Algebraic Approach to Molecular Thermodynamics

Maia Angelova† and A. Frank‡

†School of Computing and Mathematics
University of Northumbria, Newcastle upon Tyne, UK GB-NE1 8ST
‡Instituto de Ciencias Nucleares and Centro de Ciencias Físicas,
UNAM, A.P. 70-543, Mexico, D.F., 04510 Mexico.

October 24, 2018

Abstract

An algebraic model based on Lie-algebraic and discrete symmetry techniques is applied to the analysis of thermodynamic vibrational properties of molecules. The local anharmonic effects are described by a Morse-like potential and the corresponding anharmonic bosons are associated with the $SU(2)$ algebra. A vibrational high-temperature partition function and the related thermodynamic functions are derived and studied in terms of the parameters of the model. The idea of a critical temperature is introduced in relation with the specific heat. A physical interpretation of a quantum deformation associated with the model is given.

1 Introduction

The algebraic approach has been used successfully in molecular physics and has led to new insights into the nature of complex many body systems [1, 2, 3]. In the framework of the algebraic method, the Hamiltonian of a given system is written as an algebraic operator using the generators of the appropriate Lie algebra. All other operations in the model are algebraic operators, unlike the differential operators in standard wave mechanics. The technical advantage of the algebraic approach is the comparative ease of algebraic operations. Equally important, however, is the conclusion derived from comparison with experiment, that there are generic forms of symmetry-adapted algebraic Hamiltonians and that entire classes of molecules can be described by generic Hamiltonians where the parameters vary in a systematic fashion for different molecules. In its initial stage of development [4-14], 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. Later on, the SU(2) models [15]-[20] combined Lie algebraic techniques, describing the interatomic interactions, with discrete symmetry techniques associated with the local symmetry of the molecules. Recently, a clear-cut connection could be established between the Morse-SU(2) approach and the traditional potential energy surface methods [12, 13, 14].

The algebraic model [1, 2] exploits the isomorphism between the SU(2) algebra and the one-dimensional Morse oscillator,

\[ \mathcal{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + D(1 - e^{-\frac{x}{d}})^2, \]  

where \( D \) is the depth of the potential well, \( d \) is its width, \( x \) is the displacement from the equilibrium and \( \mu \) is the mass of the oscillator. The one-dimensional Morse Hamiltonian can be written in terms of the generators of SU(2),

\[ \mathcal{H}_M = \frac{A}{4} (\hat{N}^2 - 4\hat{J}_z^2) = \frac{A}{2} (\hat{J}_+ \hat{J}_- + \hat{J}_- \hat{J}_+ - \hat{N}), \]  

where \( A \) is a constant dependent on the parameters of the Morse potential. The eigenstates, \( |N, v\rangle \), correspond to the \( U(2) \supset SU(2) \) symmetry-adapted basis, where \( N \) is the total number of bosons fixed by the potential shape, and \( v \) is the number of quanta in the oscillator, \( v = 1, 2, \ldots, \lfloor \frac{N}{2} \rfloor \).

The value of \( N \) is dependent on the depth \( D \) and the width \( d \) of the Morse potential well [1, 2, 15],

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

The parameters \( A \) and \( N \) are related to the usual harmonic and anharmonic constants \( \omega_c \) and \( x_c \omega_c \) used in spectroscopy [4, 5, 21],

\[ \omega_c = A(N + 1) = \hbar \left( \frac{2D}{\mu d^2} \right)^{\frac{1}{2}}, \]  

\[ x_c \omega_c = A = \frac{\hbar^2}{2d^2D}. \]
The anharmonic effects can be described by anharmonic boson operators \( \hat{b} = \frac{\hat{J}_-}{\sqrt{N}} \), \( \hat{b}^\dagger = \frac{\hat{J}_-}{\sqrt{N}} \), \( \hat{v} = \frac{\hat{N}}{2} - \hat{J}_z \) (5)

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

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

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

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

\[
H_M \sim \frac{1}{2} \left( \hat{b}^\dagger \hat{b} + \hat{b} \hat{b}^\dagger \right)
\] (7)

which corresponds to vibrational energies

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

where \( \omega_0 \) 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 \([12]\) and through the derivation of raising and lowering operators for the Morse potential \([13]\). Note that for an infinite potential depth, \( N \to \infty \), the Morse potential cannot be distinguished from the harmonic potential. To summarize, the algebraic anharmonic model has been developed to analyze molecular vibrational spectra \([2]-[20]\). 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 which incorporate the anharmonicity at the local level.

The deformation of the harmonic oscillator algebra, associated with the Morse potential, has also been derived using a quantum analogue for the anharmonic oscillator \([22]\). We have described the anharmonic vibrations as anharmonic \( q \)-bosons using a first-order expansion of the quantum deformation. We have thus proposed a physical interpretation of quantum deformation in the framework of the algebraic model.
The aim of this paper is to apply the algebraic approach to the vibrational high-temperature thermodynamics of diatomic molecules and to obtain the basic thermodynamic functions in terms of the parameters of the algebraic model. This paper can be considered as a first step in the direction of incorporating anharmonicity and the finite number of bound vibrational states into the thermodynamic description of molecular systems. The rest of the paper is organized as follows. In Section 2, we derive a Morse-like vibrational partition function for high temperature and study its properties. In Section 3, the vibrational partition function is used to derive the basic thermodynamic functions, such as the mean vibrational energy, specific heat and free energy. The idea of critical temperature is introduced in relation with the specific heat. In Section 4, the mean number of anharmonic bosons is obtained. The concept of maximal temperature of the anharmonic vibrations is discussed. The \( q \)-bosonic deformation of first order is considered. It is shown that this quantum deformation is related to the shape of the anharmonic potential well and the fixed number of anharmonic bosons. The results are applied to the diatomic molecule H\(^1\)Cl\(^{35}\). These results must be combined with the translational and rotational thermodynamic functions in order to compare with experiment, as discussed in reference [21].

### 2 Vibrational Partition Function

The vibrational partition function of a diatomic anharmonic molecule is

\[
Z_N = \sum_{v=0}^{[N/2]} e^{-\beta \varepsilon_v}
\]

where \( \beta = 1/k_B T \), the vibrational energies \( \varepsilon_v \) are given by equation (8) and \( N \) is the fixed total number of anharmonic bosons. Introducing new parameters, \( \alpha = \frac{\hbar \omega_0}{2} \), \( N_0 = \left\lfloor \frac{N}{2} \right\rfloor \) and \( l = N_0 - v \), the exact value of vibrational partition function can be written as,

\[
Z_N = e^{-\alpha} \sum_{l=0}^{N_0} e^{-\frac{\alpha}{N_0} (N_0^2 - l^2)}.
\]

At high temperatures \( T \), for \( N_0 \) large and \( \alpha < 1 \), the sum can be replaced by the integral,

\[
Z_N = \left\lfloor \frac{N_0}{\alpha} \right\rfloor e^{-\alpha(N_0+1)} \int_0^{\sqrt{\alpha \cdot N_0}} e^{s^2} ds
\]
where \( s = \sqrt{\frac{N_0}{N_0}} \). This integral can be evaluated exactly in terms of the error function, \( \text{erf}(\sqrt{\alpha N_0}) \) (as defined in [24]),

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

Equation (12) represents the high-temperature value of the vibrational partition function in the Morse-like spectrum [24, 25, 26]. The partition function is expressed in terms of the parameters of the algebraic model \( N_0 \) and \( \alpha \). The dependence on the temperature is given by \( \alpha \),

\[
\alpha = \frac{\hbar \omega_0}{2k_B T} = \frac{\Theta}{2T}.
\]
where \( \Theta = \frac{\hbar \omega_0}{k_B} \) is the usual characteristic vibrational temperature of the molecule. The contributions of the anharmonic vibrations are essential in the high-temperature region for \( T \geq \Theta \), where \( T = \Theta \) corresponds to \( \alpha = 0.5 \).

When \( N_0 \rightarrow \infty \), the harmonic limit of the model is obtained,

\[
Z_\infty \sim \frac{N_0 e^{-\alpha}}{2\alpha N_0 - 1} \sim \frac{e^{-\alpha}}{2\alpha} \quad \Theta e^{-\frac{T}{\Theta}}
\]

which coincides with the harmonic vibrational partition function of a diatomic molecule at high temperatures. The expression for the partition function (12) 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 [14].

The diatomic molecule \( \text{H}^1\text{Cl}^{35} \) is considered as an example. Using the values of \( x_e \) and \( \omega_e \) [21] for the zero lines of this molecule and equations (3) and (4) we obtain the total number of anharmonic bosons, fixed by the shape of the Morse potential, \( N = 56 \), and the total number of quanta in the oscillator, \( N_0 = 28 \). The depth of the Morse potential is \( D = 5.32 \text{eV} \), and the width is \( d = 0.57 \times 10^{-10} \text{m} \). The characteristic vibrational temperature of the molecule is \( \Theta = 4300 \text{K} \) [27].

Substituting the value of \( N_0 = 28 \) in equation (12) we can calculate the partition function, \( Z_{56} \), for the molecule \( \text{H}^1\text{Cl}^{35} \) as a function of the parameter \( \alpha \). The graph on Figure 1 represents the partition function \( Z_{56} \) given by equation (12) for the values of the parameter \( \alpha \) between 0 and 1 (solid line). The exact partition function from equation (10) is given for comparison (double-dashed line). It is clear that in the region \( 0 < \alpha \leq 1 \), 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. The comparison between the function \( Z_{56} \) (solid line) and the harmonic limit \( Z_\infty \) (dashed line) is given on Figure 2. The finiteness of \( Z_{56} \) in the high \( T \) limit is linked, of course, with the finite number of states in the Morse potential. A more realistic description in the high \( T \) region requires the introduction of the continuum states of the Morse potential [28].

Having the partition function \( Z_N \) in terms of the parameters of the algebraic model, we are now in position to derive the corresponding thermodynamic functions. An algebraic approach has been used in [29] to study the thermodynamic properties of molecules. However, the partition function in [28] uses an approximation of the classical density of states, while we have derived an explicit function in terms of the parameters of the algebraic model.
3 Thermodynamic Vibrational Functions

3.1 Mean Vibrational Energy

The mean vibrational energy is given by

\[ U_N = -\frac{\partial}{\partial \beta} \ln Z_N = -\frac{\hbar \omega_0}{2Z_N} \frac{\partial Z_N}{\partial \alpha}. \] (15)

Taking into account that

\[ \frac{\partial Z_N}{\partial \alpha} = -\frac{Z_N}{2\alpha} \left( N_0 + 1 \right) Z_N + \frac{N_0 e^{-\alpha}}{2\alpha}, \] (16)
we obtain the following expression for the mean vibrational energy in terms of the partition function $Z_N$,

$$U_N = \frac{\hbar \omega_0}{2} \left(1 + N_0 + \frac{1}{2\alpha} - \frac{N_0 e^{-\alpha}}{2\alpha Z_N}\right).$$  \hspace{1cm} (17)

Substituting $Z_N$ with equation (12) gives the following expression for the mean energy, $U_N$, in terms of the parameter $\alpha$,

$$U_N = \frac{\hbar \omega_0}{2} \left(1 + N_0 + \frac{1}{2\alpha} - \sqrt{\frac{N_0}{\alpha \pi}} \frac{e^{\alpha N_0}}{\text{erfi} \left(\sqrt{\alpha N_0}\right)}\right).$$  \hspace{1cm} (18)

The harmonic limit is obtained from equation (17), when $N_0 \to \infty$ and $Z_N$ is given by (14),

$$U_\infty \sim \frac{\hbar \omega_0}{2} \left(1 + \frac{1}{\alpha}\right) = \frac{\hbar \omega_0}{2} + k_B T.$$  \hspace{1cm} (19)

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

The graph on Figure 3 represents the mean vibrational energy, $U_{56}/\hbar \omega_0$, of the molecule $\text{H}^1\text{Cl}^{35}$ for values of $\alpha$, $0 < \alpha \leq 1$. The high-temperature
region corresponds to $\alpha \leq 0.5$. For comparison the graph of the harmonic limit $U_\infty$ (dashed line) for $N_0 \to \infty$ is also given. As already mentioned in the previous section, the finiteness of $U_N$ in the high $T$ limit is a result of the finite number of states in the Morse potential.

### 3.2 Specific Heat

The vibrational part of the specific heat is,

$$C_N = \frac{\partial U_N}{\partial T} = -\frac{\hbar \omega_0}{2k_B T^2} \frac{\partial U_N}{\partial \alpha}. \quad (20)$$

Substituting $U_N$ with equation (17) and using equation (16), we obtain

$$C_N = k_B \left( \frac{N_0 e^{-\alpha}}{2Z_N} \right) \left( \alpha N_0 - \frac{1}{2} - \frac{N_0 e^{-\alpha}}{2Z_N} \right) \quad (21)$$

This equation represents the vibrational specific heat in the algebraic model in terms of the partition function $Z_N$. Substituting $Z_N$ in equation (21) with the expression (12), we obtain the dependence of the specific heat $C_N$ on the parameter $\alpha$,

$$C_N = k_B \left( \frac{N_0 e^{-\alpha}}{2Z_N} \right) \left( \alpha N_0 - \frac{1}{2} - \frac{N_0 e^{-\alpha}}{2Z_N} \right) \quad (22)$$

It is clear from the relation (22) that all anharmonic contributions to the vibrational part of the specific heat depend on the parameter $\alpha$ and hence on the temperature $T$. When $N_0 \to \infty$, the harmonic limit of the model gives the vibrational specific heat of a diatomic molecule at high temperatures,

$$C_\infty \sim k_B. \quad (23)$$

Figure 4 represents the dependence of the vibrational specific heat, $C_{56}/k_B$, on the parameter $\alpha$, $0 < \alpha < 1$, for the molecule H$^1$Cl$^{35}$ (solid line). The graph of the harmonic vibrational specific heat of a diatomic molecule (see e.g. [21, 27]), $C_{\text{harm}}/k_B$, is also given (double-dashed line) as well as the harmonic limit, $C_\infty/k_B$ (dashed line), where

$$C_{\text{harm}} = k_B 4\alpha^2 \frac{e^{2\alpha}}{(e^{2\alpha} - 1)^2}. \quad (24)$$
Figure 4: Vibrational specific heat $C_{56}/k_B$ (solid line) as a function of $\alpha$. For comparison, $C_{\text{harm}}/k_B$ (double-dashed line) and $C_{\infty}/k_B$ (dashed line) are also given.

The effects of the anharmonicity are strongest for values of $\alpha \leq 0.5$, where $\alpha = 0.5$ corresponds to the characteristic vibrational temperature $\Theta$ ($\Theta = 4300\text{K}$ for $\text{H}^1\text{C}^{35}$).

The graph shows an anomaly in the dependence of the vibrational specific heat on the parameter $\alpha$ (temperature $T$). The specific heat has a maximum for a value of $\alpha = \alpha_C$ which corresponds to a temperature, $T = T_C$. We shall call this temperature the critical temperature and the corresponding parameter $\alpha_C$ the critical parameter. The anomaly of the specific heat is again a result of the finite number of states in the system. The specific heat increases with the temperature as more anharmonic bosons are excited. The maximum is reached when the latter occupy the energy state with $v = N_0 = 28$. (Note that the shape of the curve is similar to the shape
associated with the Schottky anomaly of the specific heat of a two-level system \[27\]).

The maximal vibrational energy is given by the equation (8) by substituting \(v\) with its maximal value \(N_0\). Thus,

\[
\varepsilon_{\text{max}} = \hbar \omega_0 \left( \frac{N_0}{2} + \frac{1}{2} \right).
\]

while the minimum energy is,

\[
\varepsilon_0 = \frac{1}{2} \hbar \omega_0 .
\]

Thus,

\[
\Delta \varepsilon = \varepsilon_{\text{max}} - \varepsilon_0 = \frac{1}{2} \hbar \omega_0 N_0
\]

This gives \(\Delta \varepsilon = 14 \hbar \omega_0 = 5.1877 \text{eV}\) for the molecule \(\text{H}_1\text{Cl}^{35}\). Comparing \(\Delta \varepsilon\) with the dissociation energy of the molecule \(DE = 4.4703 \text{eV} \[30\], we can conclude that at the temperature \(T = T_C\), \(\Delta \varepsilon > DE\) and 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, e.g., dissociation \[28\].

We have studied the behaviour of the specific heat with respect to the combined parameter \(\alpha N_0\). The graph of \(C_N/k_B\) as a function of \(\alpha N_0\) shows a similar anomaly (Fig. 5).

Solving numerically the equation \(\frac{\partial C_N}{\partial (\alpha N_0)} = 0\) with respect to the combined parameter \(\alpha N_0\), we have found a root, \(\alpha_C N_0 = 6.1332642\). Thus, the critical value \(\alpha_C\) decreases as the number of fixed anharmonic bosons increases,

\[
\alpha_C = \frac{6.1332642}{N_0}
\]

When \(N_0 \to \infty\), \(\alpha_C \to 0\) and the anomaly of the specific heat disappears, which is in agreement with the harmonic limit of the model.

For the molecule \(\text{H}_1\text{C}^{35}, N_0 = 28\) which gives a value for \(\alpha_C = 0.219\). Thus, the value of the critical temperature for this molecule is \(T_C = 9815 \text{K}\).
3.3 Free Energy

The free vibrational energy in terms of the partition function $Z_N$ is given by

$$ F_N = -\frac{1}{\beta} \ln Z_N $$

Substituting $Z_N$ with equation (12) gives the free vibrational energy in the algebraic model at high temperatures,

$$ F_N = \hbar \omega_0 \left[ \frac{1}{\alpha} \ln 2 + \frac{1}{2\alpha} \ln \left( \frac{\alpha}{\pi N_0} \right) + (N_0 + 1) - \frac{1}{\alpha} \ln \left( \text{erf}(\alpha N_0) \right) \right] $$

When $N_0 \rightarrow \infty$, using expression (14) in equation (29), we obtain the classical harmonic result for the free vibrational energy at very high temperatures,

$$ F_\infty \sim k_B T \ln 2. $$

4 Anharmonic Bosons
4.1 Mean Number of Anharmonic Bosons

The mean vibrational energy in the anharmonic model can be written in terms of mean number \( \langle \nu_N \rangle \) of anharmonic quanta, each with energy \( \hbar \omega_0 \),

\[
U_N = \hbar \omega_0 \left( \langle \nu_N \rangle + \frac{1}{2} \right) \quad (32)
\]

Substituting \( U_N \) by equation (17), we obtain \( \langle \nu_N \rangle \) in terms of the partition function \( Z_N \),

\[
\langle \nu_N \rangle = \frac{N_0}{2} + \frac{1}{4\alpha} - \frac{N_0 e^{-\alpha}}{4\alpha Z_N}. \quad (33)
\]

Using the expression (12) in equation (33), we obtain the high-temperature value,

\[
\langle \nu_N \rangle = \frac{N_0}{2} + \frac{1}{4\alpha} - \sqrt{\frac{N_0}{4\pi \alpha}} \frac{e^{\alpha N_0}}{\text{erf}(\sqrt{\alpha N_0})}. \quad (34)
\]

The harmonic limit is obtained from equation (34) when \( N_0 \to \infty \) and \( Z_N \) is given by the expression (14),

\[
\langle \nu_\infty \rangle \sim \frac{k_B T}{\hbar \omega_0}. \quad (35)
\]

The graph of the function \( \langle \nu_{56} \rangle \) for the molecule \( H^1C_{35} \) is given on Figure 3. The dashed line represents the harmonic limit \( \langle \nu_\infty \rangle \). The same reasons apply to the finiteness of \( \langle \nu_{56} \rangle \) as those discussed for the partition function in Section 2.

4.2 Maximal Temperature

The maximal vibrational energy (25) is obtained when \( \nu = N_0 \). The maximal mean vibrational energy is given by equation (32) when \( \nu_N = \langle \nu_N \rangle_{\text{max}} \),

\[
U_{\text{max}} = \hbar \omega_0 (\langle \nu_N \rangle_{\text{max}} + \frac{1}{2}) \quad . \quad (36)
\]

Comparing the equations (25) and (36) gives the maximal mean number of anharmonic bosons,

\[
\langle \nu_N \rangle_{\text{max}} = \frac{N_0}{2} \quad (37)
\]
Figure 6: Mean number of anharmonic bosons $\nu_{56}$ as a function of $\alpha$.

(which according to the graph on Figure 6 is for a value $\alpha \to 0$). Substituting $\langle \nu_N \rangle$ by equation (34) and simplifying gives,

$$2 \sqrt{\frac{\alpha N_0}{\pi}} e^{\alpha N_0} = \text{erf} i \left( \sqrt{\alpha N_0} \right)$$

(38)

The numerical solution of the above equation has a root $\alpha N_0 \to 0$. As $N_0$ is a fixed number, this solution leads to $\alpha \to 0$. In terms of the temperature, we obtain $T_{\text{max}} \to \infty$. The result shows that in practice the system does not reach a maximal temperature, which shows the need of incorporating the continuum into the partition function (3).

4.3 Quantum Anharmonic Bosons

In [22], we have shown that the anharmonic bosons $b, b^\dagger$ from Section 1 can be obtained as an approximation of $q$-bosons [31, 32, 33]. The $q$-bosons
are defined by the following commutation relations:

\[ [a, a^\dagger] = q^\hat{n}, \quad [\hat{n}, a] = -a, \quad [\hat{n}, a^\dagger] = a^\dagger \] (39)

where the deformation parameter \( q \) is in general a complex number \[32\]. As shown in \[22\], the anharmonic commutation relations (6) can be recovered for real values of the deformation \( q \) close to 1, \( q < 1 \), and a linear expansion of \( q \) in terms of a parameter \( p \), \( p \equiv 1/(1 - q) \),

\[ q^\hat{n} = 1 - \frac{\hat{n}}{p}. \] (40)

If we now substitute the approximation for \( q^\hat{n} \) from equation (40) in the commutation relations (39) and identify 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, we recover the \( SU(2) \) anharmonic relations (6).

The form (6) of the \( SU(2) \) commutation relations can be considered as a deformation of the usual (harmonic oscillator) commutation relations, with a deformation parameter \( p = N/2 \). This gives a possible physical realization for the quantum deformation obtained in \[22\]: 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 (3) 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 \( \text{H}^1\text{C}^{35} \), \( p = 28 \) which gives \( q = 27/28 \).

Now, substituting \( N_0 = p \) in the expressions for the partition function (12), mean energy (18), specific heat (22), free energy (30) and mean number of anharmonic bosons (33), we obtain the thermodynamic properties of diatomic molecules in terms of the deformation parameter \( p \). Equation (28) gives the relation between the quantum deformation parameter and the critical parameter \( \alpha_C \) (critical temperature \( T_C \)). For large values of \( p \), \( (q \rightarrow 1) \), the classic harmonic case is restored.

5 Conclusion

We have studied the vibrational thermodynamic properties of diatomic molecules which at high temperature may strongly depend on its anharmonicity. We have derived and studied the vibrational partition function and the related thermodynamic functions, such as mean vibrational energy, specific heat and mean number of anharmonic bosons, in terms of the parameters of the
model. We have also shown that it is possible to interpret these results in terms of a quantum deformation, related to the shape of the Morse potential, and which is associated with the fixed total number of anharmonic bosons, so that the thermodynamic properties of diatomic molecules depend on the corresponding quantum deformation parameter. We believe that this paper constitutes a first step in the description of thermodynamical properties of diatomic molecules which in principle can be simply generalized to polyatomic molecules. We are currently studying the introduction of the continuum into the description, in order to take into consideration the transition to dissociation [28].

6 Acknowledgements

Maia Angelova thanks Martin Levy, Alan Jones, Derek Gardiner and Jean-Pierre Gazeau for useful discussions. This work was supported in part by Conacyt project 32 397-E.

References

[1] F. Iachello and A. Arima, The Interacting Boson Model (CUP 1987).
[2] A. Frank A and P. Van Isacker, Algebraic Methods in Molecular and Nuclear Structure Physics (John Wiley 1994).
[3] F. Iachello and R. Levine, Algebraic Theory of Molecules (OUP 1995).
[4] F. Iachello, Chem. Phys. Lett. 78 (1981) 581.
[5] F. Iachello and R.D. Levine, J. Chem. Phys. 77 (1982) 3046.
[6] O.S. van Roosmalen, F. Iachello, R.D. Levine and A.E.Dieperink, J. Chem Phys. 79 (1983) 2512.
[7] O.S. van Roosmalen, I. Benjamin and R.D. Levine, J. Chem. Phys. 81 (1984) 5986.
[8] F. Iachello and S. Oss, Phys. Rev. Lett. 66 (1991) 2976.
[9] F. Iachello and S. Oss, Chem. Phys. Lett. 187 (1991) 500.
[10] F. Iachello and S. Oss, Chem. Phys. Lett. 205 (1993) 285.
[11] J. Chem. Phys. 99 (1993) 7337.
[12] A. Frank, R. Lemus, M. Carvajal, C. Jung, E. Ziemniak, J. Chem. Phys. 308 (1999) 91.

[13] M. Carvajal, R. Lemus, A. Frank, C. Jung and E. Ziemniak, Chem. Phys. 260 (2000) 420.

[14] R. Lemus and A. Frank, J. Chem. Phys. 101 (1994) 8321.

[15] A. Frank, R. Lemus, R. Bijker, F. Pérez-Bernal and J.M. Arias, Annals of Physics 252 (1996) 211.

[16] F. Pérez-Bernal and J.M. Arias, A. Frank, R. Lemus and R. Bijker, J. Mol. Spectrosc. 184 (1997) 1.

[17] S. Oss, Adv. Chem. Phys. 43 (1996) 455.

[18] A. Frank, R. Lemus, M. Carvajal, C. Jung and E. Ziemniak, Chem. Phys. Lett. 308 (1999) 91.

[19] R. Lemus and A. Frank, Chem. Phys. Lett. 242 (1999) 25.

[20] R. Lemus and A. Frank, Chem. Phys. Lett. (in press).

[21] G. Herzberg, Molecular Spectra and Molecular Structure, volume II (Van Nostrand 1945).

[22] M. Angelova, V. Dobrev and A. Frank, J Phys A Math. Gen 34 (2001) L503-L509 , preprint cond-mat/0105193.

[23] Handbook of Mathematical Functions, Edited by M. Abramowitz and I.A. Stegun (National Bureau of Standards 1964).

[24] M. Angelova and A. Frank, 'Anharmonic Algebraic Model of Thermodynamic Properties of Diatomic Molecules’, preprint cond-mat/0105554.

[25] M. Angelova and A. Frank, Anharmonic Partition Functions in the Anharmonic Algebraic Model. Abstracts XIII International Congress of Mathematical Physics,(2000) P 20.

[26] M. Angelova and A. Frank, 'Algebraic Model of Molecular Thermodynamics’, proceedings 2nd International Symposium on Quantum Theory and Symmetries, Krakow, July 2001, World Scientific, submitted.

[27] R. Bowley and M. Sánchez, ntroductory Statistical MechanicsClarendon Press (Oxford 1999).
[28] M. Angelova, S.H. Dong and A. Frank (in preparation).

[29] D. Kusnetzov, J. Chem. Phys., 101(1994) 2289.

[30] RC Handbook of chemistry and physics 1997-1998 editor D R Lide (London CRC 1997).

[31] M. Arik and D. D. Coon, J. Math. Phys. 17 (1976) 524.

[32] L. C. Biedenharn, J. Phys. A: Math. Gen. 22, (1989) L873-L878.

[33] A. J. Macfarlane, J. Phys. A: Math. Gen. 22 (1989) 4581-4588.