

УДК 539.12.01

APPLICATIONS OF CLASSICAL AND QUANTUM ALGEBRAS TO MOLECULAR THERMODYNAMICS

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Lie-algebraic and quantum-algebraic techniques are used in the analysis of thermodynamic properties of molecules and solids. The local anharmonic effects are described by a Morse-like potential associated with the $su(2)$ algebra. A vibrational high-temperature partition function and the related thermodynamic potentials are derived in terms of the parameters of the model. Quantum analogues of anharmonic bosons, q bosons, are introduced and used to describe anharmonic properties of molecules and solids. It is shown that the quantum deformation parameter is related to the fixed number of anharmonic bosons and the shape of the anharmonic potential. A new algebraic realization of the q bosons, for the case of q being a root of unity, is given. This realization represents the symmetry of a linear lattice with periodic boundary conditions.

INTRODUCTION

The algebraic approach has been developed as an alternative to *ab initio* and Dunham-like approaches to describe the molecular vibrational degrees of freedom [1,2]. The algebraic approach provides the energy as an analytic function of the quantum numbers. The Hamiltonian is written as an algebraic operator using the appropriate Lie algebras. The technical advantage of the algebraic approach is the comparative ease of the algebraic operations. Equally important is the result obtained by comparison with the experiment, that there are generic forms of algebraic Hamiltonians and that entire class of molecules can be described by common Hamiltonian where only the parameters are different for different molecules. In its initial stage of development [3–6], the algebraic approach has sought to show why and how it provides a framework for the understanding of large-amplitude anharmonic motion. The anharmonicities are introduced by means of dynamical groups that correspond to anharmonic potentials and which constrain the total number of levels to a finite value. The current algebraic models [7–9] combine Lie algebraic techniques, describing the interatomic interactions, with discrete symmetry techniques associated with the local symmetry of the molecules. In the anharmonic oscillator symmetry model [7], the local internal coordinates are given in terms of $u(2)$ algebras. The $u(2)$ interactions correspond to anharmonic coupling of anharmonic oscillators which approximate the interactions between the Morse oscillators.

The algebraic anharmonic model has been developed to analyze molecular vibrational spectra [1–9]. It provides a systematic procedure for studying vibrational excitations in a simple form by describing the stretching and bending modes in a unified scheme based on $u(2)$ algebras which incorporate the anharmonicity at the local level.

The success of the algebraic models in the analysis of molecular vibrational spectra has led to the development of similar models for molecular thermodynamics. Kusnetzov [10] has used an algebraic approach, based on approximation of the classical density of states, to study thermodynamic properties of polyatomic molecules. Angelova and Frank [11–13] have applied the algebraic model [1, 7] to the vibrational high-temperature thermodynamics of diatomic molecules and derived the vibrational partition function and the important thermodynamic functions, such as mean energy and specific heat, in terms of the parameters of the model.

The Morse-like potential, which represents the anharmonicities at the local level, leads to a deformation of the harmonic oscillator algebra. Angelova, Dobrev, and Frank [15] have derived this deformation using quantum analogue of the anharmonic oscillator. We have described the anharmonic vibrations as anharmonic q bosons using first-order of the expansion of a quantum deformation and found relations between the parameters of the algebraic model and the quantum deformation parameter.

The aim of this paper is to review the applications of the classical and quantum algebras to molecular thermodynamics. In Section 1, the framework of the algebraic model is given. The vibrational partition function and the related thermodynamic functions, such as mean energy, specific heat and the mean number of the anharmonic bosons, are discussed in Section 2. The anharmonic q bosons are discussed in Section 3. A q -bosonic deformation of first order is considered and it is shown that the corresponding quantum deformation parameter is related to the shape of the anharmonic potential well and the fixed number of anharmonic bosons. The q bosons at roots of unity, which give rise to a finite-dimensional periodic structure are discussed and their applications to a linear lattice with periodic boundary conditions are given.

1. ALGEBRAIC MODEL

The algebraic model [1] exploits the isomorphism of $su(2)$ algebra and the one-dimensional Morse oscillator. The one-dimensional Morse Hamiltonian can be written in terms of the generators of $su(2)$,

$$\mathcal{H}_M = \frac{A}{4} (\hat{\mathcal{N}}^2 - 4\hat{J}_Z^2) = \frac{A}{2} (\hat{J}_+ \hat{J}_- + \hat{J}_- \hat{J}_+ - \hat{\mathcal{N}}), \quad (1)$$

where A is a constant dependent on the parameters of the Morse potential. The eigenstates, $|\mathcal{N}, v\rangle$,

$$|\mathcal{N}, v\rangle = \sqrt{\frac{(\mathcal{N}-v)!}{\mathcal{N}!v!}} (J_-)^v |\mathcal{N}, 0\rangle \quad (2)$$

correspond to the $u(2) \supset su(2)$ symmetry-adapted basis, where \mathcal{N} is the total number of bosons fixed by the potential shape, and v is the number of quanta in the oscillator, $v = 1, 2, \dots, [\mathcal{N}/2]$. These wave functions can be further symmetry-adapted to the local symmetry of the molecules in a way described for example in [7].

The value of \mathcal{N} is dependent on the depth D and the width d of the Morse potential well [7],

$$\mathcal{N} + 1 = \left(\frac{8\mu D d^2}{\hbar^2} \right)^{1/2}, \quad (3)$$

where μ is the mass of the oscillator. The parameters A and \mathcal{N} are related to the usual harmonic and anharmonic constants ω_e and $x_e\omega_e$ used in spectroscopy [3, 4, 14],

$$\omega_e = A(\mathcal{N} + 1) = \hbar \left(\frac{2D}{\mu d^2} \right)^{1/2}, \quad x_e\omega_e = A = \frac{\hbar^2}{2d^2 D}. \quad (4)$$

The anharmonic effects are described by anharmonic boson operators [1],

$$\hat{b} = \frac{\hat{J}_+}{\sqrt{\mathcal{N}}}, \quad \hat{b}^\dagger = \frac{\hat{J}_-}{\sqrt{\mathcal{N}}}, \quad \hat{v} = \frac{\hat{N}}{2} - \hat{J}_z, \quad (5)$$

where \hat{v} is the Morse phonon operator with an eigenvalue v . The operators satisfy the commutation relations,

$$[\hat{b}, \hat{v}] = \hat{b}, \quad [\hat{b}^\dagger, \hat{v}] = -\hat{b}^\dagger, \quad [\hat{b}, \hat{b}^\dagger] = 1 - \frac{2\hat{v}}{\mathcal{N}}. \quad (6)$$

The harmonic limit is obtained when $\mathcal{N} \rightarrow \infty$, in which case $[\hat{b}, \hat{b}^\dagger] \rightarrow 1$ giving the usual boson commutation relations.

The Morse Hamiltonian can be written in terms of the operators \hat{b} and \hat{b}^\dagger ,

$$H_M \sim \frac{1}{2} (\hat{b}\hat{b}^\dagger + \hat{b}^\dagger\hat{b}) \quad (7)$$

which corresponds to vibrational energies

$$\varepsilon_v = \hbar\omega_0 \left(v + \frac{1}{2} - \frac{v^2}{\mathcal{N}} \right), \quad v = 1, 2, \dots, \left[\frac{\mathcal{N}}{2} \right], \quad (8)$$

where ω_0 is the harmonic oscillator frequency. Thus, the spectrum of the Morse potential leads to a deformation of the harmonic oscillator algebra. A more detailed relationship between the Morse coordinates and momenta and the $su(2)$ generators can be derived through a comparison of their matrix elements [9]. Note that for an infinite potential depth, $\mathcal{N} \rightarrow \infty$, the Morse potential cannot be distinguished from the harmonic potential.

2. THERMODYNAMIC VIBRATIONAL FUNCTIONS

2.1. Vibrational Partition Function. In the anharmonic algebraic approach, the vibrational partition function of a diatomic anharmonic molecule is

$$Z_{\mathcal{N}} = \sum_{v=0}^{[\mathcal{N}/2]} e^{-\beta\varepsilon_v}, \quad (9)$$

where $\beta = 1/k_B T$; the vibrational energies ε_v are given by equation (8), and \mathcal{N} is the fixed total number of anharmonic bosons discussed in the previous section. Introducing new parameters, $\alpha = (\beta\hbar\omega_0)/2$, $\mathcal{N}_0 = [\mathcal{N}/2]$ and $l = \mathcal{N}_0 - v$, the exact value of vibrational partition function can be written as,

$$Z_{\mathcal{N}} = e^{-\alpha} \sum_{l=0}^{\mathcal{N}_0} e^{-(\alpha/\mathcal{N}_0)(\mathcal{N}_0^2 - l^2)}. \quad (10)$$

At high temperatures T , for \mathcal{N}_0 large and α small, the sum can be replaced by the integral,

$$Z_{\mathcal{N}} = \sqrt{\frac{\mathcal{N}_0}{\alpha}} e^{-\alpha(\mathcal{N}_0+1)} \int_0^{\sqrt{\alpha\mathcal{N}_0}} e^{s^2} ds, \quad (11)$$

where $s = \sqrt{(\alpha/\mathcal{N}_0)l}$. This integral can be evaluated exactly in terms of the error function, $\operatorname{erf} i(\sqrt{\alpha\mathcal{N}_0})$ (as defined in [16]),

$$Z_{\mathcal{N}} = \frac{1}{2} \sqrt{\frac{\mathcal{N}_0\pi}{\alpha}} e^{-\alpha(\mathcal{N}_0+1)} \operatorname{erf} i(\sqrt{\alpha\mathcal{N}_0}). \quad (12)$$

Equation (12) represents the high-temperature value of the vibrational partition function in the Morse-like spectrum. The partition function is expressed in terms of the parameters of the algebraic model \mathcal{N}_0 and α . When $\mathcal{N}_0 \rightarrow \infty$, the harmonic limit of the model is obtained,

$$Z_{\infty} \sim \frac{\mathcal{N}_0 e^{-\alpha}}{2\alpha\mathcal{N}_0 - 1} \sim \frac{e^{-\alpha}}{2\alpha} = \frac{T}{\Theta} e^{-(\Theta/2T)} \quad (13)$$

which coincides with the harmonic vibrational partition function of a diatomic molecule at high temperatures. Here, $\Theta = \hbar\omega_0/k_B$, is the usual characteristic vibrational temperature of the molecule and the model parameter $\alpha = \Theta/2T$. The expression for the partition function (12) can be further generalized for polyatomic molecules.

Using the values of the harmonic and anharmonic constants [14] for the zero lines of the diatomic molecule $^1\text{H}^{35}\text{Cl}$ and the equations (3) and (4), we obtain the total number of anharmonic bosons, fixed by the shape of the Morse potential, $\mathcal{N} = 56$, and the total number of quanta in the oscillator, $\mathcal{N}_0 = 28$. The characteristic vibrational temperature of the molecule is $\Theta = 4300$ K.

Substituting the value of $\mathcal{N}_0 = 28$ in equation (12) we can calculate the partition function, Z_{56} , for the molecule

$^1\text{H}^{35}\text{Cl}$ as a function of the parameter α . The anharmonic effects are essential at the high temperatures $T \geq \Theta$, i. e., $\alpha \leq 0.5$. The graph on Fig. 1 represents the partition function Z_{56} given by equation (12) for the values of the parameter α between 0 and 0.5 (solid line). The exact partition function from equation (10) is given for comparison (dashed line). It is clear, that the integral approximation is in a very good agreement with the exact representation and does not change the value and appearance of the partition function.

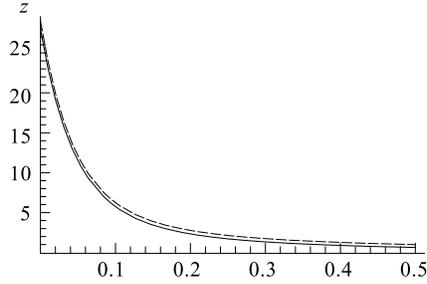


Fig. 1. Vibrational partition function Z_{56} as a function of α

2.2. Mean Vibrational Energy. The mean vibrational energy is given by

$$U_{\mathcal{N}} = -\frac{\partial}{\partial \beta} \ln Z_{\mathcal{N}} = -\frac{\hbar\omega_0}{2Z_{\mathcal{N}}} \frac{\partial Z_{\mathcal{N}}}{\partial \alpha}. \quad (14)$$

Taking into account that

$$\frac{\partial Z_{\mathcal{N}}}{\partial \alpha} = -\frac{Z_{\mathcal{N}}}{2\alpha} - (\mathcal{N}_0 + 1) Z_{\mathcal{N}} + \frac{\mathcal{N}_0 e^{-\alpha}}{2\alpha}, \quad (15)$$

we obtain the following expression for the mean vibrational energy in terms of the partition function $Z_{\mathcal{N}}$,

$$U_{\mathcal{N}} = \frac{\hbar\omega_0}{2} \left(1 + \mathcal{N}_0 + \frac{1}{2\alpha} - \frac{\mathcal{N}_0 e^{-\alpha}}{2\alpha Z_{\mathcal{N}}} \right). \quad (16)$$

Substituting $Z_{\mathcal{N}}$ with equation (12) gives the following expression for the mean energy, $U_{\mathcal{N}}$, in terms of the parameter α ,

$$U_{\mathcal{N}} = \frac{\hbar\omega_0}{2} \left(1 + \mathcal{N}_0 + \frac{1}{2\alpha} - \sqrt{\frac{\mathcal{N}_0}{\alpha\pi}} \frac{e^{\alpha\mathcal{N}_0}}{\operatorname{erf} i(\sqrt{\alpha\mathcal{N}_0})} \right). \quad (17)$$

The harmonic limit is obtained from equation (16), when $\mathcal{N}_0 \rightarrow \infty$ and $Z_{\mathcal{N}}$ is given by (13),

$$U_{\infty} \sim \frac{\hbar\omega_0}{2} \left(1 + \frac{1}{\alpha} \right) \sim \frac{\hbar\omega_0}{2} + k_B T. \quad (18)$$

This is the classical mean energy of a diatomic molecule at very high temperatures.

2.3. Specific Heat. The vibrational part of the specific heat is,

$$C_{\mathcal{N}} = \frac{\partial U_{\mathcal{N}}}{\partial T} = -\frac{\hbar\omega_0}{2k_B T^2} \frac{\partial U_{\mathcal{N}}}{\partial \alpha}. \quad (19)$$

Substituting $U_{\mathcal{N}}$ with equation (16) and using equation (15), we obtain

$$C_{\mathcal{N}} = \frac{k_B}{2} + \frac{k_B \mathcal{N}_0 e^{-\alpha}}{2Z_{\mathcal{N}}} \left(\alpha \mathcal{N}_0 - \frac{1}{2} - \frac{\mathcal{N}_0 e^{-\alpha}}{2Z_{\mathcal{N}}} \right). \quad (20)$$

The equation (20) represents the vibrational specific heat in the algebraic model in terms of the partition function $Z_{\mathcal{N}}$. Substituting $Z_{\mathcal{N}}$ with (12) in the equation (20), we obtain the dependence of the specific heat $C_{\mathcal{N}}$ on the parameters of the model α and \mathcal{N}_0 ,

$$C_{\mathcal{N}} = \frac{k_B}{2} + k_B \sqrt{\frac{\alpha \mathcal{N}_0}{\pi}} \frac{e^{\alpha \mathcal{N}_0}}{\operatorname{erf} i(\sqrt{\alpha \mathcal{N}_0})} \left(\alpha \mathcal{N}_0 - \frac{1}{2} - \sqrt{\frac{\alpha \mathcal{N}_0}{\pi}} \frac{e^{\alpha \mathcal{N}_0}}{\operatorname{erf} i(\sqrt{\alpha \mathcal{N}_0})} \right). \quad (21)$$

When $\mathcal{N}_0 \rightarrow \infty$, the harmonic limit of the model gives the vibrational specific heat of a diatomic molecule at very high temperatures,

$$C_{\infty} \sim k_B. \quad (22)$$

2.4. Mean Number of Anharmonic Bosons. The mean vibrational energy in the anharmonic model can be written in terms of mean number $\langle \nu_{\mathcal{N}} \rangle$ of anharmonic quanta, each with energy $\hbar\omega_0$,

$$U_{\mathcal{N}} = \hbar\omega_0 \left(\langle \nu_{\mathcal{N}} \rangle + \frac{1}{2} \right). \quad (23)$$

Substituting $U_{\mathcal{N}}$ by equation (16), we obtain $\langle \nu_{\mathcal{N}} \rangle$ in terms of the partition function $Z_{\mathcal{N}}$,

$$\langle \nu_{\mathcal{N}} \rangle = \frac{\mathcal{N}_0}{2} + \frac{1}{4\alpha} - \frac{\mathcal{N}_0 e^{-\alpha}}{4\alpha Z_{\mathcal{N}}}. \quad (24)$$

Using the expression (12) in equation (24), we obtain the high-temperature value,

$$\langle \nu_{\mathcal{N}} \rangle = \frac{\mathcal{N}_0}{2} + \frac{1}{4\alpha} - \sqrt{\frac{\mathcal{N}_0}{4\pi\alpha}} \frac{e^{\alpha\mathcal{N}_0}}{\operatorname{erf} i(\sqrt{\alpha\mathcal{N}_0})}. \quad (25)$$

The harmonic limit is obtained from equation (24) when $\mathcal{N}_0 \rightarrow \infty$ and $Z_{\mathcal{N}}$ is given by the expression (13),

$$\langle \nu_{\infty} \rangle \sim \frac{k_B T}{\hbar\omega_0}. \quad (26)$$

The graph of the function $\langle \nu_{56} \rangle$ for the molecule ${}^1\text{H}^{35}\text{Cl}$ is given on Fig. 2 (solid line). The harmonic limit $\langle \nu_{\infty} \rangle$ is given for comparison (dashed line).

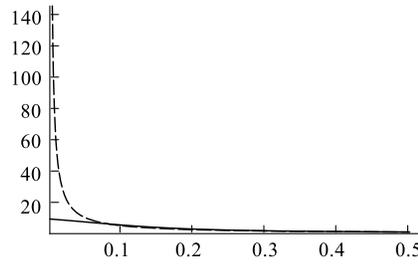


Fig. 2. Mean number of anharmonic bosons ν_{56} as a function of α

3. APPLICATIONS OF q BOSONS

3.1. Anharmonic q Bosons. We have shown in [15] that the anharmonic bosons b, b^\dagger from equations (5) can be obtained as an approximation of the q bosons [17–19]. The q bosons, enter the Heisenberg–Weyl q -algebra HW_q by the following commutation relations:

$$[a, a^\dagger] = q^{\hat{n}}, \quad [\hat{n}, a] = -a, \quad [\hat{n}, a^\dagger] = a^\dagger, \quad (27)$$

where the deformation parameter q is in general a complex number. When $q = 1$, the boson commutation relations of the harmonic oscillator are recovered.

A possible Hamiltonian for the system (27) is:

$$H = \frac{1}{2}(aa^\dagger + a^\dagger a) = \frac{1}{2}\mathcal{C} + \frac{1}{2}\frac{q^{\hat{n}+1} + q^{\hat{n}} - 2}{q - 1}, \quad (28)$$

where the Casimir operator \mathcal{C} can be written in the form:

$$\mathcal{C} = aa^\dagger + a^\dagger a - \frac{q^{\hat{n}+1} + q^{\hat{n}} - 2}{q - 1} \quad (29)$$

and satisfies the commutation relations

$$[\mathcal{C}, a] = [\mathcal{C}, a^\dagger] = [\mathcal{C}, \hat{n}] = 0. \quad (30)$$

As shown in [15], the anharmonic bosons (6) can be obtained from the q bosons (27) for real values of the deformation q close to 1, $q < 1$, using an expansion of first order of q in terms of a parameter p , $p \equiv 1/(1 - q)$,

$$q^{\hat{n}} = 1 - \frac{\hat{n}}{p}, \quad (31)$$

where $1/p \ll 1$. If we now substitute the approximation for $q^{\hat{n}}$ from equation (31) in the commutation relations (27) and identify the parameter p with $\mathcal{N}/2$, \hat{n} with \hat{v} and the creation and annihilation operators a, a^\dagger , with b, b^\dagger , respectively, we recover the $su(2)$ anharmonic relations (6).

For $q \leq 1$, the case of harmonic and anharmonic vibrations in molecules and solids is retrieved. The form (6) of the $su(2)$ commutation relations can be considered as a deformation of the usual (harmonic oscillator) commutation relations, with a quantum deformation parameter $p = \mathcal{N}/2$.

This gives a physical interpretation of the quantum deformation. The quantum deformation parameter p is the fixed number \mathcal{N}_0 of the anharmonic bosons in the oscillator. Using the relation between the fixed number of anharmonic bosons \mathcal{N} and the characteristics of the Morse potential (3), we can conclude that the quantum deformation parameter is also determined by the depth, the width and in general the shape of the Morse potential well. For the molecule ${}^1\text{H}^{35}\text{Cl}$, $p = 28$ and $q = 27/28$. Substituting $\mathcal{N}_0 = p$ in the expressions (12), (17), (21) and (25), we obtain the thermodynamic properties of diatomic molecules in terms of the deformation parameter p .

The case $q > 1$ is also very interesting and is related to Bose–Einstein condensation and superfluidity [23–25].

3.2. q Bosons at Roots of Unity. In [15], we have presented a new algebraic realization of the q bosons, for the case of q being a root of unity, $q^N \equiv 1$ (integer $N > 1$), which corresponds to a periodic structure described by a finite-dimensional representation. Note that the integer N in this section is not related in general to the total number of bosons \mathcal{N} in the previous sections.

We consider the operator $K \equiv q^{\hat{n}}$ with commutation relations,

$$[a, a^\dagger] = K, \quad K a = q^{-1} a K, \quad K a^\dagger = q a^\dagger K. \quad (32)$$

$| \rangle$ is the vacuum state which is annihilated by the operators lowering the boson number and is an eigenvector of the number operator:

$$a |0\rangle = 0, \quad K | \rangle = q^\mu |0\rangle, \quad (\text{or } \hat{n} | \rangle = \mu |0\rangle), \quad (33)$$

where μ in the generic case is an arbitrary complex number. The states of the system are built by applying the operators raising the boson number:

$$|k\rangle \equiv (a^\dagger)^k |0\rangle. \quad (34)$$

The action of the algebra on the basis $|k\rangle$ is:

$$K|k\rangle = q^{\mu+k}|k\rangle, \quad a|k\rangle = q^\mu \frac{q^k - 1}{q - 1} |k - 1\rangle, \quad a^\dagger|k\rangle = |k + 1\rangle. \quad (35)$$

The representation space, V_μ , is infinite-dimensional for a generic deformation parameter.

Now, let q is a nontrivial root of unity, i. e., $q^N = 1$ for integer $N > 1$. In this case we have:

$$a|N\rangle = q^\mu \frac{q^N - 1}{q - 1} |N - 1\rangle = 0. \quad (36)$$

All states $|k\rangle$ with $k \geq N$ form an infinite-dimensional invariant subspace, I_μ . We then obtain a finite-dimensional representation space, which is the factor-space, $F_\mu = V_\mu / I_\mu$, with dimension N . Considering the action of the algebra on the states, $|k + mN\rangle$, for fixed $k < N$ and for all non-negative integer m , we have shown in [15] that the structure is periodic, i. e., the action of the algebra on all states $|k + mN\rangle$ (for fixed k) coincides. Thus, it is sufficient to consider the states $|k\rangle$ with $k < N$. Let us denote these identified states by $\widetilde{|k\rangle}$, $k = 0, \dots, N - 1$. They form a finite-dimensional representation space \widetilde{F}_μ with dimension N . The action of the algebra on these states is:

$$\begin{aligned} K\widetilde{|k\rangle} &= q^\mu \widetilde{|k\rangle}, \quad a\widetilde{|k\rangle} = q^\mu \frac{q^k - 1}{q - 1} \widetilde{|k - 1\rangle}, \quad a^\dagger\widetilde{|k\rangle} = \widetilde{|k + 1\rangle}, \quad k < N - 1, \\ a^\dagger\widetilde{|N - 1\rangle} &= \widetilde{|0\rangle}, \quad \widetilde{|0\rangle} \equiv \widetilde{|N\rangle}. \end{aligned} \quad (37)$$

This represents a finite-dimensional system, where the boson number lowering operator acts in the usual way (in particular, it annihilates the vacuum state $|\widetilde{0}\rangle$), but the boson raising operator acts cyclicly. It has a nonzero action on all states and the vacuum state may be obtained not only by the action of the lowering operator but also by the action of the raising operator producing a jump from $|\widetilde{N-1}\rangle$ to $|\widetilde{0}\rangle$. One realization of this operator is a two-level system, obtained for $N = 2$ (equivalent to $q = -1$, fermions). For $N > 2$, systems with finite number of levels and population inversion are illustrations of possible action of these operators. In [26] the objects «quons» ($q^N = 1$) are introduced as interpolating between fermions ($N = 2$) and bosons ($N \rightarrow \infty$).

For large N periodicity of the type described above appears in crystals. We have shown that it represents the periodic boundary conditions, first proposed by Born and von Kármán [27]. The periodic boundary conditions [28] are imposed on the translational symmetry, which strictly speaking is a property of an infinite crystalline lattice, to allow its use for finite crystals. The periodic boundary conditions determine the number of the allowed wave-vector states in the Brillouin zone model and imply additional selection rules on certain frequencies.

For the classic example of a linear lattice of identical particles with periodic boundary conditions, the equilibrium positions of the particles are given by $\mathbf{t}_n = n\mathbf{t}$, $n = 0, 1, \dots, N-1$, and the periodic boundary condition requires $\mathbf{t}_N \equiv \mathbf{t}_0 \equiv \mathbf{0}$, where \mathbf{t} is the vector of primitive translations and N is a large positive number.

The symmetry operations of the linear lattice form a cyclic finite group of order N with a generator, the primitive translation $\{E|\mathbf{t}\}$. Here, the Seitz notation is used to represent a translation and E is the identity, $E \equiv \{E|0\}$.

The n th element of the group is

$$\{E|\mathbf{t}\}^n = \{E|\mathbf{t}_n\}, \quad n = 1, 2, \dots, N-1. \quad (38)$$

The product of two elements of the group is an element of the group

$$\{E|\mathbf{t}_m\}\{E|\mathbf{t}_n\} = \{E|\mathbf{t}_{m+n}\}, \quad m, n = 1, 2, \dots, N-1, \quad (39)$$

where $m+n \equiv (m+n) \pmod{N}$. The identity is

$$\{E|\mathbf{t}\}^N \equiv \{E|\mathbf{t}_0\} \equiv \{E|\mathbf{0}\}. \quad (40)$$

Using the action (37) of the operator a^\dagger on the states $|\widetilde{k}\rangle$, we have shown that the raising operator a^\dagger is isomorphic to the generator $\{E|\mathbf{t}\}$.

Thus, the symmetry group of the lattice with periodic boundary conditions is isomorphic to the finite cyclic group of order N with a generator, the operator a^\dagger . This group can be used with the other symmetry operations of one-dimensional crystalline or polymer Hamiltonians. The boundary conditions can be generalized for the three-dimensional case by introducing raising operators for each dimension.

CONCLUSION

In this paper, we have used the classical and quantum algebras to study the vibrational thermodynamic properties of molecules and solids. The algebraic approach is applied to those thermodynamic properties of diatomic molecules which at high temperatures strongly depend on the anharmonic effects. The vibrational thermodynamic functions, such as partition function, mean energy and specific heat, are derived in terms of the parameters of the algebraic model and their properties are discussed.

The application of a q algebra to physical problems is often lacking an appropriate interpretation for the deformation parameters and often applications are carried out where generalization to q -deformed versions of well-known models are made with no simple interpretation. We have shown that the $1/p$ approximation leads to the $su(2)$ algebra and to an interpretation of p in terms of the Morse potential anharmonicity. We have found a physical interpretation of the quantum deformation, showing that the deformation parameter is related to the fixed number of anharmonic bosons and the shape of the Morse potential. We have found that all vibrational thermodynamic properties (e. g., mean energy, specific heat, mean number of anharmonic bosons) of the molecules depend on the corresponding quantum deformation parameter.

A new application of the HW_q algebra when q is a root of unity is discussed, which gives a periodic structure described by a finite-dimensional representation. The raising operator belonging to this structure generates a group isomorphic to the symmetry group of a linear lattice with periodic boundary conditions. The latter may provide a useful framework for the deformation of crystalline or polymer Hamiltonians.

Acknowledgements. The results in this work are obtained in collaboration with A. Frank and V. Dobrev. The author would like to thank the Organizing Committee of the IX International Conference on Symmetry Methods in Physics for inviting her to give a plenary talk.

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