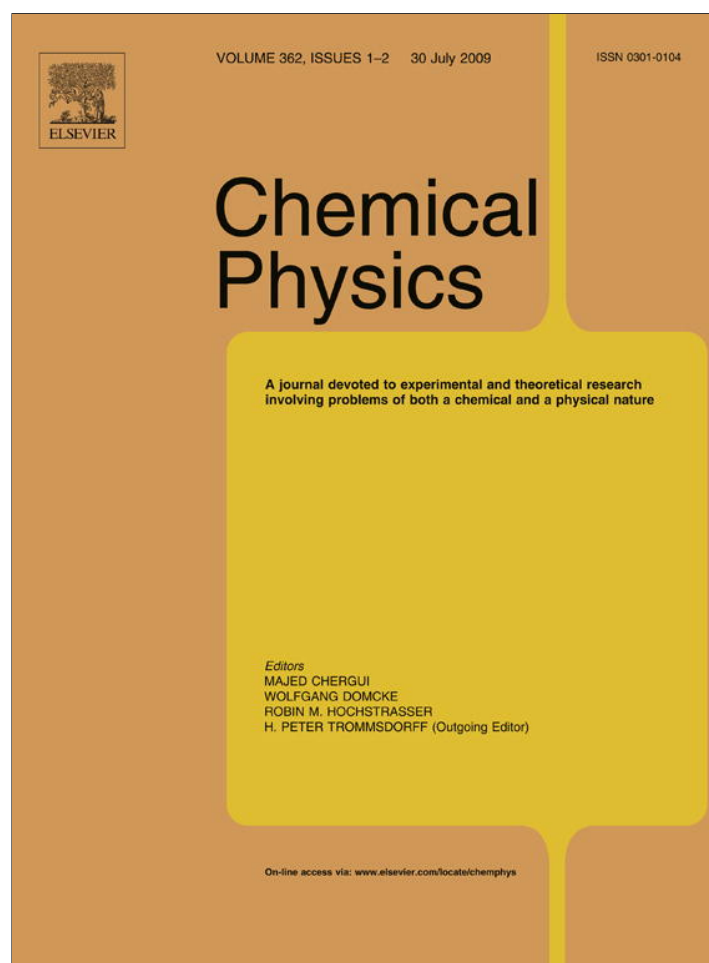


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Energy levels and partition functions of internal rotation: Analytical approximations

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ABSTRACT

A simple numerical method that has considerably simplified the calculations of torsional energy levels is proposed for one-dimensional barriers of arbitrary shape. The internal rotation constant is also permitted to vary as a function of torsional angle. In two limiting cases of high and low barriers, analytical expressions for hindered rotor state energies have been obtained. The partition function of internal rotation is then evaluated by eigenvalue summation. The derived analytical formula for the partition function of free internal rotation gives reasonable values down to the lowest temperatures. Analytical approaches give a better insight into the physical nature of the problem solvable by a rigorous method.

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1. Introduction

A quantum description of internal rotation was obtained soon after the emergence of quantum mechanics [1]. However, from the standpoint of computations, the exact solution proved to be too cumbersome for many applications even in the special case where only a one-term expansion is retained for the potential energy [1–3]. Since then numerous attempts have been made to develop simplified analytical approaches to the solution of this problem [4–12]. The detailed discussion of various approximations is given in [11]. In particular, the efforts to develop analytical approximations were successful in the case where the hindering barrier represented by a potential function depending on torsional angle ϕ in the simplest way [6–12]. Now it is common practice to represent the potential energy function by a finite Fourier series containing the minimum number of lowest-order terms that are required to give the correct number of extrema for the energy curve [13–16]. Despite the substantial amount of theoretical work accomplished in the area of internal rotation, little attention has been given to the analytic treatment of torsional energy levels appearing below or above the potential barrier of arbitrary shape.

In the present study, the focus is on methods that simplify calculations of torsional energy levels for more complex systems including the ϕ -dependence of the internal rotation constant. In the examination of torsional energy levels, it is helpful to consider two extreme cases; the barrier height is very large, and the barrier height is very small. In these limiting cases, it becomes possible to treat the problem analytically. The analytic treatment readily gives a solution, which is sufficiently accurate and enables one to phys-

ically interpret numerical results of a rigorous method. Further, the known energy levels are used to calculate the partition function of internal rotation. The approach given below is particularly attractive for the torsional vibration that can be separated from all other molecular vibrations to consider independently. The separability of internal and external rotations of a molecule is also supposed [3,17].

2. Torsional energy levels

For a molecule with s equivalent internal configurations, the potential energy $V(\phi)$ will be a periodic function in ϕ with period $2\pi/s$. The number of equivalent configurations for a complete internal revolution is obviously dependent on the symmetry of the molecule. The property of periodicity leads to a natural representation of $V(\phi)$ as a Fourier series

$$V(\phi) = \frac{1}{2} \sum_{m=1}^{\infty} V_{ms} [1 - \cos(ms\phi)]. \quad (1)$$

The kind of terms in the expansion depends on the parity of $V(\phi)$. For an asymmetric hindered rotor that has no rotational symmetry axis ($s = 1$) and a plane of symmetry, the sine terms must be taken into account due to a total lack of symmetry elements.

In the special case where the potential energy has threefold or higher symmetry, the internal rotation constant F is usually considered as constant and equal to its value of the equilibrium conformation of a molecule [4]. For potential barriers having lower symmetry than threefold one, the angular dependence of $F(\phi)$ can be represented as a Fourier series

$$F(\phi) = F_0 + \sum_{m=1}^{\infty} F_m \cos m\phi. \quad (2)$$

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If the potential energy variation with respect to ϕ is taken as given in Eq. (1), the wave equation for this problem is [18–20]

$$\frac{d}{d\phi} \left[\frac{F(\phi)}{F_0} \frac{d}{d\phi} \right] \Psi + \left[a + 2 \sum_{m=1}^{\infty} q_{ms} \cos(ms\phi) \right] \Psi = 0, \quad (3)$$

where

$$q_{ms} = \frac{V_{ms}}{4F_0} \quad \text{and} \quad q = \sum_{m=1}^{\infty} q_{ms} \quad (4)$$

and a are the eigenvalues of Eq. (3)

$$a = -2q + \frac{E}{F_0}. \quad (5)$$

Thus the solution of this differential equation yields the torsional energy levels E and the wave functions $\Psi(\phi)$. A periodic solution of Eq. (3) can be written in the following convenient form:

$$\Psi(\phi) = \sum_{k=-\infty}^{\infty} C_{ks+\sigma} e^{i(ks+\sigma)\phi}. \quad (6)$$

Appropriate periodic solutions are then obtained by choosing s integer values of σ such that $-s/2 < \sigma \leq s/2$ [2–4] (the Floquet theorem). Substitution of this expansion in Eq. (3) gives

$$\sum_{k=-\infty}^{\infty} \{ [(ks+\sigma)^2 - a] \delta_{kk'} - \sum_{m=1}^{\infty} [q_{ms} (\delta_{k,k'+m} + \delta_{k+m,k'}) - (k's+\sigma)^2 f_m (\delta_{ks,k's+m} + \delta_{ks+m,k's}) - (k's+\sigma) m f_m (\delta_{ks,k's+m} - \delta_{ks+m,k's})] \} C_{k's+\sigma} = 0, \quad (7)$$

where

$$f_m = \frac{F_m}{2F_0}. \quad (8)$$

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

$$A_{kk'} = \begin{cases} (ks+\sigma)^2, & k = k', \\ -q_{|k-k'|s} + (k's+\sigma)[k's+\sigma + (k-k')s] f_{|k-k'|s}, & k \neq k', \end{cases} \quad (9)$$

where $-\infty < k, k' < \infty$. As a rule, parameters q_{ms} characterizing the potential barrier decrease rapidly with m . This drop, together with small values of f_m , leads to the conclusion that actually A is a banded matrix with a few diagonals. As follows from Eqs. (7) and (9), the eigenvalues of this matrix will be the eigenvalues of Eq. (3). In our work, they were calculated numerically for the lowest 200 energy levels. In numerical calculations, it should be seen that each subsequent eigenvalue exceeds the preceding one.

For the barrier of a finite height, torsional energy levels are split into several sublevels. They are labeled by the quantum numbers n and σ in order of ascending energy

$$E_{n\sigma} = F_0(2q + a_{n\sigma}). \quad (10)$$

The index σ , which gives the symmetry or periodicity of the torsional wave functions, serves to distinguish torsional sublevels. For example, for $s = 6$ we have $\sigma = 0, \pm 1, \pm 2, 3$. The energy $E_{n\sigma}$ consists of successive groups of levels denoted by the number $n = 0, 1, 2, \dots$, and each group contains $(s+2)/2$ sublevels for even s and $(s+1)/2$ sublevels for odd s . 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 even s).

Thus the partition function of internal rotation may be written in the form

$$Q(\beta) = \exp(-2\beta q) \sum_{n=0}^{\infty} \sum_{\sigma=0}^{\lfloor s/2 \rfloor} g_{\sigma} \exp(-\beta a_{n\sigma}), \quad (11)$$

where $g_{\sigma} = 2/s$ except $g_0 = 1/s$ and $g_{s/2} = 1/s$ for even s . The partition function is conveniently considered as a function of the variable $\beta = F_0/k_B T$, since hindered rotor state energies are defined by the energy quantum F_0 . This is a natural unit of energy for torsional transition energies. The barrier height is responsible for the number of energy levels lying well below the barrier.

3. High barrier approximation

3.1. The barrier with s -fold symmetry

Let us examine more carefully the limit of a high barrier with threefold or higher symmetry. Here we can restrict ourselves to the calculation of the partition function counting the levels with $\sigma = 0$, i.e., nondegenerate levels of the A symmetry [1–4]. The internal motion for the A states resembles a back-and-forth oscillation localized in the potential wells. In other words, internal motion will be limited by small torsional vibrations about the potential minimum in any of the potential wells. If the position of the first potential well at $\phi = \phi_0$ is known, then the positions of other wells are given by a simple formula $\phi_0 + 2\pi i/s$, where $i = 0, 1, \dots, s-1$. Note that ϕ_0 can differ from zero, if there are other potential wells of different symmetry. Thus, the potential wells localized at these points are identical in shape, and, hence, the harmonic frequency in each of them is the same

$$\omega = \left[\frac{1}{I} \left(\frac{d^2 V}{d\phi^2} \right)_{\phi_i} \right]^{\frac{1}{2}} = \frac{2sF_0}{h} \sqrt{M_2}, \quad (12)$$

where the even derivatives are expressed in terms of the moments

$$M_k = \sum_{m=1}^{\infty} m^k q_{ms} \cos(ms\phi_0). \quad (13)$$

In Eq. (12) the second moment should be positive for the consideration of torsional vibrations with the frequency ω to be possible at all.

The zeroth-order wave function $\Psi_n(\phi)$ will be a linear combination of harmonic oscillator functions centered at s minima. It is a periodic function with period $2\pi/s$, so one can immediately write

$$\Psi_n(\phi) = \frac{1}{\sqrt{s}} \sum_{i=0}^{s-1} U_n(\phi - \phi_i), \quad (14)$$

where the harmonic oscillator functions are expressed via the Hermite polynomials

$$U_n(\phi - \phi_i) = \left(\frac{\gamma}{\pi} \right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} \exp \left[-\frac{\gamma}{2} (\phi - \phi_i)^2 \right] H_n[\sqrt{\gamma}(\phi - \phi_i)] \quad (15)$$

and

$$\gamma = \frac{I_0 \omega}{h} = \frac{h \omega}{2F_0}. \quad (16)$$

In principle, the reduced moment of inertia can depend on a torsional angle as $I(\phi_i)$; however, the parameter γ will be the same for all equivalent minima.

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 $\langle V \rangle$. In the harmonic approximation we have

$$E_n = - \int_{-\infty}^{+\infty} \Psi_n \left(F \frac{d^2 \Psi_n}{d\phi^2} + \frac{dF}{d\phi} \frac{d\Psi_n}{d\phi} \right) d\phi + \langle n|V|n \rangle. \quad (17)$$

In the case where F is independent of ϕ , the energy E_n can be rewritten as

$$E_n = \frac{\hbar\omega}{2} \left(n + \frac{1}{2} \right) \left[1 + \frac{1}{s} \sum_{\substack{ij=0 \\ i \neq j}}^{s-1} I_n(ij; 0) \right] + \langle n|V|n \rangle, \quad (18)$$

where $I_n(ij; m)$ are the necessary multicentered integrals (see Eq. (22))

$$I_n(ij; m) = \int_{-\infty}^{+\infty} U_n(\phi - \phi_i) \cos(ms\phi) U_n(\phi - \phi_j) d\phi. \quad (19)$$

Oscillator functions and their applications were discussed in the literature more than once using various mathematical methods. In particular, we employ the following result [21]:

$$\frac{1}{2^n n! \sqrt{\pi}} \int_{-\infty}^{+\infty} e^{-t^2} H_n(t-a) H_n(t+a) \cos(bt) dt = e^{-b^2/4} L_n \left(\frac{b^2}{2} + 2a^2 \right). \quad (20)$$

With Eq. (20) we easily find

$$I_n(ij; m) = \exp \left[-\frac{\gamma}{4} (\phi_i - \phi_j)^2 - \frac{m^2 s^2}{4\gamma} \right] L_n \left[\frac{\gamma}{2} (\phi_i - \phi_j)^2 + \frac{m^2 s^2}{2\gamma} \right] \times \cos \left[\frac{ms}{2} (\phi_i + \phi_j) \right]. \quad (21)$$

In these equations L_n are the Laguerre polynomials. So the average potential energy is given by the expression

$$\langle n|V|n \rangle = 2F_0 \sum_{m=1}^{\infty} q_{ms} \left\{ 1 - I_n(m) + \frac{1}{s} \sum_{\substack{ij=0 \\ i \neq j}}^{s-1} [I_n(ij; 0) - I_n(ij; m)] \right\}, \quad (22)$$

where the one-center integral $I_n(m) = I_n(ii; m)$ does not depend on the number of a potential well.

To estimate the contribution of multicentered integrals to the average torsional energy, we performed the detailed calculations with a great number of model systems. Numerical calculations show that the influence of these integrals on the calculated value $\langle V \rangle$ near the bottom of the barrier is negligibly small, while near the top of the barrier their contribution to $\langle V \rangle$ become quite noticeable. Quantum mechanically, a molecule may pass from one configuration to another by tunneling through the barrier near its top since the wave functions extend through the classically forbidden regions. However, in the vicinity of the potential maximum, the harmonic approximation is no longer valid. A comparison of calculated energy levels shows that the multicentered integrals have no pronounced effect on the accuracy of results within and beyond the limits of harmonic approximation. Therefore, in the harmonic approximation all multicentered integrals can be neglected

$$\langle n|V|n \rangle = 2F_0 \sum_{m=1}^{\infty} q_{ms} \left[1 - \exp \left(-\frac{m^2 s^2 F_0}{2\hbar\omega} \right) L_n \left(\frac{m^2 s^2 F_0}{\hbar\omega} \right) \cos(ms\phi_0) \right]. \quad (23)$$

Consider an important case following from Eq. (23) in the limit $s^2 F_0 / \hbar\omega \ll 1$. Then the expansion of the Laguerre polynomials in terms of a small argument may be used

$$e^{-z/2} L_n(z) = 1 - \left(n + \frac{1}{2} \right) z + \left[\left(n + \frac{1}{2} \right)^2 + \frac{1}{4} \right] \frac{z^2}{4} + \dots \quad (24)$$

Inserting this expansion into Eq. (23), one can recast Eq. (18) to get

$$E_n = V(\phi_0) + \hbar\omega \left(n + \frac{1}{2} \right) - \hbar x \omega \left[\left(n + \frac{1}{2} \right)^2 + \frac{1}{4} \right], \quad (25)$$

where x is the anharmonicity constant of torsional vibrations

$$x = \frac{sM_4}{16M_2^2}. \quad (26)$$

In principle, the anharmonicity constant (due to M_4) may be both positive and negative at the positive second moment. In the first case torsional oscillations resemble the vibrations of Morse oscillator, while in the second situation they appear as the vibrations of Pöschl–Teller oscillator [22]. In other words, a negative x results in a narrower potential well with more widely separated torsional levels. A positive x has just the opposite effect.

The solution of the equation $E_n = V_{\max}$ makes it possible to find the maximum quantum number N for the levels in the potential well

$$N = \frac{1}{2x} \left[1 - x - \left(1 - x^2 - \frac{4x\Delta V}{\hbar\omega} \right)^{1/2} \right], \quad (27)$$

where $\Delta V = V_{\max} - V_{\min}$ and $V_{\min} = V(\phi_0)$. To put it differently, ΔV is the barrier height from the position of the potential minimum. Note that $N + 1$ is the number of bound states below the barrier. Bound states arise at $\Delta V \geq E_0$, and the first excited level will appear below the barrier, if the barrier height satisfies the inequality

$$\Delta V \geq \frac{\hbar\omega}{2} (3 - 5x). \quad (28)$$

In a shallow potential well this inequality is reversed, and we shall consider that almost free rotation occurs in this case.

It should be noted that the general formalism allows one to make all conclusions obtained earlier [8–12] in the framework of the elementary theory, when a one-term expansion is retained for the potential energy.

In the high barrier limit, the partition function differs from the partition function of Morse oscillators solely in the form of zero-point energy [12]. Recently [22] an accurate closed-form expression for the partition function of Morse oscillators has been derived. Some limiting cases can also be found there.

3.2. Asymmetric hindered rotor

Let us consider the case of asymmetric hindered rotor for n -butane as an example. A lack of rotation symmetry axes restores s to 1; nevertheless, there is a plane of symmetry which results in an even parity for $V(\phi)$ in the standard form of Eq. (1). In n -butane (C_4H_{10}) two types of hindering potentials take place: one of them corresponds to rotations of ending methyl groups, and another is associated with CC–CC carbon torsional variations, Fig. 1. The potential of the methyl rotation has a threefold symmetry and is determined solely by the reduced barrier height q_3 ; the detailed examination is given above. The potential function governing the conformational interchange in n -butane has been more than once considered in the literature from both experimental and theoretical points of view [13,14] (and earlier references cited therein). Herrebut et al. [13] used a conventional expression for the potential function retaining the terms from V_1 to V_6 . Torsional angular dependence of the internal rotational constant $F(\phi)$ was represented as a Fourier series with coefficients from F_0 to F_6 . As is seen from Fig. 1, the *trans* equilibrium conformation (t) at $\phi = 0$ is separated from the higher energy *gauche* conformation (g) at $\phi = 2.0598$ (118°) by the t – g barrier, while direct transition between this potential well and another potential well at $\phi = 4.2235$ (242°) requires traversing the *cis* barrier ($\phi = \pi$). We employed these data to study the spectrum of energy eigenvalues applying the above analytical approach.

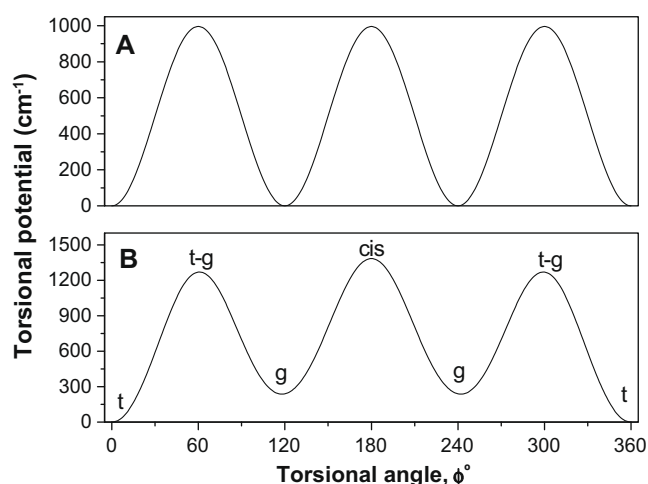


Fig. 1. Torsional potentials of the ending methyl rotation (A) and the ethyl rotation (B) in *n*-butane. The potential energy is set to zero at $\phi = 0$.

Now the harmonic frequency from Eqs. (12) and (13) and the parameter γ in Eq. (16) are calculated with the internal rotation constant for a given conformation $F(\phi_0)$ instead of F_0 . An expression of the mean kinetic energy is also changed. At small ratios $F_m/\hbar\omega$, this modification is very small. With this in mind it is convenient to express $F(\phi)$ as a power series in ϕ . Substituting this expression into Eq. (17), we have for $\langle n|T|n \rangle$ the following equation:

$$\langle n|T|n \rangle = \frac{\hbar\omega}{2} \left(n + \frac{1}{2} \right) - \frac{1}{4} \left[\left(n + \frac{1}{2} \right)^2 + \frac{5}{4} \right] \sum_{m=1}^{\infty} m^2 F_m. \quad (29)$$

The quantities $V(\phi_0)$ and x need to be substituted for $\tilde{V}(\phi_0)$ and \tilde{x} before they can be used in Eq. (25)

$$\tilde{V}(\phi_0) = V(\phi_0) - \frac{1}{4} \sum_{m=1}^{\infty} m^2 F_m \quad (30)$$

and

$$\tilde{x} = x + \frac{1}{4} \sum_{m=1}^{\infty} \frac{m^2 F_m}{\hbar\omega}. \quad (31)$$

Nondegenerate energy levels corresponding to torsional vibrations in the *t* potential well (Fig. 1) are defined by the fundamental frequency $\tilde{\omega} = 125.38 \text{ cm}^{-1}$, anharmonicity constant $\tilde{x} = 0.00853$, and rotational constant $F(0^\circ) = 1.581 \text{ cm}^{-1}$. According to Eq. (27), 13 bound states ($N_t \approx 12$) are to exist below the *cis* barrier ($V_{cis} = 1384 \text{ cm}^{-1}$).

Because of the presence of two potential wells in the *g* conformation of *n*-butane, energy levels are doubly degenerate. In reality, as a rigorous theory shows, the two potential wells are separated by the almost impenetrable barrier with level splittings of the order of 10^{-10} cm^{-1} near the barrier bottom. The *gauche* energy levels are specified by the fundamental frequency $\tilde{\omega} = 118.69 \text{ cm}^{-1}$, anharmonicity constant $\tilde{x} = 0.00889$, and rotational constant $F(118^\circ) = 1.628 \text{ cm}^{-1}$. Below the *cis* barrier ($\Delta V = 1147 \text{ cm}^{-1}$) there are eleven bound states ($N_g \approx 10$).

Energy levels, E_n^t and E_n^g , that can be calculated for each of the potential wells by Eq. (25) are related to energy levels for the entire system of potential wells, E_n , as:

(i) the *trans* conformation

$$E_n^t = \begin{cases} E_0, & n = 0, \\ E_{3n-2}, & n = 1, 2, \dots \end{cases} \quad (32)$$

(ii) the *gauche* conformation

$$E_n^g = E_{3n+2} \cong E_{3n+3}, \quad n = 0, 1, \dots \quad (33)$$

Comparison of numerically exact values E_n with approximate values is given in Table 1. Examination shows that the error does not exceed 1% for energy levels lying near the barrier bottom. In other words, torsional oscillations of asymmetric internal rotor in *n*-butane are adequately described by the Morse oscillator model. The agreement is made worse near the top of the barrier. Above 1000 cm^{-1} the degeneracy of levels is lifted. Further, the approximate theory predicts that near the top of the *cis* barrier there is the energy level with $n = N = 34$ ($3N_t - 2$), while the rigorous theory gives $N = 37$. It also shows that level splittings near the barrier top depend non-monotonically on the quantum number n owing to a complex form of the barrier and a change of internal motion from torsional oscillations to free rotation.

Now we calculate the partition function of asymmetric rotor using Eq. (11) where energy levels are labeled by the quantum number n ($\sigma = 0$ and $g_\sigma = 1$) in order of ascending energy. For comparison, let us calculate two partition functions: (i) in the first case only energy levels lying below the barrier will be taken into account ($N = 37$); (ii) in the second case all levels will be allowed for, including free rotation limit ($N = 200$). We also calculate the partition function using anharmonic model (25). Approximate expression for Q is of the form

Table 1

Calculated energy levels of torsional motion (in cm^{-1}) for the *trans* and *gauche* conformations of *n*-butane.

Trans conformation			Gauche conformation		
<i>n</i>	Exact	Eq. (25)	<i>n</i>	Exact	Eq. (25)
0	62.111	62.137	2/3	295.47	295.44
1	185.16	185.35	5/6	411.89	412.00
4	305.68	306.41	8/9	525.81	526.41
7	423.42	425.30	11/12	636.90	638.70
10	538.08	542.04	14/15	744.79	748.85
13	649.33	656.61			
Near the top of the <i>cis</i> barrier					
31	1218	1299	32	1268	1365
34	1296	1398	33	1285	1365
37	1378	1495	35	1331	1460
			36	1347	1460

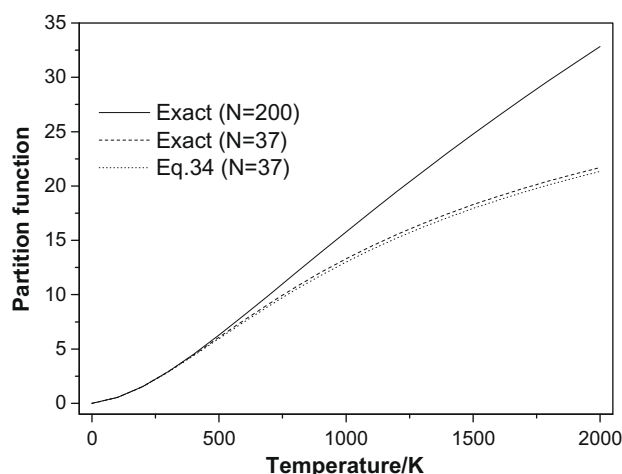


Fig. 2. Partition functions of the ethyl rotation in *n*-butane (see the text).

$$Q = \exp\left(-\frac{E_0^t}{k_B T}\right) + \sum_{n=1}^N \left[G_t(n) \exp\left(-\frac{E_{(n+2)/3}^t}{k_B T}\right) + G_{1g}(n) \exp\left(-\frac{E_{(n-2)/3}^g}{k_B T}\right) + G_{2g}(n) \exp\left(-\frac{E_{(n-3)/3}^g}{k_B T}\right) \right], \quad (34)$$

where $G_t(n) = 1$ at $n = 0, 1, 4, 7, \dots$ otherwise, it is zero. Similarly, $G_{1g}(n) = G_{2g}(n) = 1$ at $n = 2, 5, 8, \dots$ and $n = 3, 6, 9, \dots$, respectively, otherwise, they are zero. Comparison of calculated values of Q is given in Fig. 2. As is seen, there is an excellent agreement between exact and approximate partition functions, in fact, up to the temperatures, when thermal energy becomes equal to the magnitude of the *cis* barrier. An insignificant discrepancy at high temperatures reflects the fact that energy levels near the top of the barrier are described by anharmonic model (25) with an error of about 10%. It is clear from computations that above 500 K it is necessary to take into consideration the contribution of states lying above the barrier. At very high temperatures, the contribution of free internal rotation to the partition function becomes predominant (see below).

4. Low barrier approximation

Now consider the limiting case where all $q_{ms} = V_{ms}/4F_0$ tend to zero, and the barrier may be treated as a small perturbation. The effect of the variation of the internal rotation constant with torsional angle is small for molecules of interest and will be neglected.

4.1. Perturbation theory

First we find the eigenvalues of the matrix A from Eq. (9) in the limit of free internal rotation. The infinite order determinantal equation has the form

$$(\sigma^2 - a) \prod_{k=1}^{\infty} [a^2 - 2(k^2 s^2 + \sigma^2)a + (k^2 s^2 - \sigma^2)^2] = 0, \quad (35)$$

i.e., the a eigenvalues are $(ks \pm |\sigma|)^2$. According to Eq. (10), the eigenvalues are represented as a function of quantum numbers n and σ . A comparison with numerically exact values of a rigorous theory results in the conclusion that it is necessary to put $k = n/2$ for even n and $k = (n+1)/2$ for odd n . So

$$a_{n\sigma}^{(0)} = \begin{cases} \left(\frac{ns}{2} + |\sigma|\right)^2, & n = 0, 2, 4, \dots, \\ \left[\frac{(n+1)s}{2} - |\sigma|\right]^2, & n = 1, 3, \dots \end{cases} \quad (36)$$

It is convenient to choose the zeroth-order wave functions for these eigenvalues in the form

$$\Psi_{n\sigma}(\phi) = \frac{1}{\sqrt{\pi(1 + \delta_{n0}\delta_{\sigma 0})}} \begin{cases} \cos\left(\frac{ns}{2} + |\sigma|\right)\phi, & n = 0, 2, 4, \dots, \\ \sin\left[\frac{(n+1)s}{2} - |\sigma|\right]\phi, & n = 1, 3, \dots \end{cases} \quad (37)$$

If s is an even number, then σ can take a maximum value equal to $s/2$. In this case we write

$$\Psi_{n,s/2}(\phi) = \frac{1}{\sqrt{\pi}} \begin{cases} \sin\left[\frac{(n+1)s}{2}\right]\phi, & n = 0, 2, 4, \dots, \\ \cos\left(\frac{ns}{2}\right)\phi, & n = 1, 3, \dots \end{cases} \quad (38)$$

Just under this choice of eigenfunctions, calculated eigenvalues coincide with eigenvalues given in the special case $s = 2$ by the Mathieu equation [23]. For example, A_1 and E_2 levels are given by even n ; A_2 and E_1 levels are given by odd n .

For the evaluation of eigenvalues, the matrix formulation is employed in which the perturbation matrix is grouped into blocks corresponding to even and odd quantum numbers. For even n and n' we have

$$2 \int_0^{2\pi} \Psi_{n\sigma}(\phi) \cos(ms\phi) \Psi_{n'\sigma}(\phi) d\phi = \frac{1}{[(1 + \delta_{n0}\delta_{\sigma 0})(1 + \delta_{n'0}\delta_{\sigma 0})]^{1/2}} \times \left[\delta\left(m, \frac{|n - n'|}{2}\right) \pm \delta\left(m, \frac{n + n'}{2} + \frac{2|\sigma|}{s}\right) \right]. \quad (39)$$

For convenience, the delta-symbol δ_{mn} is written as $\delta(m, n)$. The lower sign refers to the case $\sigma = s/2$. For odd n and n' we get

$$2 \int_0^{2\pi} \Psi_{n\sigma}(\phi) \cos(ms\phi) \Psi_{n'\sigma}(\phi) d\phi = \delta\left(m, \frac{|n - n'|}{2}\right) \mp \delta\left(m, \frac{n + n' + 2}{2} - \frac{2|\sigma|}{s}\right), \quad (40)$$

where the lower sign means that $\sigma = s/2$. Other matrix elements different from the given ones are equal to zero.

Considering the hindering barrier as a perturbation, we find the eigenvalues by the second order perturbation theory. The problem of eigenvalues is most easily solved when $\sigma \neq 0$ and $\sigma \neq s/2$ for even n

$$a_{n\sigma} = a_{n\sigma}^{(0)} + \sum_{m=1}^{\infty} \frac{2q_{ms}^2}{4a_{n\sigma}^{(0)} - m^2 s^2}, \quad \sigma \neq 0, \frac{s}{2}. \quad (41)$$

In the case $\sigma = 0$ or $\sigma = s/2$, at any n ($n \geq 1$) linearly independent eigenfunctions are always found in pairs. These eigenvalues can be calculated by generalized perturbation theory [24] or by the methods discussed for the Mathieu equation by McLachlan [25]. The algebra required in solving this problem is lengthy, but straightforward, and one gets the final result for $a_{n\sigma}$ when $\sigma = 0$

$$a_{n0} = \begin{cases} \frac{n^2 s^2}{4} + \Delta a_e(n), & n = 0, 2, 4, \dots, \\ \frac{(n+1)^2 s^2}{4} + \Delta a_o(n), & n = 1, 3, \dots, \end{cases} \quad (42)$$

where

$$\Delta a_e(n) = |q_{ns}| - \frac{(q_{ns} + q_{2ns})^2}{2n^2 s^2} + \sum_{m=1}^{\infty} \frac{(1 - \delta_{nm})f_e(n, m)}{m(n^2 - m^2)s^2} \quad (43)$$

and

$$\Delta a_o(n) = -|q_{(n+1)s}| - \frac{(q_{(n+1)s} - q_{2(n+1)s})^2}{2(n+1)^2 s^2} + \sum_{m=1}^{\infty} \frac{(1 - \delta_{n+1,m})f_o(n, m)}{m[(n+1)^2 - m^2]s^2}. \quad (44)$$

To avoid cumbersome expressions, we introduce the notations

$$f_e(n, m) = \frac{1}{(1 + \delta_{n0})(1 + \delta_{n,2m})} [(n+m)(q_{ms} + q_{(n-m)s})^2 \theta(n-m) - (n-m)(q_{ms} + q_{(n+m)s})^2 (1 + \delta_{n,2m})] \quad (45)$$

and

$$f_o(n, m) = (n+1+m)(q_{ms} - q_{(n+1-m)s})^2 \theta(n+1-m) - (n+1-m)(q_{ms} - q_{(n+1+m)s})^2. \quad (46)$$

Here $\theta(x)$ is the step-function equal to $\theta(x) = 1$ at $x > 0$ and to $\theta(x) = 0$ at $x \leq 0$. Similar expression can be derived for $a_{n\sigma}$ at $\sigma = s/2$ if s is an even number

$$a_{n,s/2} = \begin{cases} \frac{(n+1)^2 s^2}{4} + \Delta a_o(n), & n = 0, 2, 4, \dots, \\ \frac{n^2 s^2}{4} + \Delta a_e(n), & n = 1, 3, \dots \end{cases} \quad (47)$$

Consider an important case where for the potential function only the leading term with $m = 1$ may be retained in Eq. (1). For two equivalent potential wells ($s = 2$) the wave equation of hindered rotor is similar to the Mathieu equation. Then our a_{n0} are equal to the eigenvalues of the Mathieu equation $a_n(q_s)$ for even n , and to $b_{n+1}(q_s)$ for odd n , and, vice versa, a_{n1} coincide with

$b_{n+1}(q_s)$ at even n and with $a_n(q_s)$ at odd n (designations are taken from [23]). The eigenvalues a_{n0} were found earlier in [12] for the simplest type of potential functions (with $m = 1$).

The above approximation corresponds to the case of quasi-free internal rotation where there are no excited energy levels below the barrier. In other words, the criterion of applicability reduces to the inequality $\Delta V < \hbar\omega(3 - 5x)/2$ following from Eq. (28). On the other hand, the theory may be applied to the high barrier limit for such quantum numbers when the correction quadratic in perturbation is essentially less than the zeroth-order eigenvalue at $n = N$ [12]. Evidently, the limit of free internal rotation is always reached when $n \gg N$, i.e., high above the barrier.

4.2. Partition function in a low barrier approximation

Since the potential barrier is treated as a perturbation, Eq. (11) is conveniently recast as

$$Q = \exp(-2\beta q)(Q^{(0)} + \Delta Q_0 + \Delta Q_1 + \Delta Q_2 + \dots), \quad (48)$$

where $Q^{(0)}$ is the partition function of free internal rotation

$$Q^{(0)} = \sum_{n=0}^{\infty} \sum_{\sigma} g_{\sigma} \exp(-\beta a_{n\sigma}^{(0)}) \quad (49)$$

and ΔQ_n are small corrections to $Q^{(0)}$

$$\Delta Q_n = \sum_{\sigma} g_{\sigma} [\exp(-\beta a_{n\sigma}) - \exp(-\beta a_{n\sigma}^{(0)})]. \quad (50)$$

It is sufficient to allow for only the first two or three corrections at low temperatures. The lower the temperature, the greater accuracy in ΔQ_0 is needed, since almost all molecules are in the ground state. At high temperatures, the internal motion shows up as free rotation, all corrections vanish, just the leading term $Q^{(0)}$ remains. Apparently, at rather high temperatures this limit is reached whatever the barrier height.

Now let us derive the expression for $Q^{(0)}$ using the zeroth-order eigenvalues (36) in Eq. (49). For the potential barrier with s -fold symmetry, we easily find

$$Q^{(0)} = \sum_{\sigma} g_{\sigma} e^{-\beta\sigma^2} \sum_{n=-\infty}^{\infty} e^{-\beta s^2 n^2} \cosh(2\beta s \sigma n). \quad (51)$$

The theta functions of Jacobi [26] seem to be ideally suited for treating this partition function. By the use of the Jacobi imaginary transformation

$$\sum_{n=-\infty}^{\infty} \exp(i\pi\tau n^2 + i2nz) = \frac{1}{\sqrt{-i\tau}} \sum_{n=-\infty}^{\infty} \exp\left[\frac{(z - \pi n)^2}{i\pi\tau}\right], \quad (52)$$

one can readily produce a series that is rapidly convergent at high temperatures by setting $-i\tau = \beta s^2/\pi$ and $z = \pm i\beta s\sigma$:

$$Q^{(0)} = \frac{1}{s} \sqrt{\frac{\pi}{\beta}} \sum_{n=-\infty}^{\infty} \exp\left(-\frac{\pi^2 n^2}{\beta s^2}\right) \sum_{\sigma} g_{\sigma} \cos\left(\frac{2\pi\sigma}{s}n\right). \quad (53)$$

Substitution of $n = ks$ gives the final result

$$Q^{(0)} = \frac{1}{s} \sqrt{\frac{\pi}{\beta}} \sum_{k=-\infty}^{\infty} \exp\left(-\frac{\pi^2 k^2}{\beta}\right). \quad (54)$$

Retaining the first three terms in Eq. (54), we approximately obtain

$$Q^{(0)} \cong \frac{1}{s} \sqrt{\frac{\pi}{\beta}} \left[1 + 2 \exp\left(-\frac{\pi^2}{\beta}\right) + 2 \exp\left(-\frac{4\pi^2}{\beta}\right)\right]. \quad (55)$$

Note that the first term is the classical partition function that Euler–Maclaurin summation gives exactly [3,27]. As is seen, this formula gives reasonable values even at $\beta \approx 1$, when thermal energy is of the order of the internal rotation constant. At $\beta \gg 1$ the series from

(54) converges slowly, thus the Jacobi imaginary transformation ($-i\tau = \pi/\beta$, $z = 0$) may be applied once again to obtain a rapidly convergent series in this limit

$$Q^{(0)} = \frac{1}{s} \sum_{k=-\infty}^{\infty} e^{-\beta k^2}. \quad (56)$$

Just this expression for the partition function of free internal rotation is well-known in the literature [27].

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 $\beta^{-1/2}$. However, in our calculations, we take 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. Relation (55) 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.

Consider the temperature dependence of small corrections to $Q^{(0)}$ given by Eq. (50). The molecules chosen for this study are fluorotoluene ($C_6H_4FCH_3$) and deuterated toluene ($C_6H_5CH_2D$) as a typical example of molecules with low barriers. The internal rotation of the methyl group in *p*-fluorotoluene is hindered by the sixfold barrier with $V_6 = -4.8 \text{ cm}^{-1}$ ($F_0 = 5.460 \text{ cm}^{-1}$), but in *m*-fluorotoluene the barrier has a threefold symmetry with $V_3 = 16.9$, $V_6 = -5.3 \text{ cm}^{-1}$ ($F_0 = 5.479 \text{ cm}^{-1}$) [15]. From symmetry considerations toluene-*d*₁ has just the twofold barrier with $V_2 = 23$, $V_4 = 3$, $V_6 = -5 \text{ cm}^{-1}$ ($F_0 = 4.323 \text{ cm}^{-1}$) [16]. Typical behavior of corrections ΔQ_n depending on the parameter β is shown in Fig. 3. In the high temperature limit all corrections vanish, and only free internal rotation takes place. At low temperatures all corrections with $n \geq 1$ also tend to zero, since almost all molecules accumulate in the ground state with $n = 0$, $\sigma = 0$. For this reason the main contribution is given by the positive correction ΔQ_0 . Good agreement between exact and approximate values for ΔQ_2 is not accidental. For other ΔQ_n the perturbation theory makes it possible to calculate the eigenvalues almost with the same accuracy as a rigorous method.

Fig. 4 shows the relative difference between approximate and exact values of the partition function as a function of temperature. *p*-Fluorotoluene has the low reduced barrier height $q_6 = -0.22$, thereby justifying the use of the perturbation theory. The relative difference is better than $2.5 \times 10^{-5}\%$ even at $k_B T = F_0$. Such an extreme accuracy is achieved due to a small error in the correction ΔQ_0 at this temperature (0.0085%). For comparison, in toluene-*d*₁

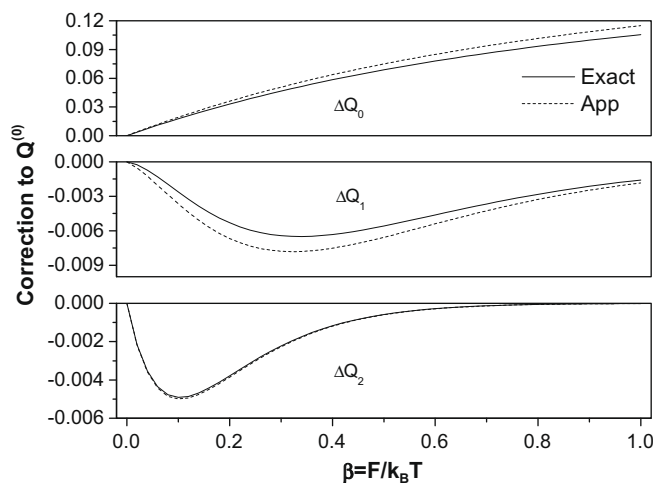


Fig. 3. Corrections to the partition function of free internal rotation for *m*-fluorotoluene calculated with the exact values of energy levels (Exact) and by the perturbation theory (App).

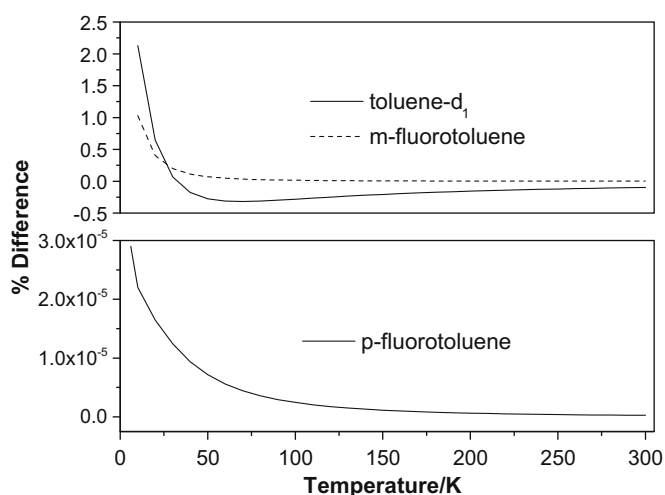


Fig. 4. Comparison of the values of the hindered rotor partition function calculated by the exact method and the perturbation theory. Deviations are defined as $(Q^{pp} - Q)/Q$.

this error is 5.6% and gives 3.7% relative difference in the partition function. In principle, the developed perturbation theory is suitable for molecules with high potential barriers but at fairly high temperatures. For example, *o*-fluorotoluene has a rather high barrier ($V_3 = 228.1 \text{ cm}^{-1}$) [15], so the adequate accuracy of computations, say 5%, is possible beginning with temperatures above 550 K.

5. Concluding remarks

The numerical method described in this work enables us to find energy levels of an internal rotor for practically any periodic potential function. The key equations of the method are Eqs. (9) and (10) that give explicitly hindered rotor state energies. The method incorporates the lowest 200 energy levels; however, more levels can easily be included if needed. As with any numerical method, there are many parameters that can be varied to enhance the accuracy of calculations. Just one of them is used in our method; it consists only in the number of necessary levels. The internal rotation constant, which is entered in the mean kinetic energy, is also permitted to vary as a function of torsional angle. Mathematically, this task is equivalent to the problem of position dependent mass in the one-dimensional Schrödinger equation. A useful generalization to this case opens the way to analyze asymmetric hindered rotors both numerically and analytically. The problem of finding the eigenvalues of a banded matrix with three, five, and more diagonals with almost identical elements along each secondary diagonal is very simple for numerical calculations, and may be solved with modest computer aids. Then partition functions are obtained by direct eigenvalue summation.

The availability of rigorous numerical method does not eliminate the need for simple models providing a better insight into the nature of the phenomenon and giving informed predictions. In the framework of analytical approach, one can raise a natural question why a solution depends on a given parameter in this or that way, and receive answers. Such a property is particularly useful when one tries to fit the parameters of a model to experimental data, for example. 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.

The analytical expressions for energy levels of this work can be very useful for the estimation of torsional anharmonicity in transition state theory (TST) calculations. By this means, an explicit treatment of torsional anharmonicity may be included in the TST rate constants and the magnitude of these effects can be assessed. Torsions are typically the lowest frequency modes of vibration in a molecule, and since partition functions are most sensitive to low frequency vibrations it is important that they are treated as accurately as possible to improve theoretical reproduction of thermodynamic properties.

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