Anharmonic Algebraic Model of Thermodynamic Properties of Diatomic Molecules

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Abstract

An algebraic model based on Lie-algebraic techniques is applied to the analysis of thermodynamic vibrational properties of diatomic molecules. The local anharmonic effects are described by a Morse-like potential and corresponding anharmonic bosons associated with the \( U(2) \) algebra. A vibrational high temperature partition function and the related thermodynamic functions are derived in terms of the parameters of the model. The thermal expansion operator is defined and obtained using the renormalized frequency of the model.

1. Anharmonic Algebraic Model

Algebraic models have been used very successfully in nuclear physics and have led to new insights into the nature of complex many body systems [1]. Similar methods have been proposed to describe molecular excitations [2,3]. The methods combine Lie algebraic techniques, describing the interatomic interactions, with discrete symmetry techniques associated with the molecules. In the framework of the algebraic model [2], the anharmonic effects of the local interactions are described by substituting the local harmonic potentials by Morse-like potential, associated with the \( U(2) \) algebra. The one-dimensional Morse Hamiltonian is written in terms of the generators of \( U(2) \),

\[
H_M = \frac{A}{4} (\hat{N}^2 - 4\hat{J}^2_Z) = \frac{A}{2}(\hat{J}_+ \hat{J}_- + \hat{J}_- \hat{J}_+) - \hat{N}
\]  

(1)
where $A$ is a constant. 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, $v = 1, 2, \ldots, \left[ \frac{N}{2} \right]$.

The anharmonic effects are described by anharmonic boson operators $[2]$

$$\hat{b} = \frac{\hat{J}_z}{\sqrt{N}}, \quad \hat{b}^\dagger = \frac{\hat{J}_z}{\sqrt{N}}, \quad \hat{v} = \frac{N}{2} - \hat{J}_z$$

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

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

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 Morse Hamiltonian can be written in terms of the operators $\hat{b}$ and $\hat{b}^\dagger$, $H_M \sim \frac{1}{2} \left( \hat{b} \hat{b}^\dagger + \hat{b}^\dagger \hat{b} \right)$

which corresponds to vibrational energies

$$\varepsilon_v = \hbar \omega_0 \left( v + \frac{1}{2} - \frac{v^2}{N} \right).$$

where $\omega_0$ is the harmonic oscillator frequency. The Morse potential spectrum thus 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 $[5]$. Note that for an infinite potential depth, $N \to \infty$, the Morse potential cannot be distinguished from the harmonic potential.

The anharmonic model has been developed to analyze molecular vibrational spectra $[2-8]$. 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 $U(2)$ algebras which incorporate the anharmonicity at the local level.

The aim of this paper is to apply the algebraic approach to the vibrational high-temperature thermodynamics of a diatomic molecule and obtain the basic thermodynamic functions in terms of the parameters of the anharmonic model. These results must be combined with the translational and rotational thermodynamic functions in order to compare with experiment, in a fashion similar to that of reference $[9]$. Here, we concentrate our attention on the derivation of analytic results which will be applied in a subsequent paper $[10]$.

2. Vibrational Partition Function

The vibrational partition function of a diatomic anharmonic molecule is
\[ Z_N = \sum_{v=0}^{[N/2]} e^{-\beta \varepsilon_v} \] (6)

where \( \beta = 1/k_B T \), the vibrational energies \( \varepsilon_v \) are given in equation (5) 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 \( l = \left\lfloor \frac{N}{2} \right\rfloor - v \), the vibrational partition function can be written as,

\[ Z_N = e^{-\alpha N_0} \sum_{l=0}^{N_0} e^{-\frac{\alpha}{N_0}} (N_0^2 - l^2). \] (7)

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

\[ Z_N = \sqrt{\frac{N_0}{\alpha}} e^{-\alpha(N_0+1)} \int_0^{\sqrt{\alpha N_0}} e^s ds \] (8)

where \( s = \sqrt{\frac{\alpha}{N_0}} l \). This integral can be evaluated exactly in terms of the error function, \( \text{erf} i \left( \sqrt{\alpha N_0} \right) \) (see [11]),

\[ Z_N = \frac{1}{2} \sqrt{\frac{N_0 \pi}{\alpha}} e^{-\alpha(N_0+1)} \text{erf} i \left( \sqrt{\alpha N_0} \right). \] (9)

Equation (9) represents the high-temperature value of the vibrational partition function in the Morse-like spectrum. When \( N_0 \to \infty \), \( \alpha N_0 \gg 1 \), the harmonic limit of the model is obtained,

\[ Z_\infty \sim \frac{N_0 e^{-\alpha}}{2\alpha N_0 - 1} \sim \frac{e^{-\alpha}}{2\alpha} \frac{k_B T}{h\omega_0} e^{-\frac{h\omega_0}{2k_B T}}. \] (10)

which coincides with the harmonic vibrational partition function of a diatomic molecule at high temperatures.

Having the partition function \( Z_N \) in terms of the parameters of the algebraic model, we are now in position to derive the basic thermodynamic functions. An algebraic approach has been used in [12] to study the thermodynamic properties of molecules. However, the partition function in [12] 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 which can now be used to compute the high-temperature thermodynamic functions in analytic form.
3. Thermodynamic Vibrational Functions

3.1. Mean Vibrational Energy

The mean vibrational energy is given by

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

(11)

Taking into account that

\[ \frac{\partial Z_N}{\partial \alpha} = -\frac{Z_N}{2\alpha} - (N_0 + 1) Z_N + \frac{N_0 e^{-\alpha}}{2\alpha} \]  

(12)

we obtain the following expression for the mean vibrational energy in terms of the partition function \( Z_N \),

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

(13)

Substituting \( Z_N \) by expression (9) gives,

\[ U_N = \frac{\hbar \omega_0}{2} \left( 1 + N_0 + \frac{1}{2\alpha} - \frac{N_0 e^{-\alpha}}{2\alpha Z_N} \right) \]  

(14)

The harmonic limit is obtained from equation (13), when \( N_0 \to \infty \) and \( Z_N \) is given by (10),

\[ U_\infty \sim \frac{\hbar \omega_0}{2} + k_B T. \]  

(15)

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

3.2. Specific Heat

The vibrational part of the specific heat is,

\[ C_N = \frac{\partial U_N}{\partial T} = -\frac{\hbar \omega_0}{2k_B T^2} \frac{\partial U_N}{\partial \alpha}. \]  

(16)

Substituting \( U_N \) with equation (13) and using (12), we obtain

\[ C_N = \frac{k_B}{2} + \frac{k_B N_0 e^{-\alpha}}{2Z_N} \left( N_0 \alpha - \frac{1}{2} - \frac{N_0 e^{-\alpha}}{2Z_N} \right). \]  

(17)

This represents the vibrational specific heat in the anharmonic model in terms of the partition function \( Z_N \). All anharmonic contributions depend on the temperature. The explicit value is obtained from equation (17) by substituting \( Z_N \) by expression (9).
$N_0 \to \infty$, the harmonic limit of the model gives the vibrational specific heat of a diatomic molecule at very high temperatures,

$$C_\infty \sim k_B.$$  \hfill (18)

3.3. 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 $\hbar \omega_0$,

$$U_N = \hbar \omega_0 \left( \langle \nu_N \rangle + \frac{1}{2} \right)$$  \hfill (19)

Substituting $U_N$ by equation (13), we obtain $\langle \nu_N \rangle$ in terms of the partition function $Z_N$,

$$\langle \nu_N \rangle = \frac{N_0}{2} + \frac{1}{4\alpha} - \frac{N_0 e^{-\alpha}}{4\alpha Z_N}.$$  \hfill (20)

Using expression (9) in equation (20), we obtain the high-temperature value,

$$\langle \nu_N \rangle = \frac{N_0}{2} + \frac{k_B T}{\hbar \omega_0} - \sqrt{\frac{N_0}{\pi}} \left( \frac{k_B T}{\hbar \omega_0} \right)^\frac{3}{2} e^{\frac{N_0}{4\alpha \hbar T}} \frac{N_0}{2} e^{-\frac{1}{2} \left( \sqrt{\frac{\hbar \omega_0 N_0}{2\pi k_B T}} \right)}. $$  \hfill (21)

The harmonic limit is obtained from equation (20) when $N_0 \to \infty$ and $Z_N$ is given by expression (10),

$$\langle \nu_\infty \rangle \sim \frac{k_B T}{\hbar \omega_0}.$$  \hfill (22)

3.4. Free Energy

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

$$F_N = -\frac{1}{\beta} \ln Z_N$$  \hfill (23)

Substituting $Z_N$ with equation (9) gives the free vibrational energy in the algebraic model at high temperatures,

$$F_N = k_B T \ln 2 + k_B T \ln \left( \frac{\hbar \omega_0}{2\pi N_0 k_B T} \right) - \frac{\hbar \omega_0}{2} \left( N_0 + 1 \right) - k_B T \ln \left( \text{erf} \left( \frac{\hbar \omega_0 N_0}{2k_B T} \right) \right). $$  \hfill (24)

Using expression (10) in equation (23), we obtain the classical harmonic result for the free vibrational energy at very high temperatures,

$$F_\infty \sim k_B T \ln 2.$$  \hfill (25)
4. Thermal Expansion

It is well-known that the thermal expansion in a molecule is a result of the local anharmonic effects and cannot be explained by the harmonic models. It depends on the positions of the atoms and their displacement from the equilibrium. As an approximation, we can write the coordinate operator \( \hat{x} \) in terms of the anharmonic operators \( \hat{b} \) and \( \hat{b}^\dagger \) (see also [5]) as

\[
\hat{x} = \sqrt{\frac{\hbar}{2 \mu \omega}} \left( \hat{b} + \hat{b}^\dagger \right)
\]  

(26)

Here, \( \omega \) depends on the number of quanta in the oscillator [4-7],

\[
\omega = \omega_0 \left( \frac{N + 1}{N} - \frac{2\nu}{N} \right)
\]  

(27)

Now, we define the thermal expansion operator,

\[
\hat{X}_N = \sqrt{\frac{\hbar}{2 \mu \omega}} \left( \hat{b} + \hat{b}^\dagger + \frac{\gamma}{N} \right)
\]  

(28)

where \( \frac{\gamma}{N} \) represents the displacement from the equilibrium position. The harmonic limit is obtained when \( N \to \infty \), in which case \( \omega \to \omega_0 \) and \( \frac{\gamma}{N} \to 0 \).

Evaluating the mean value of the operator, \( \hat{X}_N \), between the states \( |N\nu\rangle \) and taking into account (27), we obtain the mean thermal expansion \( X_N \) in terms of the parameters of the anharmonic model,

\[
X_N = \sqrt{\frac{\hbar}{2 \mu \omega_0}} \frac{\gamma}{\sqrt{N(N + 1)}} \left( 1 - \frac{2\nu}{N} \frac{1}{N + 1} \right)^{-\frac{1}{2}}
\]  

(29)

The anharmonic effects are essential at high temperatures \( T \). When \( N \gg \nu \), equation (29) becomes,

\[
X_N \sim \sqrt{\frac{\hbar}{2 \mu \omega_0}} \frac{\gamma}{N} \left( 1 + \frac{\nu}{N} \right)
\]  

(30)

Taking into account the high-temperature value of the mean number of quanta (22),

\[
X_N \sim \sqrt{\frac{\hbar}{2 \mu \omega_0}} \frac{\gamma}{N} \left( 1 + \frac{k_B T}{\hbar \omega_0 N} \right)
\]  

(31)

The thermal expansion of anharmonic diatomic molecule has been obtained in [13], using a Morse-type potential and classical methods. The comparison of equations (29)
and (30)-(31) with the results in [13] at high temperatures shows very good agreement. It also shows that $\gamma_N$ is proportional to the mean separation between the atoms at $T = 0$ and that $N^2$ is proportional to the depth of the potential well, the latter being in agreement with the algebraic model [4-7].

5. Conclusion

We have applied the algebraic model to those thermodynamic properties of diatomic molecule which at high temperature strongly depend on its anharmonicity. We have derived the vibrational partition function and the related thermodynamic functions, such as mean vibrational energy and specific heat, in terms of the parameters of the model. The next step is to consider the rotational excitations of the molecule. The thermal expansion, which is a typical anharmonic effect, has been derived in terms of the parameters of the model and its high-temperature value is in a good agreement with classical anharmonic results. The model can be further applied to the thermodynamics of polyatomic molecules. This and other applications will be discussed elsewhere.

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