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Analytical Solution of Non-Linear Oscillator and Thermal Properties of Interacting System of Real Polyatomic Molecules

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ABSTRACT

The study examined the solution of nonlinear oscillator and thermal properties of interacting system of real polyatomic molecules. A nonlinear oscillator potential was substituted into the radial part of the Schrodinger wave equation and solved using the Frobenius method to obtain the energy eigenvalues of the system. The partition function and the energy eigenvalues are used to determine three thermal properties for four polyatomic molecules which showed that added energy is required in the absence of the nonlinear term as the orbital and magnetic quantum numbers are increased and degeneracy completely removed. Other findings also reveal that as the virial coefficients of the four polyatomic molecules vary, the additive property of entropy is observed as well as the enhancement of the mean energy approximately proportional to the volume of the molecules. The four polyatomic molecules under consideration are environmentally impactful and are indispensable to man.

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Introduction

It is a popular fact that microscopic systems are tackled theoretically with the use of the Schrodinger wave equation, Klein – Gordon equation, Dirac equation and their modifications, particularly in physics and chemistry [1-3]. In broad terms, to describe a given physical system, a potential model use cannot be overemphasized because the model provides information needed and from which some or all of the needed physical quantities can be computed. In the consideration of potential models, it has been observed that closed form solution of the Schrodinger wave equation is available or possible for few, and one of them is the linear harmonic oscillator. According to [4], the linear harmonic oscillator problem, offer us an opportunity to understand the basic features of a quantum system along with its transition to classical domain. It can be applied to study the vibrational spectra of molecules, quantum theory of radiation, high energy physics and the state with zero-point energy is reinterpreted as the vacuum [5]. Its use in other branches of physics is abounded [6]. Works on a combination or variations of harmonic oscillators are also listed [7-10]. As the study of the harmonic oscillator progresses, its inversion and modifications are also abounded [11-16]. Motivated by the recent advances in harmonic oscillator, inverted harmonic oscillator and their variations, as well as following the work of [17], the present study introduces a modified nonlinear harmonic oscillator of the form

$$V(r) = \frac{1}{2}\mu\omega^2 r^2 - \frac{1}{3r}\mu\varsigma \qquad (1)$$

where μ is the mass of oscillator, ω is the frequency, r is the radius and ς is a small positive nonlinear parameter.

This potential appears to be a generalized harmonic oscillator because it could be adjusted to the harmonic oscillator, the inverted harmonic oscillator and other variations or combinations.

Most of the studies on thermal properties of interacting systems are for ideal gases or molecules which are diatomic. However, the interaction of man, its environment and to account for the deviation between rarefied gases and real gases, values of Van der Waals constants for four polyatomic molecules which are environmentally indispensable to man and theoretical correct up to the second virial coefficient are chosen to among other considerations, determine some of its thermal properties and its relation to man.

Some thermodynamic functions of several potential models' study are abounded [18-26]. However, their application to polyatomic molecules is scanty. The choice of the four polyatomic molecules (Water, carbon(iv)oxide, Hydrogen sulphide and Sulphur(iv)oxide) are predicated on not only playing a crucial role in climate change and maintenance of environmental equilibrium balance but also, having greater range of shapes that are possible than the diatomic molecules, makes spin pairing of electrons very clear with valence – bond description of water and possess several modes of vibration because all bonds lengths and angles may change as oppose to diatomic molecules with only one mode of vibration.

Basically, the research is to describe the nonlinear harmonic oscillator potential with the thermal properties of four polyatomic molecules owing to the importance of some of their cycles, and an extension from ideal gases to real gases with a view to comparing the deviation.

Formalism

The work considers the radial Schrodinger wave equation of the form

$$\frac{1}{r}dr\left(r^2\frac{dR(r)}{dr}\right)+\frac{2\mu}{\hbar^2}\left(E-V(r)-\frac{l(l+1)\hbar^2}{2\mu r^2}\right)R(r)=0 \qquad (2)$$

Where l is the orbital quantum number, E is the eigenvalues and $\hbar$ is the Planck's constant.

Equation (1) is put into equation (2) and simplify, results in

$$\frac{d^2R(r)}{dr^2}+\frac{2}{r}\frac{dR(r)}{\hbar^2}+\frac{2\mu}{\hbar^2}\left(E-\frac{1}{2}\mu\omega^2r^2+\frac{1}{3r}\mu\varsigma-\frac{l(l+1)\hbar^2}{2\mu r^2}\right)R(r)=0 \qquad (3)$$

Equation (3) is transformed into the form

$$\left[\frac{d}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{\vartheta}{r^2}\right]R(r)+\left[A-Br^2+\frac{C}{r}\right]R(r)=0 \qquad (4)$$

Where

$$\vartheta=l(l+1)$$

$$A=\frac{2\mu E}{\hbar^2}$$

$$B=\frac{\mu^2\omega^2}{\hbar^2}$$

$$C=\frac{2\mu^2\varsigma}{3\hbar^2}$$

Method of Solution

The study assumed a radial wave function of the form

$$R(r)=Exp\left(-\alpha r^2-\beta rF(r)\right) \qquad (5)$$

where α and β are constants.

Equation (5) is put into equation (4) and simplify, results into

$$F''(r)+\left[-4\alpha r-2\beta+\frac{2}{r}\right]+$$
$$\left[-(4\alpha-\beta)r^2+4\alpha\beta r-6\alpha+\beta^2+A-\frac{2\beta}{r}-\frac{\vartheta}{r^2}+\frac{C}{r}\right]F(r)=0 \qquad (6)$$

To determine for real feasible solution, equation (6) is tested for the existence of ordinary points, singularities and Frobenius series solution and was satisfied [27-28]. Therefore, the study assumed a solution of the form

$$F(r)=\sum_{n=0}^{\infty}a_nr^{n+\varsigma} \qquad (7)$$

Equation (7) is put into equation (6) and equate coefficients of $r^{n+\varsigma}$, $r^{n+\varsigma-1}$, $r^{n+\varsigma-2}$ and $r^{n+\varsigma+2}$ respectively to zero, the following expressions result

$$(n+\varsigma)(-4\alpha)-(6\alpha-\beta^2-A)=0 \qquad (8)$$

$$(n+\varsigma)(-2\beta)-2\beta+C=0 \qquad (9)$$

$$2(n+\varsigma)+(n+\varsigma)(n+\varsigma-1)-\vartheta=0 \qquad (10)$$

$$(4\alpha-B)=0 \qquad (11)$$

Equations (11) and (9) are substituted into equation (8) and using the expressions for A, B and C results into

$$E_{n,l}=-\frac{\hbar^2(n+1)^2}{4\mu}+\frac{\hbar^2}{4\mu}\sqrt{(n+1)^2+\frac{4\mu^2\varsigma}{3\hbar^2}}-\left(\frac{2\mu\varsigma}{3}\right)-$$
$$\frac{\mu\omega^2}{\hbar^2}\left(-n-l(l+1)-\frac{3}{2}\right) \qquad (12)$$

When $\varsigma=0$

$$E_{n,l}=-\frac{\hbar^2(n+1)^2}{4\mu}+\frac{\hbar^2(n+1)}{4\mu}-\frac{\mu\omega^2}{\hbar^2}\left(-n-l(l+1)-\frac{3}{2}\right) \qquad (13)$$

For simplicity, if $\mu=\hbar=1$ ([5], [29 – 30]), equations (12) and (13) respectively reduced to the form

$$E_{n,l}=-\frac{(n+1)^2}{4}+\frac{1}{4}\sqrt{(n+1)^2+\frac{4\varsigma}{3}}-\left(\frac{2\varsigma}{3}\right)-\omega^2\left(-n-l(l+1)-\frac{3}{2}\right) \qquad (14)$$

and

$$E_{n,l}=-\frac{(n+1)^2}{4}+\frac{(n+1)}{4}-\omega^2\left(-n-l(l+1)-\frac{3}{2}\right) \qquad (15)$$

Thermal Properties

Thermal properties of a system consist of parameters such as specific heat, entropy. Mean energy, pressure and enthalpy just to mention a few. According to [31], to determine the thermal properties of a system, the partition function is needed and is given as

$$Z=\sum_{i=1}^{\infty}g_iExp\left(-\frac{E_{n,l}}{kT}\right) \qquad (16)$$

where g is the degeneracy of the ith level, k is the Boltzmann constant and T is the temperature.

The kernel of the thermodynamic properties is the partition function from which the thermal functions are obtained [32].

However, to determine the thermal functions of real gases or molecules, we make use of the expression following [33]

$$Z=\frac{(2\mu E_{n,l})^{\frac{3N}{2}}}{N!2\pi\hbar^{3N}}\int Exp\left(-\frac{U}{kT}\right)dq \qquad (17)$$

Where N is the number of particles and U is the potential energy.

To determine the integral $\int Exp\left(-\frac{U}{kT}\right)dq$ is challenging, therefore the Van der Waals assumptions as reported in [33] is adopted. The assumption is that the particles are rigid spheres and they attract each other with a weak force which decreases rapidly.

The Helmholtz free energy F(T) of the system is stated as

$$F(T) = -\frac{1}{T}\ln Z(T) = -\frac{1}{T}\ln Z(T) + \frac{N}{TV}B(T) \qquad (18)$$

where B(T) is the second virial coefficients

Using equation (17), equation (18) can be written as

$$F(T) = -\frac{\ln V^{N}}{N!\lambda^{3N}T} + \frac{N}{TV}\left(b - \frac{a}{NkT}\right) \qquad (19)$$

where $\lambda = \frac{2\pi\hbar}{\sqrt{2\mu E}}$ is the thermal wavelength and $B(T) = b - \frac{a}{NKT}$

The entropy S(T) of the system is given as

$$S(T) = -k\frac{\partial F(T)}{\partial T} = \frac{k\ln V^{N}}{N!\lambda^{3N}T^{2}} + \frac{kNb}{VT^{2}} - \frac{a}{kT^{3}} \qquad (20)$$

The pressure P(V) of the system is given by the expression

$$P(V) = -\frac{\partial F(T)}{\partial V} = \frac{N}{V\left(\ln N!\lambda^{3N}\right)T} + \frac{N}{TV^{2}}\left(b - \frac{a}{NKT}\right)$$

Table 1: Values of Van der Waals Constants a and b for Four Polyatomic Molecules [33,34]

Molecule	$a\left(atm-m^{6}/mol^{2}\right)$	$b\left(m^{3}/mol\right)$
CO_2	3.610	4.290
H_2O	5.464	3.049
H_2S	4.484	4.340
SO_2	6.775	5.680

Table 2: Values of Energies (J) obtained from Equations (14) and (15) for Increasing Orbital and Quantum Numbers

n	l	$E_{n,l}$	$E_{n,l}(\varsigma=0)$
0	0	58.6976	58.7176
1	0	97.1744	97.1960
	1	176.131	176.153
2	0	135.152	135.174
	1	214.109	214.131
	2	372.023	372.045
3	0	172.630	172.653
	1	251.587	251.610
	2	409.501	409.523
	3	646.371	646.394
4	0	209.609	209.631
	1	288.565	288.588
	2	446.479	446.502
	3	683.350	683.372
	4	999.177	999.200
5	0	246.087	246.110
	1	325.044	325.067
	2	482.957	482.980
	3	719.828	719.851
	4	1035.660	1035.680
	5	1430.440	1430.460

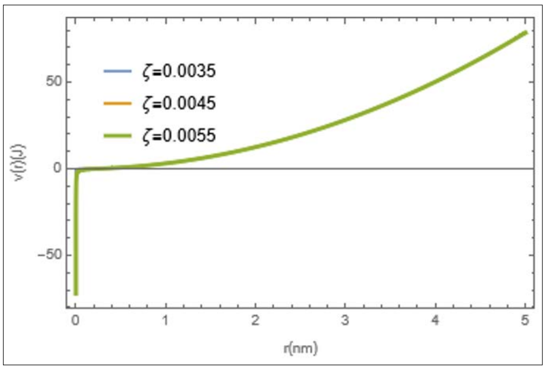

Figure 1: Potential Function Dependence on Radius of Oscillator with Nonlinear Parameter Varying

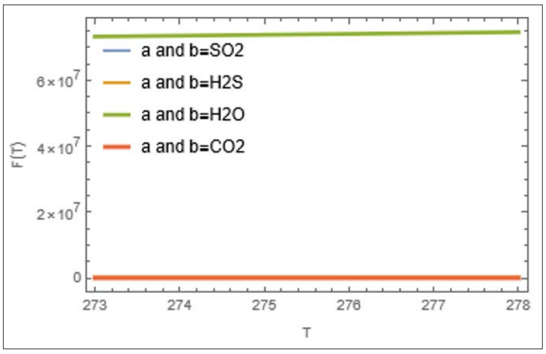

Figure 2: Dependence of Helmholtz Free Energy on Temperature with Varying Virial Coefficients.

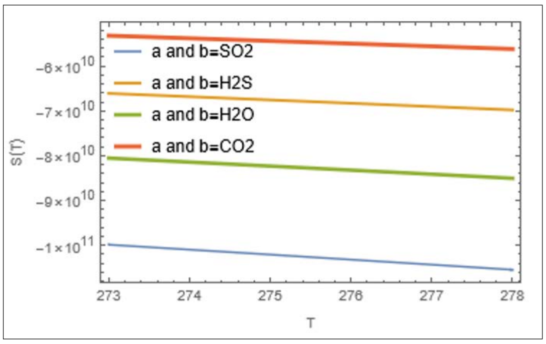

Figure 3: Dependence of Entropy on Temperature with Varying Virial Coefficients

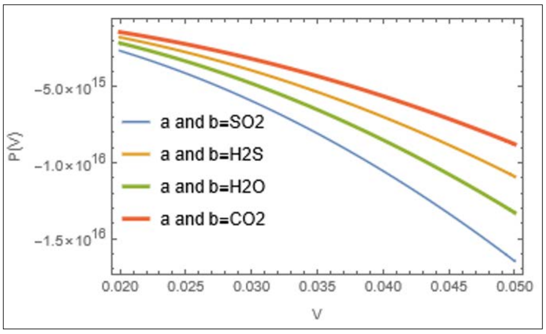

Figure 4: Dependence of Pressure on Volume with Varying Virial Coefficients

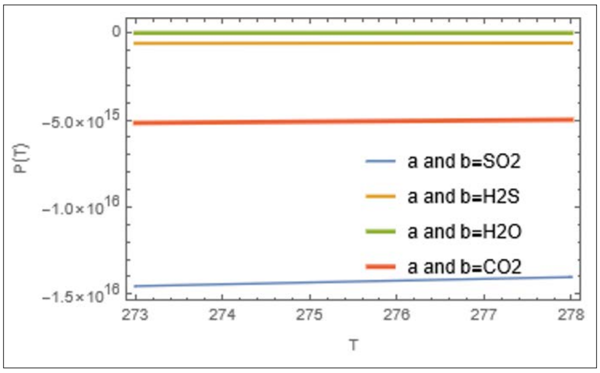

Figure 5: Dependence of Pressure on Temperature with Varying Virial Coefficients

Discussion

Table 2 reveals that as the magnetic and orbital quantum number increases, the energy eigenvalues increases but when the nonlinearity parameter is removed, added energy is required. It is also observed that degeneracy is completely removed and this is consistent with the study of [16] and [18]. Figure 1 shows that increase in the nonlinear parameter got the potential function enhanced initially and tends to a saturation point. Figure 2 depict the relationship between the temperature and the free energy which shows that variation of the virial coefficients of the polyatomic molecules, enhanced the free energy that is proportional to the volume of the molecules. Although, the free energy of H_2O is greater than CO_2 with saturation reached in the free energy of H_2S and SO_2. Figure 3 shows that the additive property of entropy was observed as the varying virial coefficients of the molecules are introduced. It is however shown that the increase is in the order of $SO_2 > H_2S > H_2O > CO_2$. This suggest that of the four polyatomic molecules under consideration, the entropy of SO_2 is the highest while that of CO_2 is the least. Figure 4 reveals that as the virial coefficients of the molecules vary, the pressure is enhanced and the trend showed that $CO_2 > H_2S > H_2O > SO_2$. A complete reversal of the molecules effect on the entropy. Figure 5 shows the relationship between the pressure and the temperature as the virial coefficients of the polyatomic molecules vary, the pressure is improved but the trend is $H_2O > H_2S > CO_2 > SO_2$ which is consistent with the work of [33].

Conclusion

The study determined the energy eigenvalues of a nonlinear oscillator and used it to describe some select thermodynamic functions of four dominant environmentally impactful polyatomic molecules. A fluctuation of their behaviour on the P–T and P–V diagrams, illustrated the differences in the virial coefficients and their improved or enhanced properties over diatomic molecules.

References

1. Milanovic V, Ikovic Z (1999) Generation of isospectral combinations of the potential and the effective-mass variations by supersymmetric quantum mechanics. J Phys A Math Gen 32: 7001-7016.
2. Kumar R, Fakir C (2012) Series solutions to the N-dimensional radial Schrödinger equation for the quark–antiquark interaction potential. Phys Scr 85: 055008.
3. Roy B and Roy P (2002) A Lie algebraic approach to effective mass Schrödinger equations. J Phys A Math Gen 35: 3961.
4. Ghatak A, Lokanathan S (2002) Quantum mechanics (Theory and applications (Fourth Edition) Macmillan India Limited, New Delhi. https://books.google.com.nf/books?id=GC0vc22hlxEC&printsec=copyright#v=onepage&q&f=false.
5. Yuce C, Kilic A, Coruh A (2006) Inverted oscillator. Phys Scr 74: 114.
6. Monteiro MR, Rodrigues LMCS, Wulck S (1996) Quantum Algebraic Nature of the Phonon Spectrum in 4He. Phys Rev Lett 76: 1089.
7. Marin JL, Cruz CA (1988) On the harmonic oscillator inside an infinite potential well. Am J Phys 56: 1134-1136.
8. Mirhashem S, Ferrell RA (1991) Variational approach to the stationary states of the double-oscillator potential. Am J Phys 59: 425-433.
9. Gettys WE, Graben HW (1975) Quantum solution for the biharmonic oscillator. Am J Phys 43: 626-629.
10. Skal L, Cizek J, Weniger EJ, Zamastil A (1999) Large-order behavior of the convergent perturbation theory for anharmonic oscillators. Phys Rev A 59: 102.
11. Guth A, Pi SY (1985) Quantum mechanics of the scalar field in the new inflationary universe. Phis Rev D 32: 1899-1920.
12. Boyanovsky D, Holman R, Lee DS, Silva JP (1995) A note on thermal activation. Nucl Phys B 441: 595-608.
13. Miller PA, Sarkar S (1998) Fingerprints of classical instability in open quantum dynamics.Phys Rev E 58: 4217.
14. Gaioli FH, GarciaAlvarez ET, Castagnino MA (1997) The Gamow vectors and the Schwinger effect. Int J Theor Phys 36: 2371-2389.
15. Ngiangia AT, Harry ST (2016) Inverted Isotropic Harmonic Oscillator with a δ −function Potential J NAMP 36: 239-244.
16. Ngangia AT, Amadi O, Lawson TWJ (2023) thermodynamic properties of inverted isotropic oscillator with delta function potential in a magnetic field. J NAMP 65: 103-110.
17. Cahn SB, Nadgorny (2004) A guide to Physics Problems Part 1. Mechanics, Relativity and Electrodynamics. Kluwer Academic Publishers 63: 861.
18. Ikot AN, Lutfuoglu BC, Ngwueke MI, Udoh ME, Zare S, et al. (2016) Klein-Gordon equation particles in exponential-type molecule potentials and their thermodynamic properties in D dimensions. Eur Phys J Plus 131: 419.
19. Ikot AN, Chukwuocha EO, Onyeaju MC, Onate CA, Ita BI (2018) Thermodynamics properties of diatomic molecules with general molecular potential. Pramana J Phys 90: 22.
20. Ikot AN, Okorie US, Sever R, Rampho GJ (2019) Eigensolution, expectation values and thermodynamic properties of the screened Kratzer potential. Eur Phys J Plus 134: 386.
21. Okorie US, Ibekwe EE, Ikot AN, Onyeaju MC, Chukwuocha EO (2018) Thermodynamic Properties of the Modified Yukawa Potential. J Korean Phys Soc 73: 1211-1218.
22. Wang J, Jia CS, Li CJ, Peng XL, Zhang LH, et al. (2019) Thermodynamic Properties for Carbon Dioxide. ACS Omega 4: 19193-19198.
23. Yahya WA, Oyewumi KJ (2016) Thermodynamic properties and approximate solutions of the ℓ-state Pöschl–Teller-type potential. J Assoc of Arab Univ for Basic and Appl Sci 21: 53-58.
24. Lumb Sonia, Lumb Shalini, Prasad V (2013) Response of a Harmonically Confined System to Short Laser Pulses. Quantum Matter 2: 314-320.
25. Lumb Sonia, Lumb Shalini, Prasad V Sugny D (2018) Effect of electric field on thermodynamic properties of confined molecules. J Chemical Physics 510: 37-46.
26. Lumb S, Lumb S, Prasad V (2017) Rovibrational spectra of bounded diatomic molecules. Int. J Quant. Chem 117: e25339.
27. Gupta BD (2004) Mathematical Physics: Third Edition

(Viskas Publishing House PVT LTD). https://books.google.co.in/books/about/Mathematical_Physics_3Rd_Revised_Edition.html?id=W4ZOKWWGjDYC&redir_esc=y.
28. Zettili N (2001) Quantum Mechanics: Concepts and applications. http://www.mmmut.ac.in/News_content/02110tpnews_11232020.pdf
29. Hassanabadi H, Yazarloo BH, Ikot AN, Zarrinkamar S (2014) Exact Solution of KleinGordon with the Pöschl-Teller Double-Ring-Shaped Coulomb Potential. Acta Phys Pol A 126: 1-5.
30. Patil SH (2006) Harmonic oscillator with a δ-function potential. Eur J Phys 27: 899-913.
31. Tiwari S, Tandon P, Uttam KN (2012) Thermodynamical Quantities of Chalcogenide Dimers (O2, S2, Se2, and Te2) from Spectroscopic Data. Journal of Spectroscopy 2013: 1-7.
32. Oliveira RRS, AraujoFilho AA, Lima FCE, Maluf RV, Almeida CAS (2018) Thermodynamic properties of an Aharonov-Bohm quantum ring. Eur Phys J Plus 134: 495.
33. Chandra S (2008) A Textbook of Statistical Mechanics. https://www.amazon.in/Textbook-Statistical-Mechanics-S-Chandra-ebook/dp/B07NDCNYMZ.
34. Atkins P and Paula J D (2006) Physical Chemistry 8th Edition. http://www.rnlkwc.ac.in/pdf/study-material/chemistry/Peter_Atkins__Julio_de_Paula__Physical_Chemistry__1_.pdf