

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/253598051>

An accurate closed-form expression for the partition function of Morse oscillators

Article in *Chemical Physics Letters* · May 2007

DOI: 10.1016/j.cplett.2007.03.052

CITATIONS

56

READS

119

1 author:



[M. L. Strekalov](#)

Russian Academy of Sciences

75 PUBLICATIONS **470** CITATIONS

SEE PROFILE

An accurate closed-form expression for the partition function of Morse oscillators

M.L. Strekalov *

Institute of Chemical Kinetics and Combustion, Siberian Branch of Russian Academy of Sciences, 630090 Novosibirsk, Russia

Received 6 February 2007; in final form 12 March 2007

Available online 21 March 2007

Abstract

On the basis of the Poisson summation formula, an explicit expression is proposed to evaluate the vibrational partition function for a mode with either negative or positive anharmonicity. This formula gives numerical values almost identical to exact values over the entire temperature range from zero to infinity. The developed approximation will also be available in numerical calculations of the whole vibrational partition function for polyatomic molecules.

© 2007 Elsevier B.V. All rights reserved.

1. Introduction

Vibrational contribution to various thermodynamic functions of a molecular gas is expressed in terms of a partition function and its first two derivatives with respect to temperature. The partition function can be either calculated by direct method or evaluated by approximate analytical approach, provided that molecular energy levels are known. Calculations of vibrational energy levels and vibrational partition functions for a given potential energy surface are the basic problems in molecular spectroscopy and statistical mechanics. Harmonic vibrational frequencies are obtained by normal mode analysis, while anharmonic ones are calculated by the vibrational self-consistent field method or by second order perturbation theory [1–4]. It has been mentioned more than once that the anharmonicity of molecular vibrations can play an important role in calculations of thermodynamic functions [4].

This raises the question of whether the use of approximate methods for the calculation of partition functions of polyatomic molecules. In most cases the common harmonic approximation is employed for which the energy lev-

els and partition functions are given by simple functions of the normal mode frequencies. Unfortunately, this approximation proves to be very inaccurate at high temperatures. With anharmonic frequencies used in the harmonic approximation, Truhlar and Isaacson [5] have developed a simple approximation that provides much better agreement with more rigorous calculations. Independent anharmonic mode approximation [6] can also lead to considerable errors. The situation reverses when the mode–mode coupling is taken into account by cumulant expansion [7]. In this case one can apply simple analytical expressions derived in the present work to the partition functions of fundamental vibrations. They can be calculated with extremely high accuracy at any temperatures, thus we can focus our attention on errors brought about solely by intermode couplings.

The Morse oscillator is the most simple and realistic anharmonic oscillator model that has found wide application in the description of vibrational motion of diatomic molecules. On the other hand, as a zero-order approximation, vibrational modes of polyatomic molecules may be treated as uncoupled anharmonic ones. They can be described using the Morse oscillators for stretching vibrations, and Pöschl–Teller oscillators for bending ones. The calculated partition functions may be then employed as building blocks to obtain the whole vibrational partition

* Fax: +7 3832 330 73 50.

E-mail address: strekalov@ns.kinetics.nsc.ru

function with allowance for intermode couplings. To correctly estimate the arising errors, the partition functions of uncoupled modes should be calculated as accurately as possible.

Recently [7] a simple analytical formula for the partition function of Morse oscillators has been derived. With cumulant expansion method, the approximation equally suitable within the whole range of temperatures where a molecule exists as a bound system has been obtained. The largest difference did not exceed 8%. This Letter proposes another approach using the Poisson summation formula. This formula seems to be ideally suited for treating the partition functions of many simple statistical-mechanical systems, such as the Morse oscillator and Pöschl–Teller one. Note that for the characteristic value $x_e \approx 0.01$ of anharmonicity constant the newly obtained analytical expression yields the maximum deviation 0.05% at all temperatures from zero to infinity.

2. The case of Morse oscillators

Write the Poisson summation formula as [8]

$$\sum_{n=0}^{\infty} f(n) = \frac{1}{2}f(0) + \sum_{m=-\infty}^{\infty} \int_0^{\infty} f(x) e^{-i2\pi mx} dx \quad (1)$$

Eq. (1) is exact for well-behaved functions f . For a finite sum with the upper bound N , Eq. (1) is no longer valid in this form. An obvious modification of (1) for this case is

$$\sum_{n=0}^N f(n) = \sum_{n=0}^{\infty} f(n) - \sum_{n=0}^{\infty} f(n+N+1) \quad (2)$$

With Eq. (1) in the right-hand side of (2), we immediately get

$$\sum_{n=0}^N f(n) = \frac{1}{2}[f(0) - f(N+1)] + \sum_{m=-\infty}^{\infty} \int_0^{N+1} f(x) e^{-i2\pi mx} dx \quad (3)$$

Let us use the above summation formula for the evaluation of the partition function of Morse oscillators

$$Q(a, b) = \sum_{n=0}^N \exp(an^2 - bn) \quad (4)$$

where $a = x_e \theta$, $b = \theta(1 - x_e)$ and $\theta = \omega/k_B T$. Here ω is the harmonic frequency, x_e is the anharmonicity constant; ω and $k_B T$ are given in cm^{-1} . There are only N vibrational energy levels where

$$N = \left[\frac{1 - x_e}{2x_e} \right] \quad (5)$$

and angular brackets represent the integer part of the number. The partition function is specified relative to the zero point energy. This requires multiplying the partition function by $\exp(-E_0/k_B T)$ where E_0 is the zero point energy.

With Eq. (3), $Q(a, b)$ becomes

$$Q(a, b) = \frac{1}{2}(1 - c_N) + \sum_{m=-\infty}^{\infty} \int_0^{N+1} \exp[(\sqrt{a}x - \gamma)^2 - \gamma^2] dx \quad (6)$$

where

$$c_N = \exp[a(N+1)^2 - b(N+1)] \quad (7)$$

For brevity we introduce the designation

$$\gamma = \frac{b + i2\pi m}{2\sqrt{a}} \quad (8)$$

The integral in the right-hand side of Eq. (6) is expressed in terms of Dawson's integral. So

$$Q(a, b) = \frac{1}{2}(1 - c_N) + \frac{1}{\sqrt{a}} \left[F\left(\frac{b}{2\sqrt{a}}\right) + c_N F\left(\frac{2a(N+1) - b}{2\sqrt{a}}\right) \right] + \frac{2Re}{\sqrt{a}} \sum_{m=1}^{\infty} [F(\gamma) + c_N F(\sqrt{a}(N+1) - \gamma)] \quad (9)$$

where

$$F(x) = e^{-x^2} \int_0^x e^{t^2} dt \quad (10)$$

Here $F(x)$ is Dawson's integral, which is tabulated [9] or can easily be calculated numerically. At small x its behavior is given by the expansion

$$F(x) = x - \frac{2}{3}x^3 + \dots \quad (11)$$

For large x we also write two terms of the asymptotic expansion

$$F(x) = \frac{1}{2x} + \frac{1}{4x^3} + \dots \quad (12)$$

The lowest-order approximation which retains only the term with $m=0$ is recognized as the classical partition function, the terms with $m \neq 0$ give the quantum corrections. Simple estimations show that the argument of the function $F(x)$ is always large for the terms with $m \neq 0$. For this reason one can take into account all quantum corrections in Eq. (9) using Dawson's integral asymptotic expansion. Note that the use of the first term of asymptotic expansion for Dawson's integral is the only approximation necessary for an analytical derivation. Summation of all quantum corrections can be made in the explicit form by the formula

$$\frac{1}{2} + \sum_{m=1}^{\infty} \frac{2x}{x^2 + 4\pi^2 m^2} = -\frac{1}{x} + \frac{1}{1 - e^{-x}} \quad (13)$$

So we have

$$Q(a, b) = \frac{1}{1 - e^{-b}} + \frac{1}{\sqrt{a}} F\left(\frac{b}{2\sqrt{a}}\right) - \frac{1}{b} + Q_N(a, b) \quad (14)$$

where all terms depending on N are collected in the expression

$$Q_N(a, b) = c_N \left[\frac{1}{e^{2a(N+1)-b} - 1} + \frac{1}{\sqrt{a}} F\left(\frac{2a(N+1)-b}{2\sqrt{a}}\right) - \frac{1}{2a(N+1)-b} \right] \quad (15)$$

This is our principal result. Note that Eq. (14) together with (15) is valid for all numerical values of the parameters a and b varying from zero to infinity. At large N the term Q_N tends to zero.

Consider some particular cases following from general formula (14). Let $x_e = 0$, however, the number of the bound states remains finite and equal to N ('truncated' oscillators). In this case, by substituting $a = 0$ and $b = \theta$ into Eq. (14), one obtains

$$Q(0, \theta) = \frac{1 - e^{-\theta(N+1)}}{1 - e^{-\theta}} \quad (16)$$

This is the exact result for the partition function of truncated harmonic oscillators. The concept of truncated oscillators arises when one uses the harmonic approximation for vibrations in a system that dissociates above certain energy. Input Eq. (9) shows that this result can be obtained only when all quantum corrections with $m \neq 0$ are taken into account.

Now consider the high temperature limit when the parameters a and b tend to zero. In view of Eqs. (11) and (12), we find

$$Q(a, b) = N + 1 + \frac{a}{3}(N + 1)^3 - \frac{b}{2}(N + 1)^2 \quad (17)$$

This is the approximate result. The right answer is obtained directly from Eq. (4)

$$Q(a, b) = N + 1 + \frac{a}{6}(N + 1)N(2N + 1) - \frac{b}{2}N(N + 1) \quad (18)$$

As is seen, for large N both equations coincide.

Now examine the low temperature limit when the parameters a and b are very large but $a \ll b$. For clarity we represent them as $a = \theta/(2N + 1)$ and $b = 2Na$, where $\theta \gg 1$. Thus

$$Q(a, b) = 1 + e^{-b} + \frac{2a}{b^3} \quad (19)$$

Eq. (19) holds when $\theta > x_e^{-1} = 2N + 1$. A characteristic feature of this equation is that it involves the power-behaved term that varies proportionally with T^2 . This is due to a very large but finite number of terms in state sum (4).

Finally, let us write the partition function of Morse oscillators with allowance for the zero point energy

$$Q_M = Q[x_e\theta, \theta(1 - x_e)] \exp\left[-\frac{\theta}{2}\left(1 - \frac{x_e}{2}\right)\right], \quad (20)$$

where $Q(a, b)$ is given by Eq. (14). Fig. 1 represents the relative difference between the exact and approximate partition functions versus $\theta = \omega/k_B T$ for different values of the anharmonicity parameter $x_e = (2N + 1)^{-1}$. The relative error is seen to decrease with increasing N (at large N) as $1/N$. For diatomic molecules $x_e \approx 0.01$ (or $N \approx 50$) is the

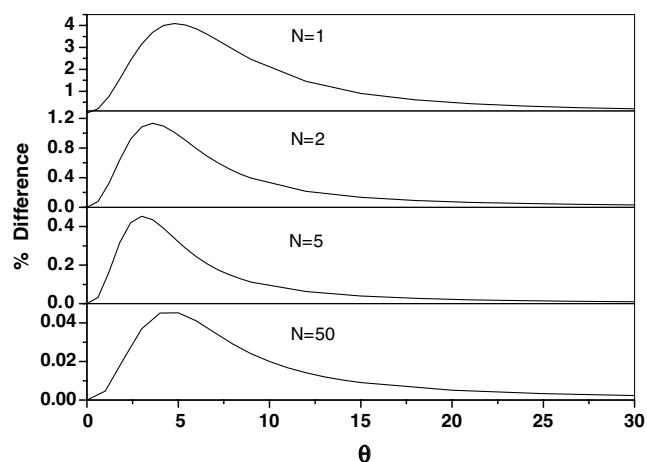


Fig. 1. Percent difference between the exact and approximate partition functions of Morse oscillators is plotted against $\theta = \omega/k_B T$.

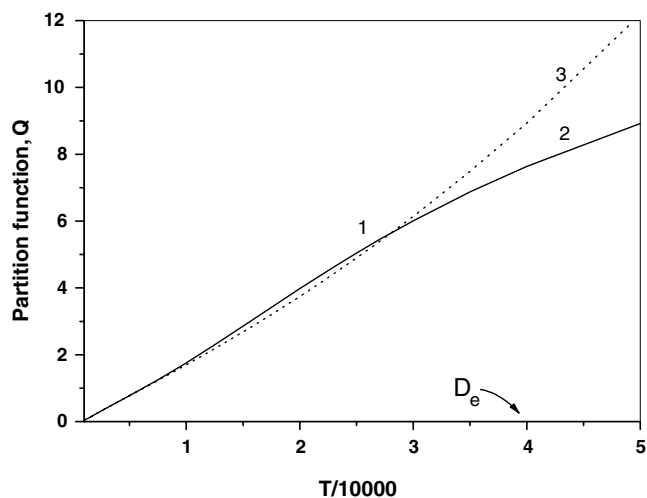


Fig. 2. Vibrational partition functions for H_2 as a function of temperature. (1) and (2) the exact summation and Eq. (20); (3) the first cumulant approximation.

characteristic value. The maximal deviation does not exceed 0.05% in this case. Commonly, anharmonicity constants for polyatomic molecules are considerably less than the above value. As an example, Fig. 2 shows the calculations of vibrational partition function of hydrogen with $\omega = 4401 \text{ cm}^{-1}$ and $x_e\omega = 121 \text{ cm}^{-1}$; $E_N = D_e$ is the dissociation energy. At $x_e = 0.0275$ the Eq. (20) gives numerical values almost identical to exact values with the difference less than 0.13%. The first cumulant approximation, Eq. (19) of Ref. [7], provides a reasonably accurate behavior of Q_M at temperatures below the dissociation energy with the difference less than 7.5%. Nevertheless, this approximation proves to be very inaccurate near the dissociation limit.

3. The case of Pöschl–Teller oscillators

Formally the Pöschl–Teller Hamiltonian with trigonometric type potential [10] has the same eigen-spectrum as the Morse Hamiltonian

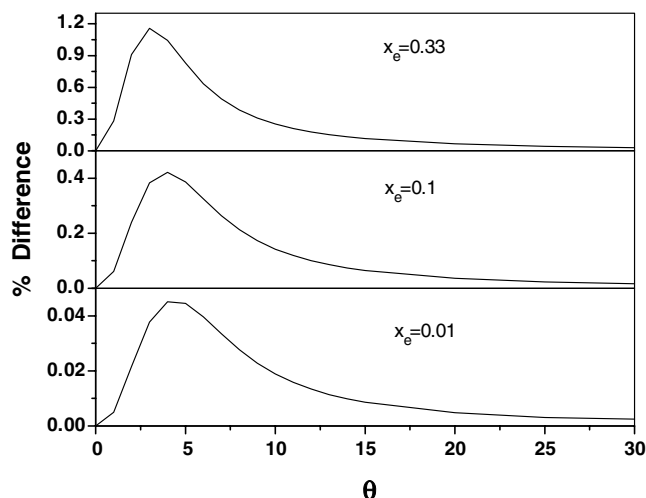


Fig. 3. Percent difference between the exact and approximate partition functions of Pöschl–Teller oscillators is shown versus $\theta = \omega/k_B T$.

$$E_n = E_0 + \omega(1 + x_e)n + x_e \omega n^2 \quad (21)$$

Fundamental difference is that the anharmonicity constant is positive, while the Morse oscillator constant is negative. For this reason bending vibrations (with $x_{ii} > 0$) can be modeled by the Pöschl–Teller oscillators.

The partition function is of the form

$$Q'(a, b) = \sum_{n=0}^{\infty} \exp(-an^2 - bn) \quad (22)$$

In this case $a = x_e \theta$ and $b = \theta(1 + x_e)$. There is no necessity of calculating this partition function again, since the desired result is easily given by general formula (14) with negative a and $N = \infty$. The integral $F(x)$ is transformed into the error function for complex values of the argument [9]

$$\frac{-i}{\sqrt{a}} F\left(\frac{-ib}{2\sqrt{a}}\right) = \frac{1}{2} \sqrt{\frac{\pi}{a}} \exp\left(\frac{b^2}{4a}\right) \operatorname{erfc}\left(\frac{b}{2\sqrt{a}}\right) \quad (23)$$

The error function is tabulated in [9] and is easy to calculate numerically. Using this equality in Eq. (14) and taking into account that $Q_N(a, b) = 0$ at $N = \infty$, we immediately find

$$Q'(a, b) = \frac{1}{1 - e^{-b}} + \frac{1}{2} \sqrt{\frac{\pi}{a}} \exp\left(\frac{b^2}{4a}\right) \operatorname{erfc}\left(\frac{b}{2\sqrt{a}}\right) - \frac{1}{b} \quad (24)$$

Consider some particular cases following from Eq. (24). The harmonic oscillator limit is obtained at $a = 0$ and $b = \theta$

$$Q'(0, \theta) = \frac{1}{1 - e^{-\theta}} \quad (25)$$

The partition function is represented as the sum of infinite series in (22); therefore the high temperature limit is equal to

$$Q'(a, b) = \frac{1}{2} \sqrt{\frac{\pi}{a}} \quad (26)$$

instead of Eq. (17). The low temperature limit for $Q'(a, b)$ is found in perfect analogy to Eq. (19)

$$Q'(a, b) = 1 + e^{-b} - \frac{2a}{b^3} \quad (27)$$

Eq. (27) is derived based on two terms in the asymptotic expansion of the error function, thus the range of applicability of this equation is severely limited. At low temperatures one should use Eq. (24) without any approximations. Fig. 3 shows the relative difference between the exact and approximate partition functions versus θ at different values of the anharmonicity parameter x_e . As is seen, there is a good agreement between Q' and the exact summation of (22) even in the case of speculative anharmonicity $x_e = 0.33$.

4. Concluding remarks

For diatomic molecules the vibrational partition function is given by Eq. (14) (or more general Eq. (20)), and is easily calculated at any temperatures, given the parameters ω and x_e . Analytical formula makes it possible to study the partition function behavior in the range of high and low temperatures for arbitrary number N of the sum terms. Due to a finite number of terms, only analytical approach (Eq. (19)) could be employed to study its behavior at low temperatures. Thus formula (14) is actually very convenient to use. The above analysis can be extended easily to the case of polyatomic molecules when the mode–mode coupling is taken into account by cumulant expansion. Studies in this direction are presently under way.

References

- [1] K.M. Kuhler, D.G. Truhlar, A.D. Isaacson, J. Chem. Phys. 104 (1996) 4664.
- [2] A.D. Isaacson, J. Chem. Phys. 108 (1998) 9978.
- [3] K. Yagi, K. Hirao, T. Taketsugu, M.W. Schmidt, M.S. Gordon, J. Chem. Phys. 121 (2004) 1383.
- [4] B. Njagic, M.S. Gordon, J. Chem. Phys. 125 (2006) 224102.
- [5] D.G. Truhlar, A.D. Isaacson, J. Chem. Phys. 94 (1991) 357.
- [6] A.D. Isaacson, D.G. Truhlar, J. Chem. Phys. 76 (1982) 1380.
- [7] M.L. Strelakov, Chem. Phys. Lett. 393 (2004) 192.
- [8] P.M. Morse, H. Feshbach, Methods of Theoretical Physics, McGraw-Hill, New York, 1953.
- [9] M. Abramowitz, I. Stegun, Handbook of Mathematical Functions, Dover, New York, 1964.
- [10] G. Pöschl, E. Teller, Z. Phys. 83 (1933) 143.