Algebraic Models and Quantum Deformations in Molecular Thermodynamics

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Abstract. Lie-algebraic and quantum-algebraic techniques are used in the analysis of thermodynamic properties of molecules and solids at high temperatures. In the framework of the algebraic models, the local anharmonic effects are described by a Morse-like potential, associated with the $SU(2)$ algebra. The vibrational high-temperature properties, such as mean energy and specific heat, are studied in terms of the parameters of the algebraic models. The concept of a critical temperature associated with the anharmonic vibrations is introduced. $q$-bosons are applied to molecular thermodynamics. A quantum deformation, associated with the model is discussed and its effect on the thermodynamic properties is studied.

1. Introduction/ Algebraic Model

The algebraic models have been successfully used in molecular physics and have led to new understanding of the interactions in complex molecules [1, 2]. The algebraic models exploit the isomorphism between the $SU(2)$ algebra and the one-dimensional Morse oscillator. The $SU(2)$ models [1]-[8] combine Lie algebraic techniques, describing the interatomic interactions, with discrete symmetry techniques associated with the local symmetry of the molecules. The anharmonic effects in the molecule are described by boson operators written in terms of the generators of $SU(2)$ [1],

\[
\hat{b} = \frac{\hat{J}_+}{\sqrt{N}}, \quad \hat{b}^\dagger = \frac{\hat{J}_-}{\sqrt{N}}, \quad \hat{\nu} = \frac{\hat{N}}{2} - \hat{J}_z
\]

where $\hat{N}$ is the boson number operator and $N$ is the total number of bosons fixed by the potential shape. The value of $\hat{N}$ is dependent on the depth $D$, the width $d$ of the Morse potential well and the reduced mass $\mu$ of the oscillator [1, 6],

\[
N + 1 = \left( \frac{8\mu Dd^2}{\hbar^2} \right)^{\frac{1}{2}}.
\]

The operators $\hat{b}$ and $\hat{b}^\dagger$ satisfy the commutation relations,

\[
\left[ \hat{b}, \hat{\nu} \right] = \hat{b}, \quad \left[ \hat{b}^\dagger, \hat{\nu} \right] = -\hat{b}^\dagger, \quad \left[ \hat{b}, \hat{b}^\dagger \right] = 1 - \frac{2\hat{\nu}}{N}
\]

The harmonic limit is obtained when $N \to \infty$, in which case $\left[ \hat{b}, \hat{b}^\dagger \right] \to 1$ giving the usual boson commutation relations. The one-dimensional Morse Hamiltonian can be written in terms of the anharmonic boson operators $\hat{b}$ and $\hat{b}^\dagger$,

\[
H_M \sim \frac{1}{2} \left( \hat{b} \hat{b}^\dagger + \hat{b}^\dagger \hat{b} \right)
\]
which corresponds to vibrational energies

\[ \varepsilon_v = \hbar \omega_0 \left( v + \frac{1}{2} - \frac{v^2}{N} \right), \quad v = 1, 2, \ldots, \left\lfloor \frac{N}{2} \right\rfloor \]  

where \( \omega_0 \) is the harmonic oscillator frequency. The Morse phonon operator \( \hat{v} \) has an eigenvalue \( v \) which gives the number of quanta in the oscillator. For the diatomic molecule \(^1\)H\(^{35}\)Cl, the total number of anharmonic bosons, fixed by the shape of the Morse potential, is \( N = 56 \) and the total number of quanta in the oscillator is 28.

The algebraic anharmonic model has been developed to analyze molecular vibrational spectra [1]-[8]. 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 SU(2) algebras. The spectrum of the Morse potential leads to a deformation of the harmonic oscillator algebra. For an infinite potential depth, \( N \to \infty \), the Morse potential cannot be distinguished from the harmonic potential. This deformation of the harmonic oscillator algebra has been derived using a quantum analogue for the anharmonic oscillator [10], where the anharmonic vibrations are described as anharmonic \( q \)-bosons. The first steps in applying the algebraic approach to molecular thermodynamics are made in [13, 12] where the partition function and the basic thermodynamic functions for diatomic molecules are derived in terms of the parameters of the model. In this paper we will discuss further application of the algebraic approach to the vibrational high-temperature thermodynamics of diatomic molecules and the impact of the quantum deformations onto basic thermodynamic functions. We will introduce the idea of critical temperature and consider a possible physical interpretation of a \( q \)-bosonic deformation.

2. Applications of the algebraic approach to vibrational thermodynamics

The algebraic approach is applied to molecular thermodynamics by deriving the appropriate partition functions. Having the partition function in terms of the parameter of the model, the derivation of the thermodynamic potentials such as mean energy, specific heat, mean number of bosons, is a straightforward procedure. Here, we will summarise and discuss the results for diatomic molecules.

At high temperatures the vibrational partition function in the Morse-like spectrum is [13, 12],

\[ Z_N = \frac{1}{2} \sqrt{\frac{N_0 \pi}{\alpha}} e^{-\alpha (N_0 + 1)} \text{erf} \left( \sqrt{\alpha N_0} \right). \]  

where \( \alpha = \frac{\hbar \omega_0}{2k_B T} \) and \( N_0 = \left\lfloor \frac{N}{2} \right\rfloor \) are the parameters of the algebraic model and \( \text{erf} \left( \sqrt{\alpha N_0} \right) \) is the error function as defined in [11]. The dependance on the temperature \( T \) is given by the parameter \( \alpha \). When \( N_0 \to \infty \), the harmonic limit of the model is obtained, \( Z_\infty \sim e^{-\alpha / 2\alpha} \), which is precisely the harmonic vibrational partition function of a diatomic molecule at high temperatures. The expression for the partition function (6) can be generalised to polyatomic molecules, by combining the present results with the use of a local-mode model where each interatomic potential is of the Morse form [5].

The mean vibrational energy is \( U_N = -\frac{\hbar \omega_0}{2Z_N} \frac{\partial Z_N}{\partial \alpha} \). For high temperatures, substituting \( Z_N \) with (6) we obtain,

\[ U_N = \frac{\hbar \omega_0}{2} \left( 1 + N_0 + \frac{1}{2\alpha} - \sqrt{\frac{N_0}{\alpha \pi}} \frac{e^{\alpha N_0}}{\text{erf} \left( \sqrt{\alpha N_0} \right)} \right). \]  

(7)
When $N_0 \to \infty$, the classical mean energy of a diatomic molecule at high temperatures is obtained.

The vibrational part of the specific heat is $C_N = \frac{\partial U_N}{\partial T}$, which gives the following dependence of $C_N$ on the parameter $\alpha$ at high-temperatures,

$$C_N = \frac{k_B}{2} + k_B \sqrt{\frac{\alpha N_0}{\pi}} \frac{e^{\alpha N_0}}{\text{erf} \left( \sqrt{\alpha N_0} \right)} \left( \alpha N_0 - \frac{1}{2} - \sqrt{\frac{\alpha N_0}{\pi}} \frac{e^{\alpha N_0}}{\text{erf} \left( \sqrt{\alpha N_0} \right)} \right)$$ (8)

When $N_0 \to \infty$, the harmonic limit of the model gives $C_\infty \sim k_B$.

Figure 1 represents the vibrational specific heat, $C_{56}/k_B$, for the molecule $^1\text{H}^{35}\text{Cl}$ as a function of the parameter $\alpha$ (solid line). It includes the contributions of the harmonic and anharmonic vibrations. The anharmonic contributions are strongest for $0 < \alpha < 0.5$, where $\alpha = 0.5$ corresponds to the characteristic vibrational temperature 4300K of this molecule. The harmonic vibrational specific heat of a diatomic molecule (see e.g. [9]), $C_{\text{harm}}/k_B$, is also given (double-dashed line) as well as the harmonic limit, $C_\infty/k_B$ (dashed line). The graph shows an anomaly in the vibrational specific heat: it has a maximum for a value of $\alpha_C$ which corresponds to a temperature $T_C$. We call this temperature a critical temperature for the model and the corresponding parameter $\alpha_C$ a critical parameter. The anomaly of the specific heat is a result of the finite number $N$ of bosons in the system. The numerical solution gives a root, $\alpha_C N_0 = 6.133$. Thus, the critical value $\alpha_C$ decreases as the number of fixed anharmonic bosons increases. The anomaly of the specific heat disappears as $N_0 \to \infty$, $\alpha_C \to 0$.

For the molecule $^1\text{H}^{35}\text{Cl}$, $N_0 = 28$, $\alpha_C = 0.219$ which gives $T_C = 9815K$. The comparison of $\Delta \varepsilon = \varepsilon_{N_0} - \varepsilon_0$ with the dissociation energy of the molecule shows that

![Figure 1](image-url)
$\Delta \varepsilon > DE$ for all temperatures. At $T_C$ when all bosons in the system could be excited, some of the molecules might have started to dissociate while others may still be in stable molecular states. Our model, in its present form, does not account for the effects of the dissociation. In addition, this simple version of the model does not yet include the contributions of the translational and rotational degrees of freedom which at temperatures close to $T_C$ may be substantial. The critical temperature $T_C$ can be considered as a temperature above which the model is no longer valid in its current form and other effects take place.

3. Quantum deformations

In [10], we have shown that the anharmonic bosons $b, b^\dagger$ from equation (9) can be obtained as an approximation of $q$-bosons (see e.g. [14]). The $q$-bosons are defined by the following commutation relations:

\[ [a, a^\dagger] = q \hat{n}, \quad [\hat{n}, a] = -a, \quad [\hat{n}, a^\dagger] = a^\dagger \]  

(9)

where the deformation parameter $q$ is in general a complex number [14]. As shown in [10], the anharmonic commutation relations (3) can be recovered for real values of the deformation $q$ close to 1, $q < 1$, and an expansion of $q$ in terms of the first-order of a parameter $p$, $p \equiv 1/(1 - q)$,

\[ q \hat{n} = 1 - \frac{\hat{n}}{p} \]  

(10)

The expansion 10 will be referred to as a linear deformation $q$. Substituting the approximation for $q^{\hat{n}}$ from equation (10) in the commutation relations (9) and identifying the parameter $p$ with $N/2$, $\hat{n}$ with $\hat{v}$ and the creation and annihilation operators $a, a^\dagger$, with $b, b^\dagger$ respectively, the $SU(2)$ anharmonic commutation relations (3) are recovered.

The $SU(2)$ commutation relations (3) can be considered as a deformation of the harmonic oscillator commutation relations, with a deformation parameter $p = N/2$. This gives a possible physical realization for the quantum deformation obtained in [10]: the quantum deformation parameter $p$ is the fixed number $N_0$ of the anharmonic bosons in the oscillator. Using the relation between the fixed number of anharmonic bosons $N$ and the characteristics of the Morse potential (2) we arrive to the conclusion that the quantum deformation is also determined by the depth, the width and in general the shape of the Morse potential well. For the molecule $^3$H$^{35}$Cl, $p = 28$ which gives $q = 27/28$.

Using the linear deformation $q$, we can write the Morse Hamiltonian (4) and the vibrational energies (5) in terms of the quantum deformation parameter $p$. Further, substituting $N_0 = p$ in the expressions for the partition function (6), mean energy (7) and specific heat (8), we obtain the basic thermodynamic properties of the diatomic molecules as functions of the deformation parameter $p$. The critical parameter $\alpha_C$ (critical temperature $T_C$) is inversely proportional to the quantum deformation parameter. For large values of $p$, $(q \to 1)$, the classic harmonic case is restored. Work is in progress on expansions of $q$ in terms of higher orders of the deformation parameter $p$ and the effect of the higher order parameter on the Hamiltonian, vibrational energies and the related thermodynamic properties.

References