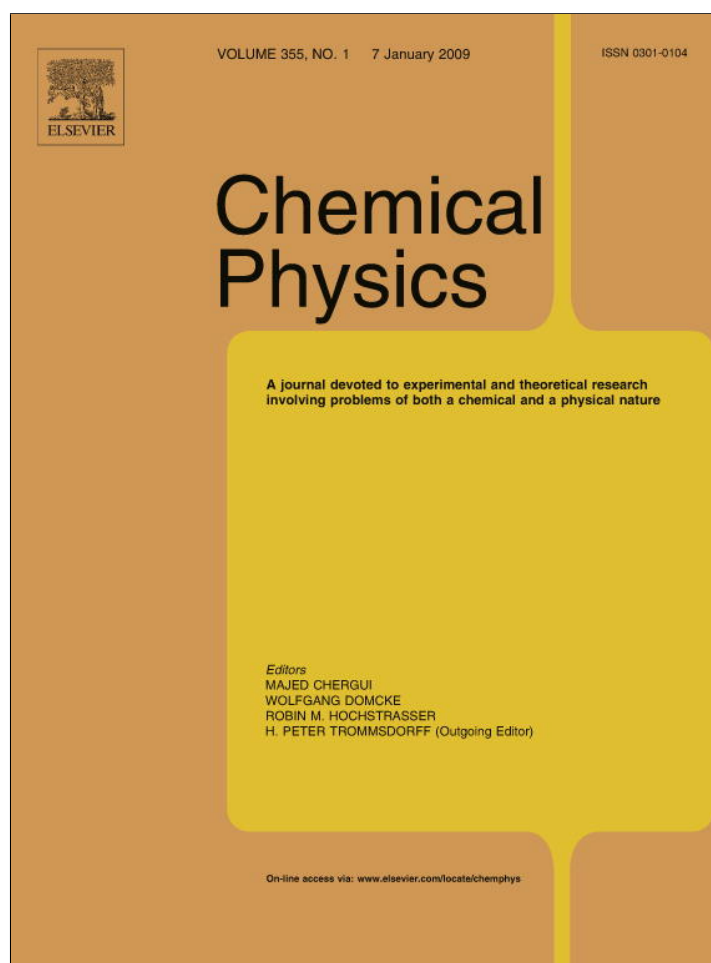


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Chemical Physics

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Partition function of the hindered rotor: Analytical solutions

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ARTICLE INFO

Article history:

Received 8 September 2008

Accepted 5 November 2008

Available online 12 November 2008

Keywords:

Torsional oscillations
Intramolecular dynamics
Internal rotation
Partition function

ABSTRACT

A simple numerical method that has considerably simplified the calculations of torsional energy levels is proposed. Approximate expressions of the hindered-rotor partition function have been derived, analytically interpreted, and compared with numerically exact values. The accuracy of the previously developed approximations is estimated.

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1. Introduction

Internal rotation effects are inherent in most molecules, when one part of a molecule can rotate with respect to the other through considerable angles, and at high excitation energies begins to rotate freely. High-resolution microwave and infrared spectroscopy open up opportunities to examine this phenomenon with a high accuracy [1]. A quantum description of hindered rotation was made soon after the emergence of quantum mechanics [2], however, mathematically speaking the theory [2–4] proved to be too cumbersome for many applications. Since then numerous attempts have been made to develop more simple approaches to the same problems [5–13]. In the framework of analytical approach, one can raise a natural question why a partition function Q depends on a given parameter in this or that way, and receive answers. It cannot be doubted that analytical models are a reliable guidance in theory and make it possible to extract reasonable information from the calculation data. Obviously, such models are necessary for this purpose.

There are several publications, beginning with the Pitzer and Gwinn pioneer work [4], that present analytical calculations of the hindered-rotor partition function [6,9–12]. In this work, we give a detailed comparison of numerically exact calculations with various approximations developed to solve this problem. It turns out that the classical partition function [4] gives sufficiently accurate values of Q for the barriers with an arbitrary number of minima. However, this conclusion is valid only for the high temperature limit with $\beta = B/k_B T \ll 1$, where B is the effective rotational constant. The Wigner–Kirkwood approximation of partition function used in [10] strongly improves the accuracy of the Q

values calculated at high temperatures, but leads to even greater errors in comparison with the classical approximation at low temperatures. The Pitzer–Gwinn approximation modified in [11] in terms of the Padé approximant gives good results at temperatures for $\beta < 0.1$, i.e., over a wide temperature range sufficient for many practical purposes. It should be noted that disagreement with exact values begins to increase approximately at $\beta > 0.1$, but this demerit is typical for all approximations that ignore an accurate value of the zero-point energy [13].

A comparison with the numerically exact calculations shows that all approximations are inapplicable in the limit of very small barriers at intermediate and low temperatures. The well-known expression for a free-rotor partition function can be used only in the high temperature limit and needs considerable correction at intermediate and low temperatures. In the present paper, we derive a simple analytical formula to describe this case. A closed-form expression will be derived analytically for the hindered-rotor partition function to obtain the accurate values of Q both in high and low temperature limits.

2. Exact solution

The potential energy of the hindered internal rotor for the barrier with s -fold symmetry may be written as [1]

$$V(\phi) = \frac{V_s}{2} [1 - \cos(s\phi)], \quad 0 \leq \phi \leq 2\pi \quad (1)$$

where s is the number of potential minima and V_s is the barrier height. A wave function of internal rotation satisfies the equation similar to the Mathieu equation

$$\frac{d^2 \Psi}{d\phi^2} + [a + 2q \cos(s\phi)] \Psi = 0, \quad (2)$$

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where q is the reduced barrier height

$$q = \frac{V_s}{4B}, \quad (3)$$

and a are the eigenvalues of Eq. (2) (see below Eq. (8))

$$a = \frac{1}{B} \left(E - \frac{V_s}{2} \right). \quad (4)$$

Here $B = \hbar^2/2I$ is the effective rotational constant and I is the reduced moment of inertia for a relative motion of two groups of atoms in a molecule [1]. A periodic solution of Eq. (2) may be represented by a Fourier expansion [3]

$$\Psi(\phi) = \sum_{k=-\infty}^{\infty} C_{sk+\sigma} e^{i(sk+\sigma)\phi}. \quad (5)$$

For the molecule with s equivalent internal configurations the appropriate periodic solutions are obtained by choosing s integer values of σ , such that $-s/2 < \sigma \leq s/2$. Substituting this expansion in Eq. (2) yields

$$\left[(sk + \sigma)^2 - a \right] C_{sk+\sigma} - q [C_{s(k+1)+\sigma} + C_{s(k-1)+\sigma}] = 0. \quad (6)$$

If this infinite set of linear homogeneous equations has a nontrivial solution for $C_{sk+\sigma}$, the determinant of coefficients must vanish. Let us consider the following tridiagonal matrix

$$A_{ij} = (si + \sigma)^2 \delta_{ij} - q(\delta_{i,j+1} + \delta_{i+1,j}) - \infty < i, j < \infty. \quad (7)$$

As follows from Eqs. (6) and (7), the eigenvalues of this matrix will be the eigenvalues of Eq. (2). In our work, they were calculated numerically for the lowest 200 energy levels. A comparison with the tables [14] demonstrates that, as a minimum, the first ten decimal points are exact. In numerical calculations, one should take care that the next eigenvalue is greater than the preceding one.

An appropriate solution of the torsional wave equation leads to a set of torsional levels n , each of which is split into several sublevels and, therefore, is specified by quantum numbers n and σ

$$E_{n\sigma} = \frac{V_s}{2} + Ba_{n\sigma} \quad (8)$$

For example, for $s = 6$ we have $\sigma = 0, \pm 1, \pm 2, 3$. The energy levels with $\pm\sigma$ are doubly degenerate and correspond to two possible directions of internal rotation; the exceptions, which give nondegenerate levels, are $\sigma = 0$ and $\sigma = s/2$ (only for s even). For the molecules with a threefold barrier, the $\sigma = 0$ levels are nondegenerate levels corresponding to the symmetry species A , and $\sigma = \pm 1$ are the degenerate levels of species E (for details, see [1]). The number of distinct sublevels for any n will be $(s+2)/2$ for s even and $(s+1)/2$ for s odd. Hence, for the quantum partition function of the hindered rotor the following equation may be written

$$Q(\beta) = \sum_{n=0}^{\infty} \sum_{\sigma=0}^{\lfloor s/2 \rfloor} g_{\sigma} \exp\left(-\beta \frac{E_{n\sigma}}{B}\right), \quad (9)$$

where $g_{\sigma} = 2/s$ except $g_0 = 1/s$ and $g_{s/2} = 1/s$ for s even.

Consider now the influence of energy level splittings on the partition function with respect to temperature. In the infinite barrier limit each torsional level will be s -fold degenerate, since the internal motion is a torsional oscillation in any of the s equivalent potential wells. For a finite barrier, the tunneling effect results in level splittings, because the probability of tunneling through the barrier is finite due to finite V_s . On the other hand, the number of bound states in any potential well is also finite and depends on the anharmonicity constant of torsional vibrations. Therefore, for the barrier with a height of 1 kcal/mol, two or three levels arise in the potential well depending on the rotational constant value. These effects start to produce a pronounced effect on the partition

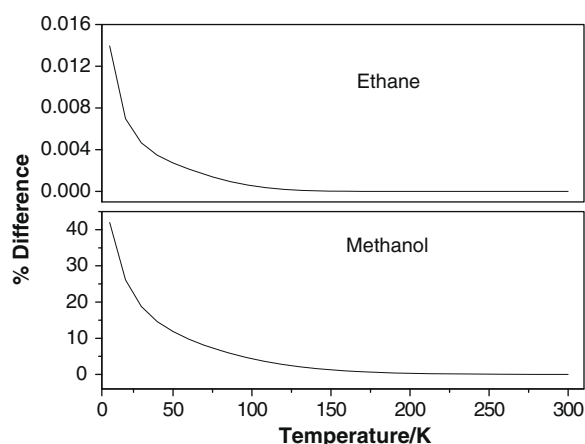


Fig. 1. Percent difference between the Q_A and Q partition functions vs. temperature. Deviations are defined as $(Q_A - Q)/Q_A$.

Table 1

Parameters of molecules used in the calculations. Rotational constants and torsional barriers are in kcal/mol.

Molecule	s	B	V_s	q^a	N^b	Source
HN_2^+	2	0.0204	48.96	600	28	[21]
CH_3OH	3	0.071	1.073	3.778	1	[3,22]
C_2H_6	3	0.026	2.93	28.17	3	[23]
CH_3NO_2	6	0.028	0.006	0.054	0	[24]
CF_3NO_2	6	0.018	0.0744	1.033	0	[25]

^{a,b} Calculated from Eqs. (3) and (16), respectively.

function, when energy state separations become comparable to the thermal motion energy $k_B T$. The level splittings also increase with $|\sigma|$ and, therefore, with the number of potential wells. Thus, the greater the splittings, the greater the difference between partition functions when all sublevels of the torsional energy (Q) or just the A levels (Q_A) are counted. This difference becomes particularly significant at low temperatures either for the molecules with just one or two levels below the barrier or for those deprived of the bound states (free rotation).

Fig. 1 shows the relative difference between the partition functions Q_A and Q as a function of temperature. The necessary molecular parameters are given in Table 1. As is seen, this difference may be neglected for ethane even at very low temperatures. At room temperature, the relative difference decreases to the value of the order of $10^{-9}\%$. On the contrary, for methanol the relative difference reaches tens of percent for low temperatures decreasing to 0.017% at 300 K. Inspection of the Table 1 shows that methanol has only two levels below the barrier (i.e., $N+1$), while ethane has four of them. However, the fundamental difference results from the large value of the effective rotational constant of methanol.

3. High barrier solution (torsion oscillator)

Consider now in detail the limit of very high barrier when it is sufficient to calculate the partition function counting the levels with $\sigma = 0$, i.e., the A levels. In this case, the internal motion will be restricted to small torsional oscillations with the frequency of harmonic vibrations equal to [1]

$$\omega = s\sqrt{BV_s}. \quad (10)$$

Hereafter $\hbar = 1$. The total energy of the molecule undergoing hindered internal rotation is equal to the sum of the mean kinetic energy $\langle T \rangle$ and the average potential energy $\langle V \rangle$. With the wave function $\Psi_n(\phi)$ written in the harmonic approximation we have

$$\langle n|T|n \rangle = \frac{\omega}{2} \left(n + \frac{1}{2} \right) \quad (11)$$

and

$$\langle n|V(\phi)|n \rangle = \frac{V_s}{2} [1 - e^{-4x} L_n(8x)], \quad (12)$$

where

$$x = \frac{\omega}{8V_s} = \frac{s}{8} \sqrt{\frac{B}{V_s}} = \frac{s}{16\sqrt{q}} \quad (13)$$

In Eq. (12) $L_n(x)$ are the Laguerre polynomials; the integral used to evaluate the matrix element is given in [15]. Then for torsional energy levels we find

$$E_n = \frac{\omega}{2} \left(n + \frac{1}{2} \right) + \frac{\omega}{16x} [1 - e^{-4x} L_n(8x)], \quad (14)$$

where $\omega = 8xV_s$. To analyze this equation, we restrict ourselves to the case where the harmonic approximation is applicable, i.e., $x \ll 1$. Thus, we get

$$E_n = \omega \left(n + \frac{1}{2} \right) - x\omega \left[\left(n + \frac{1}{2} \right)^2 + \frac{1}{4} \right] \quad (15)$$

As is easy to see, the introduced parameter x plays the role of an anharmonicity constant of torsional vibrations.

Solving equation $E_n = V_s$, we find the maximum quantum number N for the levels in the potential well

$$N = \frac{1}{2x} \left(1 - x - \sqrt{1 - x^2} \right) \quad (16)$$

Note that $N + 1$ will be the number of bound states below the barrier. As $N \geq 0$, the bound states arise at $x < 1/2$. The first excited level arises at $x \leq 1/10$. In the shallow potential well at $x > 1/2$ there are no bound states at all and only free rotation takes place.

In the high barrier limit, the partition function takes the form

$$Q_N^\omega = \exp \left[-\frac{\theta}{2} (1 - x) \right] \sum_{n=0}^N \exp [-\theta(1 - x)n + x\theta n^2], \quad N = 1, 2, \dots \quad (17)$$

where $\theta = \beta\omega/B$. The upper index ω means that the partition function is the result of quantum torsional vibrations with the frequency ω . The case where $x > 1/10$ (or $N = 0$) calls for a more careful examination and will be discussed below. Eq. (17) differs from the partition function of Morse oscillators only in the form of zero-point energy. Recently [16] an accurate closed-form expression for the partition function of Morse oscillators has been derived. A more simple but less accurate equation is presented in [17] for the same case.

The molecular ion HN_2^+ provides a useful accuracy check of Eq. (17) (see Table 1). The results are shown in Fig. 2. The behavior of Q at very high temperatures is determined by the energy levels that lie above the barrier even if it is very high. Just for this reason the partition function Q diverges in the limit $\beta \rightarrow 0$, while Q_N^ω has the limit $N + 1$. However, at low temperatures one can put $Q \approx Q_N^\omega \approx Q_1^\omega$ to a good approximation. Note that for a high barrier of a two-fold symmetry the difference between the partition functions Q and Q_A may be ignored.

4. Small barrier solution (quasi-free rotation)

Consider now the limit of small barrier when $q \rightarrow 0$ in Eq. (2). In this case, the eigenfunctions giving the periodic solution with a period of $2\pi/s$ take the form

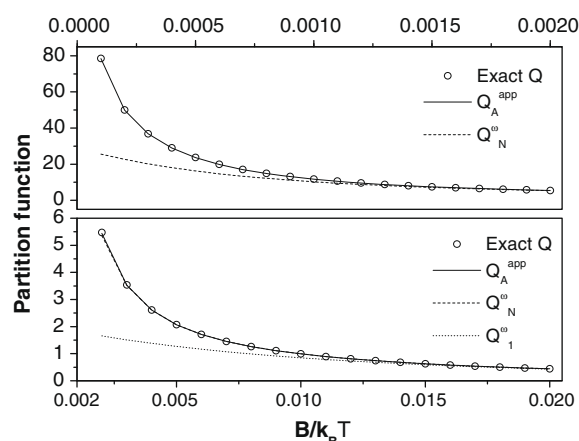


Fig. 2. Partition functions of internal rotation for HN_2^+ are plotted against $\beta = B/k_B T$.

$$\Psi_n(\phi) = \frac{1}{\sqrt{\pi(1 + \delta_{n,0})}} \begin{cases} \cos\left(\frac{\sigma n}{2}\phi\right), & n = 0, 2, 4, \dots \\ \sin\left[\frac{s(n+1)}{2}\phi\right], & n = 1, 2, \dots \end{cases} \quad (18)$$

With Eq. (18), the zeroth-order eigenvalues are given simply by

$$a_n^{(0)} = \begin{cases} \frac{s^2 n^2}{4}, & n = 0, 2, 4, \dots \\ \frac{s^2 (n+1)^2}{4}, & n = 1, 3, \dots \end{cases} \quad (19)$$

As was apparent after the numerical computations, the eigenvalues of matrix A from Eq. (7) are given by relationship (19) in the limit of very large n (with $\sigma = 0$), regardless of the parameter q values. In the small barrier approximation, the free internal rotational problem is solved exactly and then the barrier is added as perturbation. The matrix elements of the perturbation are solely off-diagonal

$$2q \int_0^{2\pi} \cos(s\phi) \Psi_n(\phi) \Psi_k(\phi) d\phi = \begin{cases} q, & k = n \pm 2 \\ \sqrt{2}q, & k = 0 \text{ or } n = 0 \end{cases}, \quad (20)$$

where k is a positive number. The eigenvalues at $q \neq 0$ can be calculated by ordinary perturbation theory as power series in the parameter q or by the methods discussed for the Mathieu equation by McLachlan [18]. With an accuracy to q^2 , one obtains

$$a_n = \frac{s^2 n^2}{4} + \frac{q^2}{s^2} \delta_{n,2} + \frac{2q^2}{s^2 (n^2 - 1)}, \quad n = 0, 2, 4, \dots \quad (21)$$

and

$$a_n = \frac{s^2 (n+1)^2}{4} - \frac{q^2}{s^2} \delta_{n,1} + \frac{2q^2}{s^2 [(n+1)^2 - 1]}, \quad n = 1, 3, \dots \quad (22)$$

The solution of ordinary Mathieu equation with a period of π has these eigenvalues in the case of even n [14,19]. It should be noted that the applicability condition for these equations is not restricted to a trivial requirement $q \ll 1$, moreover, above the barrier at $n \geq N + 1$; the last term in (22) must be essentially less than the first one

$$\frac{8q^2}{s^4 (N+1)^2 [(N+1)^2 - 1]} \ll 1 \quad (23)$$

Further, note that the number of levels below the barrier depends on the barrier height. That is why the left-hand side of inequality (23) remains finite even for very high barrier. At $q \rightarrow \infty$ (or $N \rightarrow \infty$) the left-hand side of the inequality yields a numerical value (≈ 0.265) that is still less than unity.

Now let us count all the levels above the barrier and denote their contribution to the partition function as Q_N^B . We have

$$Q_N^B = e^{-2\beta q} \sum_{n=N+1}^{\infty} e^{-\beta a_n} \quad (24)$$

The total partition function is

$$Q_A^{app} = Q_N^{(0)} + Q_N^B, \quad N = 1, 2, \dots \quad (25)$$

The lower index A means that the levels with $\sigma = 0$, i.e., the A levels are counted. This expression is valid for $x < 1/10$ or $q > (5s/8)^2$ where the bound states arise below the barrier. Fig. 2 demonstrates the accuracy of this approximation. It should be noted that the upper limit for sum (24) is taken as equal to 200, i.e., the number of levels used to calculate the numerically exact Q (see below). The limit of low temperatures is obtained from Eq. (24) where only the first term with $n = N + 1$ should be retained. The limit of high temperatures is more difficult to analyze. This will be the subject of the next section.

5. Partition function of free internal rotation

We examine the case of free internal rotation in the absence of excited levels below the barrier, i.e., at $q < (5s/8)^2$. Instead of (24) the total partition function is given by the expression

$$Q_f = e^{-2\beta q} \sum_{n=0}^{\infty} e^{-\beta a_n}. \quad (26)$$

The series can be evaluated analytically if we make the following. First, add up the terms with $n = 0, 1, 2$, then sum up the remainder of terms taking into consideration either even n beginning at $n = 4$ or odd n beginning at $n = 3$. The two series in even and odd n are equal; therefore, we can apply this property to give

$$Q_f = e^{-2\beta q} \left[\exp\left(\frac{2\beta q^2}{s^2}\right) + 2 \cosh\left(\frac{\beta q^2}{s^2}\right) \exp\left(-\beta s^2 - \frac{2\beta q^2}{3s^2}\right) + \sum_{n=3}^{\infty} [1 - (-1)^n] e^{-\beta a_n} \right] \quad (27)$$

Evaluating the remaining sum in (27), we neglect all terms in Eq. (22) except the first one. This neglect leads to the inequality similar to (23) with $N = 3$ or $q^2 < 30s^4$. This inequality is weaker than the initial inequality $q < (5s/8)^2$.

The theta functions of Jacobi [19] seem to be ideally suited for treating this partition function. To proceed further, use the Jacobi imaginary transformation

$$\sum_{n=-\infty}^{\infty} \exp(i\pi\tau n^2 + i2nz) = \frac{1}{\sqrt{-i\tau}} \sum_{n=-\infty}^{\infty} \exp\left[\frac{(z - \pi n)^2}{i\pi\tau}\right] \quad (28)$$

The above transformation enables one to readily produce a rapidly convergent series at small β . Substituting $z = 0$ and $-i\tau = \beta s^2/4\pi$ we find

$$\sum_{n=0}^{\infty} \exp\left(-\beta \frac{s^2 n^2}{4}\right) \cong \frac{1}{2} + \frac{1}{s} \sqrt{\frac{\pi}{\beta}} \left[1 + 2 \exp\left(-\frac{4\pi^2}{s^2 \beta}\right)\right] \quad (29)$$

Substitution of $z = \pi/2$ and $-i\tau = \beta s^2/4\pi$ gives

$$\sum_{n=0}^{\infty} (-1)^n \exp\left(-\beta \frac{s^2 n^2}{4}\right) \cong \frac{1}{2} + \frac{2}{s} \sqrt{\frac{\pi}{\beta}} \exp\left(-\frac{\pi^2}{s^2 \beta}\right) \quad (30)$$

Simple manipulations yield

$$Q_f = e^{-2\beta q} \left\{ \frac{1}{s} \sqrt{\frac{\pi}{\beta}} \left[1 + 2 \exp\left(-\frac{\pi^2}{s^2 \beta}\right) + 2 \exp\left(-\frac{4\pi^2}{s^2 \beta}\right)\right] - 1 + \exp\left(\frac{2\beta q^2}{s^2}\right) \right\} \quad (31)$$

In this expression, the two terms proportional to $\exp(-\beta s^2)$ are omitted, because if taken together, they give a very small contribution to Q_f at all β .

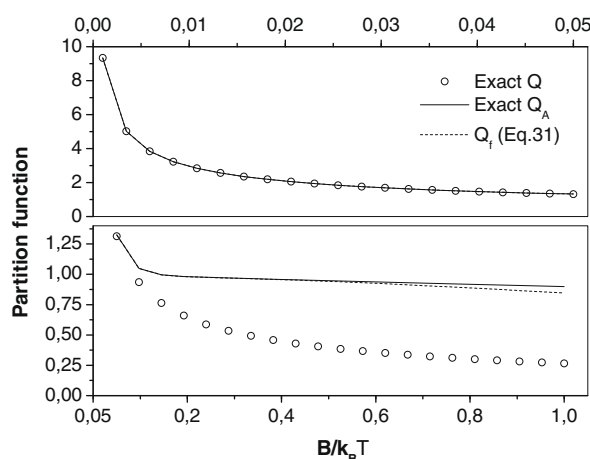


Fig. 3. Partition functions of internal rotation for CH_3NO_2 are plotted against $\beta = B/k_B T$.

In the high temperature limit $2\beta q \ll 1$ we arrive at the well-known expression for the classical partition function of free internal rotation [4]

$$Q_f = \frac{1}{s} \sqrt{\frac{\pi}{\beta}} = \frac{1}{s} \sqrt{\frac{2\pi I k_B T}{h^2}} \quad (32)$$

In the limit of low temperatures Q_f becomes

$$Q_f = \exp\left[-2\beta q \left(1 - \frac{q}{s^2}\right)\right] \quad (33)$$

Remember that the reduced barrier height should be restricted to the inequality $q < (5s/8)^2$ for the case of free internal rotation. To reverse this inequality, the partition function should be calculated from general Eq. (25) with the bound states below the barrier taken into account.

Fig. 3 compares the calculated values of Q , Q_A and Q_f for nitromethane with the barrier of a sixfold symmetry with a height of 6.03 cal/mol. The previous partition function Q_f is observed to coincide with the numerically exact Q_A to very low temperatures when $k_B T \approx B$. For nitromethane the essential difference between Q and Q_A at low temperatures (below 280 K) is evident.

Let us discuss the accuracy with which the partition function Q is calculated at high temperatures with $\beta \rightarrow 0$. In this limit Q diverges as $\beta^{-1/2}$. In the calculations, we take, however, into account a finite number of energy levels above the barrier. We allow the lowest 200 energy levels to obtain $Q = 201$ in this limit. Eq. (32) between Q and β gives the confidence limit $\beta \approx 8 \times 10^{-5}/s^2$ up to which the numerical calculations of the partition function with this number of levels will be valid.

6. Comparison with other approximations

Usually, when a new phenomenon is discovered, many approximations are developed to simplify a solution of the hindered-rotor problem [1–4], and yet interest continues [5–13]. Although the hindered-rotor problem can be solved exactly, the solutions [2–4] are cumbersome for many applications. There is a need for methods that are more convenient and sufficiently accurate.

We have made systematic comparisons of the numerically exact values of the partition function with the classical approximation [4], the Wigner–Kirkwood approximation developed in [10], and the Pitzer–Gwinn approximation [4] modified in [11] using a particular approximation of the zero-point energy. The typical results are given in Fig. 4 for ethane as an example. Comparisons are made

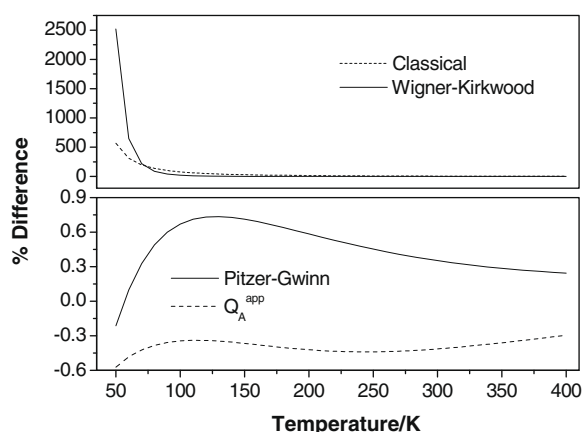


Fig. 4. Comparison of the values of the hindered-rotor partition function calculated with various approximations for C_2H_6 . Deviations are defined as $(Q_A - Q^{app})/Q_A$.

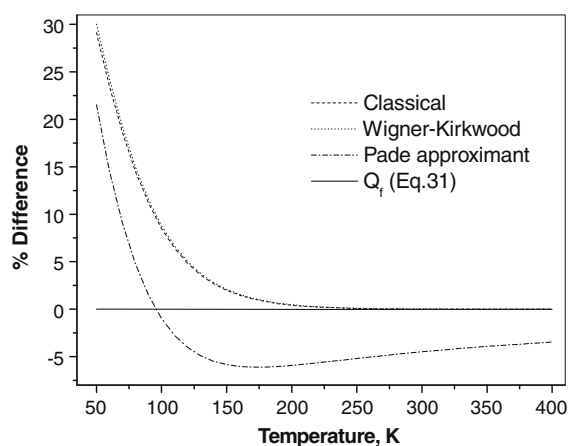


Fig. 5. Comparison of the values of the hindered-rotor partition function calculated with various approximations for CF_3NO_2 . Deviations are defined as $(Q_A - Q^{app})/Q_A$.

with the partition function Q_A only, since, the level splittings of torsional energy are ignored in all approximations. Moreover, for ethane this difference is negligibly small to very low temperatures (Fig. 1). Despite its simplicity, the classical approximation is sufficiently accurate for many purposes. The relative difference equal to -3.0% at 400 K increases slowly with decreasing temperature up to $\beta \approx 0.05$, then an essential deviation takes place pointing to non-applicability of classical mechanics at low temperatures. The Wigner–Kirkwood approximation strongly improves the classical results at high temperatures, leading to an accuracy of -0.0051% at 400 K. Nevertheless, the quantum corrections responsible for high accuracy at high temperatures lead to even greater errors in

comparison with the classical approximation at low temperatures. Such defect of these approximations is eliminated in the Pitzer–Gwinn approximation modified by McClurg and co-workers [11] (for more details, see [20]). For ethane, our approximation (25) gives slightly higher accuracy at low temperatures and comparable results at high temperatures.

Quite different results are obtained when the approximations considered above are applied to the CF_3NO_2 molecule having a low barrier, as indicated by Fig. 5. None of these approximations are applicable at intermediate and low temperatures. In all approximations Eq. (32) is used for the free-rotor partition function, while, actually, Q_f decreases exponentially with increasing β . Comparison of the values given by Eq. (31) with the numerically exact values shows that a relative difference of -0.0024% at 50 K does not exceed 5.5% even at 9 K where $k_B T \approx B$.

7. Conclusion

The problem of finding tridiagonal matrix eigenvalues is easy to solve numerically using modest computer aids. The analytical approximations developed to estimate a partition function, such as Eqs. (17), (24), and (31), provide physical interpretation of the results obtained. The developed treatment of the one-dimensional hindered rotor provides a reliable basis for solving the multidimensional problem. This formidable task will be considered in the nearest future.

References

- [1] C.C. Lin, J.D. Swalen, *Rev. Mod. Phys.* 31 (1959) 841.
- [2] H.H. Nielsen, *Phys. Rev.* 40 (1932) 445.
- [3] J.S. Koehler, D.M. Dennison, *Phys. Rev.* 57 (1940) 1006.
- [4] K.S. Pitzer, W.D. Gwinn, *J. Chem. Phys.* 10 (1942) 428.
- [5] J. Troe, *J. Chem. Phys.* 66 (1977) 4758.
- [6] D.G. Truhlar, *J. Comput. Chem.* 12 (1991) 266.
- [7] V.D. Knyazev, I.A. Dubinsky, I.R. Slagle, D. Gutman, *J. Phys. Chem.* 98 (1994) 5279.
- [8] S. Schmatz, *Chem. Phys.* 346 (2008) 198.
- [9] S.C. King, J.F. Leblanc, P.D. Pacey, *Chem. Phys.* 123 (1988) 329.
- [10] W. Witschel, C. Hartwigsen, *Chem. Phys. Lett.* 273 (1997) 304.
- [11] R.B. McClurg, R.C. Flagan, W.A. Goddard, *J. Chem. Phys.* 106 (1997) 6675.
- [12] P.Y. Ayala, H.B. Schlegel, *J. Chem. Phys.* 108 (1998) 2314.
- [13] A.D. Isaacson, D.G. Truhlar, *J. Chem. Phys.* 75 (1981) 4090.
- [14] M. Abramowitz, I.A. Stegun (Eds.), *Handbook of Mathematical Functions*, Dover, New York, 1965.
- [15] I.S. Gradshteyn, I.M. Ryzhik, *Tables of Integrals Series and Products*, Academic, San Diego, 1994.
- [16] M.L. Strelalov, *Chem. Phys. Lett.* 439 (2007) 209.
- [17] M.L. Strelalov, *Chem. Phys. Lett.* 393 (2004) 192.
- [18] N.W. McLachlan, *Theory and Application of Mathieu Functions*, Dover, New York, 1964.
- [19] E.T. Whittaker, G.N. Watson, *Modern Analysis*, Cambridge University, Cambridge, 1952.
- [20] V.D. Knyazev, *J. Chem. Phys.* 111 (1999) 7161.
- [21] S. Schmatz, M. Mladenović, *Ber. Bunsenges. Phys. Chem.* 101 (1997) 372.
- [22] R.M. Lees, J.G. Baker, *J. Chem. Phys.* 48 (1968) 5299.
- [23] S. Weiss, G.E. Leroi, *J. Chem. Phys.* 48 (1968) 962.
- [24] E. Tannenbaum, R.J. Myers, W.D. Gwinn, *J. Chem. Phys.* 25 (1956) 42.
- [25] W.M. Tolles, E.T. Handelman, W.D. Gwinn, *J. Chem. Phys.* 43 (1965) 3019.