt{\frac{n(n+\mu+v-1)(n+a+b-1)(n+\mu+a)(n+\mu+b-1)(n+v+a-1)(n+v+b-1)(n+\mu+v+a+b-2)}{(2n+\mu+v+a+b-3)(2n+\mu+v+a+b-1)}}W_{n-1}^{\mu}$$
$$-\frac{1}{2n+\mu+v+a+b}\sqrt{\frac{(n+1)(n+\mu+v)(n+a+b)(n+\mu+a)(n+\mu+b)(n+v+a)(n+v+b)(n+\mu+v+a+b-1)}{(2n+\mu+v+a+b-1)(2n+\mu+v+a+b-1)}}W_{n+1}^{\mu} \quad \text{(A5)}$$

Using the Gauss Sum eq. (7) to evaluate the hypergeometric function ${}_2F_1$ at $t=1$ in eq. (9),

$$(1-t)^{-iy}\left[(1-t)^{-iy}\frac{\Gamma(\mu+v)\Gamma(2iy)}{\Gamma(\mu+iy)\Gamma(v+iy)}+complexconjugate\right]$$

$$=(1-t)^{-iy}\frac{\Gamma(\mu+v)\left|\Gamma(2iy)\right|}{\left|\Gamma(\mu+iy)\Gamma(v+iy)\right|}\left[(1-t)^{-iy}e^{i\alpha}+c.c\right] \quad \text{(A6)}$$

Using eq. (13) in the Wilson polynomial changes it to become the discrete Racah Polynomial defined as

$$\tilde{R}_n^N(m;\alpha,\beta,\gamma)=\frac{(\alpha+1)_n(\gamma+1)_n}{(\alpha+\beta+N+2)_n\,n!}\;{}_4F_3\left(\left.\begin{matrix}-n,-m,n+\alpha+\beta+1,m-\beta+\gamma-N\\ \alpha+1,\gamma+1,-N\end{matrix}\right|1\right) \quad \text{(A7)}$$

Like the Wilson polynomial, the discrete Racah polynomial has an orthonormal version defined as follows:

$$R_n^N\left(m;\alpha,\beta,\gamma\right)=\sqrt{\frac{2n+\alpha+\beta+1}{n+\alpha+\beta+1}\frac{\left(-N\right)_n\left(\alpha+1\right)_n\left(\gamma+1\right)_n\left(\alpha+\beta+2\right)_n}{\left(\beta+1\right)_n\left(\alpha+\beta-\gamma+1\right)_n\left(\alpha+\beta+N+2\right)_n n!}}$$

$$\times{}_4F_3\left(\left.\begin{matrix}-n,-m,n+\alpha+\beta+1,m-\beta+\gamma-N\\ \alpha+1,\gamma+1,-N\end{matrix}\right|1\right) \tag{A8}$$

with orthogonality

$$\sum_{m=0}^{N}\rho^N\left(m;\alpha,\beta,\gamma\right)R_n^N\left(m;\alpha,\beta,\gamma\right)R_{n'}^N\left(m;\alpha,\beta,\gamma\right)=\delta_{n,n'} \tag{A9}$$

Note Alhaidari and Taiwo (2017) made use of the following identities in their calculations:

$$\frac{\left(a+1\right)_n}{\left(a\right)_n}=\frac{n+a}{a},\ \frac{\left(a\right)_{n+1}}{\left(a\right)_n}=n+a\ ,(n+a)_n=\frac{\Gamma(2n+a)}{\Gamma(2n+a)},\ \frac{\left(n+a\right)_n}{\left(a+1\right)_{2n}}=\frac{a/\left(a\right)_n}{2n+a} \tag{A10}$$

And

$$\left(a-n\right)_n=\frac{\Gamma\left(a\right)}{\Gamma\left(a-n\right)}. \tag{A11}$$