

Hindered internal rotation in molecular systems: quantum statistics of equilibrium and rate constants in the Wigner function formalism

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Summary. The quantum statistics of a symmetric hindered internal rotator in a molecule or molecular complex is developed within the Wigner function formalism. Different shapes of the rotational barrier are considered. The partition function and the thermodynamic functions are given as Wigner–Kirkwood series expansions in terms of powers of Planck's constant squared. One gets simple closed expressions containing the modified Bessel functions J_0 and J_1 of the argument $iV_0/2kT$ where V_0 is the barrier height. Some problems concerning the evaluation of equilibrium and rate constants of chemical reactions are discussed.

Key words: Hindered rotation – Wigner–Kirkwood series – Partition functions – Thermodynamic functions

1. Introduction

The internal rotation of molecular groups (e.g. the methyl group) within molecules (e.g. ethane, polymers) or molecular complexes (e.g. $C_3H_6OH_2$) has been a topic of interest for many years [1, 2]. Related motions are the rotation of molecules adsorbed on solid surfaces [3, 4] and the torsional oscillations of molecules or ions in the interior of molecular crystals [5, 6]. The contributions of the corresponding degrees of freedom to the thermodynamic functions and to the equilibrium and rate constants are, generally, important. In calculations in the frame of statistical thermodynamics these rotators were mostly treated as (classical) free rotators [7] or sometimes as (harmonic) torsional oscillators [8].

However, the rotators have to be classified, in most cases, as hindered rotators or strongly anharmonic torsional oscillators, the more the lower the temperature is. There exists only a small number of papers on the quantum statistics of hindered rotators [9–13] whereas the literature on the quantum statistics of various types of anharmonic oscillators is abundant [14, 15]. The reason is that the Schrödinger equation for a hindered rotator is of the Mathieu–Hill type whose energy eigenvalues can be calculated only approxi-

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mately. Therefore, the evaluation of the partition function and the thermodynamic functions is possible only with numerical methods; closed general formulae cannot be derived from this approach [9, 10].

There exists, however, another general method to do quantum mechanics and quantum statistics: the Wigner function formalism [16, 17]. In this formalism, all expectation values of quantum mechanical observables and the partition function are calculated as phase space averages in analogy to classical statistical thermodynamics. The equivalent of the classical phase space distribution function is the Wigner quasi-probability distribution function. Energy eigenvalues or eigenvalues of other operators are not at all needed. The Wigner function formalism operates, in principle, without any approximation and includes zero-point energy and tunneling automatically. It is, therefore, a very suitable tool for the quantum statistics of nontrivial systems and has found wide applications in many different areas of physics and physical chemistry, see e.g. [11–13, 18–20].

The main quantities characterizing a hindered rotator are the shape and the strength of the potential barrier. For a symmetric rotator, the hindering potential can be given by:

$$V(\phi) = \frac{1}{2}V_0(1 - \cos n\phi) \quad (1)$$

where n is the symmetry number (e.g. $n = 3$ for the methyl group) or, more generally, by Fourier series [21]:

$$V(\phi) = \frac{1}{2}V_0 \left(1 - \sum_k a_k \cos kn\phi \right). \quad (2)$$

In the most simple case $V(\phi)$ is dominated by the repulsive interaction with a single near-neighbour atom within the molecule (or crystal) considered; then all coefficients a_k for $k \geq 2$ are zero. The presumption is also that the cosine series converges rather rapidly. A reasonable representation of the barrier can then be made with the first two terms. For the important case of $n = 3$ one has:

$$V(\phi) = \frac{1}{2}[V_3(1 - \cos 3\phi) - V_6 \cos 6\phi]. \quad (3)$$

The effect of adding a small sixfold potential $V_6 \cos 6\phi$ to the threefold main potential $V_3 \cos 3\phi$ is to broaden the potential wells at the expense of the barriers. (If V_6 is negative then the wells are narrowed and the barriers broadened.) For many acetates and other molecules and complexes containing the methyl group we have $V_6 \ll V_3$ (e.g. $V_6/V_3 \approx 0.15$ for acetates) [21].

The purpose of this paper is twofold:

- To show the utility and flexibility of the Wigner function formalism by means of another example
- To derive closed approximative expressions for the partition function and the thermodynamic functions for systems of (independent) symmetric hindered quantum rotators and to discuss their influence on the evaluation of equilibrium and rate constants.

The rest of the paper is organized as follows: In Sect. 2 we explain the Wigner function formalism and derive formulae for the partition function by means of the Wigner–Kirkwood series expansion in terms of even powers of Planck's constant. Section 3 contains the evaluation of the thermodynamic functions free energy, internal energy, entropy, and heat capacity. In Sect. 4 some problems concerning the statistical evaluation of chemical equilibrium and rate constants are discussed.

2. Wigner function formalism for the partition function of a hindered rotator

The starting point of the Wigner function formalism is the state space equivalent (the so-called Wigner equivalent) $A_w(p, q)$ of any quantum operator (observable) $A(\hat{P}, \hat{Q})$. If the operator \hat{A} is given in the coordinate representation by $\hat{A}(q, \hat{q}) = \langle q | \hat{A} | q' \rangle$ then its Wigner equivalent is defined by means of the Wigner transformation as:

$$A_w(p, q) = \int dz e^{ipz/\hbar} \left\langle q - \frac{z}{2} | \hat{A} | q + \frac{z}{2} \right\rangle. \quad (4)$$

The Wigner function $f_w(p, q)$ is essentially the Wigner equivalent of the density operator $\hat{\rho}$ and is given as:

$$f_w(p, q) = \frac{1}{(2\pi\hbar)^f} \int dz e^{ipz/\hbar} \left\langle q - \frac{z}{2} | \hat{\rho} | q + \frac{z}{2} \right\rangle. \quad (5)$$

Here f denotes the number of degrees of freedom of the system considered, p, q, z are corresponding vectors with f components, pz means the scalar product (in an Euclidean space), and $\int dz$ is an f -fold integral. For a single rotator with a fixed axis one has $f = 1$.

A key result of the Wigner approach is the formula for the expectation value $\langle \hat{A} \rangle$ of any operator \hat{A} in terms of a phase space integral [16, 17]:

$$\langle \hat{A} \rangle = \text{Tr}(\hat{\rho} \hat{A}) = \iint dp dq f_w(p, q) A_w(p, q). \quad (6)$$

This expression looks like a corresponding formula in the classical phase space statistics. The Wigner function $f_w(p, q)$ is, however, generally not a proper probability distribution and may become locally negative which is clearly a consequence of the Heisenberg uncertainty relations.

In equilibrium statistical thermodynamics the most important quantity is the partition function:

$$Z(T, V) = \text{Tr} e^{-\beta \hat{H}} = \sum_n e^{-\beta E_n} \quad (7)$$

where \hat{H} is the Hamiltonian of the system considered, E_n are its eigenvalues, and $\beta = 1/kT$. Now we introduce the Boltzmann operator $\hat{\Omega}$ and its Wigner equivalent Ω_w :

$$\hat{\Omega} = e^{-\beta \hat{H}}, \quad \Omega_w = (e^{-\beta \hat{H}})_w. \quad (8)$$

Then the partition function is given as:

$$Z = \iint dp dq \Omega_w(p, q; \beta).$$

The Bloch equation for the evaluation of $\hat{\Omega}$ reads:

$$\partial \hat{\Omega} / \partial \beta = -\hat{H} \hat{\Omega} = -\hat{\Omega} \hat{H} = -\frac{1}{2} [\hat{H}, \hat{\Omega}]_+$$

where $[\cdot, \cdot]_+$ denotes the anticommutator. The Wigner equivalent of Eq. (8) becomes [16]:

$$\frac{\partial \Omega_w}{\partial \beta} = -H_w \cos\left(\frac{\hbar}{2} A\right) \Omega_w \quad (9)$$

with the Poisson bracket operator or symplectic differential operator:

$$A = \frac{\partial'}{\partial p} \frac{\bar{\partial}}{\partial q} - \frac{\partial'}{\partial q} \frac{\bar{\partial}}{\partial p}. \tag{10}$$

For a system with one degree of freedom and a Hamiltonian:

$$H(\hat{P}, \hat{Q}) \Rightarrow H_w(p, q) = \frac{p^2}{2m} + V(q) \tag{11}$$

where $V(q)$ is potential energy the Bloch equation reads explicitly:

$$\frac{\partial \Omega_w}{\partial \beta} = - \left(\frac{\hbar^2}{8m} \frac{\partial^2}{\partial q^2} \right) \Omega_w - \cos \left(\frac{\hbar}{2} \frac{\partial}{\partial p} \frac{\partial'}{\partial q} \right) V(q) \Omega_w \tag{12}$$

here $\partial'/\partial q$ operates only on $V(q)$ and not on Ω_w .

The solution of Eq. (12) can be represented by the famous Wigner–Kirkwood series, an expansion in powers of \hbar^2 . With Eq. (7) this series reads for the partition function:

$$Z = \frac{1}{2\pi\hbar} \iint dp dq e^{-\beta(p^2/2m + V(q))} \sum_{n=0}^{\infty} \hbar^{2n} \Phi_n \tag{13}$$

with $\Phi_0 = 1$, and the terms Φ_n giving the quantum corrections to the classical partition function are to be calculated recursively according to:

$$\begin{aligned} \Phi_n(p, q; \beta) = & - \int_0^\beta d\beta' \left\{ e^{\beta'V} \frac{1}{8m} \frac{\partial^2}{\partial q^2} (\Phi_{n-1} e^{-\beta'V}) \right. \\ & \left. + e^{\beta'p^2/2m} \sum_{k=0}^{n-1} \frac{(-1)^{n+k-1}}{[2(n-k)]!} \left(\frac{1}{2} \frac{\partial}{\partial p} \frac{\partial'}{\partial q} \right)^{2(n-k)} V e^{-\beta'p^2/2m} \Phi_k \right\}. \end{aligned} \tag{14}$$

After integration over the momentum p , we get the partition function as:

$$\begin{aligned} Z = & \frac{1}{\hbar} \sqrt{\frac{m}{2\pi\beta}} \int dq e^{-\beta V} \left\{ 1 + \hbar^2 \frac{\beta^2}{12m} \left[-V'' + \frac{\beta}{2} (V')^2 \right] \right. \\ & + \hbar^4 \frac{\beta^4}{240m^2} \left[-V'''' + \beta \left(2V'V''' + \frac{3}{2}V''^2 \right) - \frac{11}{6} \beta^2 V'^2 V'' + \frac{5}{24} \beta^3 V'^4 \right] \\ & \left. + O(\hbar^6) + \dots \right\} \end{aligned} \tag{15}$$

where $V' = \partial V/\partial q$ and so forth. The advantage of this series expansion is that it gives the partition function as classical partition function plus quantum corrections $Z(\hbar^2)$:

$$Z = Z_{cl} + Z(\hbar^2) + Z(\hbar^4) + \dots \tag{16}$$

Because of the factors β^2, β^4, \dots this expansion converges rapidly for not too low temperatures [22, 23].

For a hindered rotator with a simple cosine potential the canonically conjugate coordinates are given by the rotation angle ϕ and the angular momentum L , respectively; and the mass is to be replaced by the moment of inertia I . The potential energy (hindering potential) $V(\phi)$ is in the most simple case specified as (cf. Eq. (1))

$$V(\phi) = \frac{1}{2} V_0 (1 - \cos n\phi). \tag{17}$$

In order to have a convenient comparison with the limiting case of a harmonic oscillator ($V_0 \rightarrow \infty$) we introduce the angular frequency ω of the harmonically oscillating torsional vibrator by:

$$\omega = \sqrt{\frac{V_0}{2I}} n. \quad (18)$$

With Eq. (17) the classical partition function is written as:

$$Z_{cl} = \frac{\sqrt{2\pi I/\beta}}{hn} e^{-x} \int_0^{2\pi} e^{x \cos n\phi} d\phi \quad (19)$$

where $x = \beta V_0/2$. We get the well-known expression:

$$Z_{cl} = Z_f e^{-x} I_0(x) \quad (20)$$

where

$$Z_f = \frac{\sqrt{2\pi I/\beta}}{h} \frac{2\pi}{n} \quad (21)$$

is the classical partition function of a free internal rotator of symmetry number n , and:

$$I_0(x) = J_0(ix) = \frac{1}{2\pi} \int_0^{2\pi} e^{x \cos n\phi} d\phi \quad (22)$$

is the modified Bessel function $I_0(x)$ (or the Bessel function $J_0(ix)$ of the purely imaginary argument ix) of order zero [24].

The evaluation of the quantum corrections $Z(\hbar^2)$ and $Z(\hbar^4)$ yields with $u = \beta\hbar\omega$

$$Z(\hbar^2) = Z_f e^{-x} \frac{u^2}{2\pi} \int_0^{2\pi} e^{x \cos n\phi} \left(-\frac{1}{12} \cos n\phi + \frac{1}{24} x \sin^2 n\phi \right) d\phi, \quad (23)$$

$$Z(\hbar^4) = Z_f e^{-x} \frac{u^4}{2\pi} \int_0^{2\pi} e^{x \cos n\phi} \frac{1}{240} \left(\frac{1}{x} \cos n\phi - 2 \sin^2 n\phi + \frac{3}{2} \cos^2 n\phi - \frac{11}{6} x \sin^2 n\phi \cos n\phi + \frac{5}{24} x^2 \sin^4 n\phi \right) d\phi. \quad (24)$$

All integrals in Eqs. (23) and (24) can be expressed by Bessel functions $J_\nu(z)$ of purely imaginary argument $z = ix$, where ν is a positive integer index [24]:

$$J_\nu(ix) = \frac{i^{-\nu}}{2\pi} \int_0^{2\pi} e^{ix \cos n\phi} \cos \nu n\phi d\phi \quad (25)$$

or by the modified Bessel functions:

$$I_\nu(x) = i^{-\nu} J_\nu(ix). \quad (26)$$

One gets:

$$Z(\hbar^2) = -Z_f e^{-x} \frac{1}{24} \beta^2 (\hbar\omega)^2 I_1(x), \quad (27)$$

$$Z(\hbar^4) = +Z_f e^{-x} \frac{1}{240} \beta^4 (\hbar\omega)^4 \left\{ -\frac{1}{x} I_1(x) + \frac{3}{2} \left[I_0(x) - \frac{1}{x} I_1(x) \right] - \frac{11}{24} x [I_1(x) - I_3(x)] + \frac{5}{8} I_2(x) \right\}. \quad (28)$$

By means of the recursive relations [24]:

$$I_{v-1}(x) - I_{v+1}(x) = 2vI_v(x)/x \quad (29)$$

we have finally the total partition function as a compact expression:

$$Z = Z_f e^{-x} I_0(x) \left\{ 1 - \frac{\beta^2(\hbar\omega)^2}{24} \frac{I_1(x)}{I_0(x)} + \frac{\beta^4(\hbar\omega)^4}{5760} \left(7 - \frac{2}{x} \frac{I_1(x)}{I_0(x)} \right) \right\}. \quad (30)$$

The factor in curly brackets represents the quantum correction to the classical partition of function of Eq. (20).

In the case of a modulated cosine potential given by:

$$V(\phi) = \frac{1}{2} V_0 (1 - \cos n\phi - \varepsilon \cos 2n\phi) \quad (31)$$

where $\varepsilon \approx 0.1$ for most molecules or molecular complexes, at first we calculate the classical partition function written in the shape:

$$Z_{cl} = Z_f e^{-x} \frac{1}{2\pi} \int_0^{2\pi} e^{x \cos n\phi} \left[1 + \sum_{v=1}^{\infty} \frac{x^v \varepsilon^v}{v!} \cos^v 2n\phi \right] d\phi. \quad (32)$$

With [24]:

$$\cos^{2\mu-1} 2n\phi = \frac{1}{2^{2\mu-2}} \sum_{k=0}^{\mu-1} \binom{2\mu-1}{k} \cos(2\mu-2k-1) 2n\phi, \quad (33)$$

$$\cos^{2\mu} 2n\phi = \frac{1}{2^{2\mu}} \left\{ \sum_{k=0}^{\mu-1} 2 \binom{2\mu}{k} \cos 2(\mu-k) 2n\phi + \binom{2\mu}{\mu} \right\} \quad (34)$$

one gets for Z_{cl} a series expansion in terms of Bessel functions $I_{2(2\mu-2k-1)}(x)$ and $I_{4(\mu-k)}(x)$, respectively. Clearly this series converges rather rapidly, and in practice one needs only terms up to the order ε or ε^2 . Therefore we use the approximation:

$$Z_{cl} = Z_f e^{-x} \frac{1}{2\pi} \int_0^{2\pi} e^{x \cos n\phi} \left[1 + \varepsilon x \cos 2n\phi + \varepsilon^2 \frac{x^2}{2} \cos^2 2n\phi \right] d\phi \quad (35)$$

and get, by use of (25), after elementary transformations

$$Z = Z_f e^{-x} I_0(x) \left[1 + \varepsilon x \frac{I_2(x)}{I_0(x)} + \varepsilon^2 \frac{x^2}{4} \left(1 + \frac{I_4(x)}{I_0(x)} \right) \right]. \quad (36)$$

Comparing this expression with the classical partition function of Eq. (20) without the potential proportional to $\varepsilon \cos 2n\phi$, we identify the factor in square brackets in Eq. (36) as the potential modulation correction factor in Z_{cl} . With the help of the recursive relations of Eq. (29) it is again possible to express the whole correction factor in terms of the Bessel functions $I_0(x)$ and $I_1(x)$ only:

$$Z_{cl} = Z_f e^{-x} I_0(x) \left[1 + \varepsilon x \left(1 - \frac{2I_1}{xI_0} \right) - \varepsilon^2 \frac{x^2}{2} \left\{ \left(1 + \frac{12}{x^2} \right) \frac{I_1}{I_0} - \frac{4}{x} \left(1 - \frac{6}{x^2} \right) \frac{I_1}{I_0} \right\} \right].$$

The full partition function is given by Eq. (16). We content ourselves with the first quantum correction $Z(\hbar^2)$ and write:

$$Z(\hbar^2) = Z_f e^{-x} \frac{1}{2\pi} \int_0^{2\pi} e^{x \cos n\phi} [1 + \varepsilon A_1 + \varepsilon^2 A_2] \frac{\hbar^2 \beta^2}{12I} \left\{ -V'' + \frac{\beta}{2} V'^2 \right\} d\phi \quad (37)$$

where

$$\begin{aligned} A_1 &= x \cos 2n\phi, \\ A_2 &= \frac{x^2}{2} \cos^2 2n\phi = \frac{x^2}{4} (1 + \cos 4n\phi), \end{aligned} \quad (38)$$

$$\begin{aligned} V' &= \frac{1}{2}V_0(n \sin n\phi + \varepsilon 2n \sin 2n\phi), \\ V'' &= \frac{1}{2}V_0(n^2 \cos n\phi + \varepsilon 4n^2 \cos 2n\phi). \end{aligned} \quad (39)$$

After somewhat lengthy calculations using elementary formulae for trigonometric functions of multiple arcs and Eqs. (25), (26), one ends with:

$$Z(\hbar^2) = -\frac{(\hbar\omega)^2\beta^2}{24} Z_f e^{-x} \{I_1(x) + \varepsilon x(\frac{3}{2}I_1(x) + I_3(x)) - \varepsilon^2 a\} \quad (40)$$

with

$$a = x(6I_0(x) - \frac{3}{2}I_1(x) + 4I_2(x) - I_3(x) - 2I_4(x)) + x^2(I_3(x) - I_5(x)).$$

This quantum correction again contains terms proportional to ε and ε^2 due to the potential modulation. From now on we neglect the term $\varepsilon^2 a$.

3. Thermodynamic functions

All thermodynamic functions for a system of hindered rotators without mutual interaction follow from the partition functions (30), and Eqs. (36) together with (40), respectively, by use of well-known formulae [13]. We derive the (Helmholtz) free energy F , the internal energy U , the entropy S , and the heat capacity C for one mole of rotators:

$$\begin{aligned} F &= -RT \ln Z, \\ U &= RT^2 \frac{\partial}{\partial T} \ln Z, \\ S &= R \left(\ln Z + T \frac{\partial}{\partial T} \ln Z \right), \\ C &= R \frac{\partial}{\partial T} \left(T^2 \frac{\partial}{\partial T} \ln Z \right). \end{aligned} \quad (41)$$

For the thermodynamic functions we restrict ourselves to the first quantum corrections and give again all thermodynamic functions as a sum of the classical contribution and the quantum correction, using the approximation $\ln(1+x) = x - x^2/2$.

For the simple hindered rotator we first get the free energy:

$$F = F_{cl} + F(\hbar^2) \quad (42)$$

where

$$F_{cl} = -RT \ln Z_f - RT(\ln I_0(x) - x) \quad (43)$$

is the free energy of the semiclassical approximation [56], and:

$$F(\hbar^2) = RT \frac{(\hbar\omega)^2\beta^2}{24} \frac{I_1(x)}{I_0(x)}. \quad (44)$$

(Notice that $\beta = 1/kT$, $x = V_0/2kT$). The internal energy U (that means, for the set of rotators, the enthalpy H likewise) is given by:

$$U = U_{cl} + U(\hbar^2) \quad (45)$$

with

$$U_{cl} = \frac{1}{2}RT + RTx \left(1 - \frac{I_1(x)}{I_0(x)} \right), \quad (46)$$

$$U(\hbar^2) = RT \frac{(\hbar\omega)^2\beta^2}{24} \left[\frac{I_1(x)}{I_0(x)} + x \left(1 - \left(\frac{I_1(x)}{I_0(x)} \right)^2 \right) \right]. \quad (47)$$

The entropy becomes:

$$S = S_{cl} + S(\hbar^2) \quad (48)$$

with

$$S_{cl} = R(\ln Z_f + \frac{1}{2}) + R \left[\ln I_0(x) - x \frac{I_1(x)}{I_0(x)} \right], \quad (49)$$

$$S(\hbar^2) = R \frac{(\hbar\omega)^2\beta^2}{24} x \left[1 - \left(\frac{I_1(x)}{I_0(x)} \right)^2 \right]. \quad (50)$$

Finally, the molar heat capacity is given by:

$$C = C_{cl} + C(\hbar^2) \quad (51)$$

with

$$C_{cl} = \frac{1}{2}R - R \left\{ x \frac{I_1(x)}{I_0(x)} - x^2 \left[1 - \left(\frac{I_1(x)}{I_0(x)} \right)^2 \right] \right\}, \quad (52)$$

$$C(\hbar^2) = -R \frac{(\hbar\omega)^2\beta^2}{24} x \left\{ 3 - \left(\frac{I_1(x)}{I_0(x)} \right)^2 - 2x \frac{I_1(x)}{I_0(x)} \left[1 - \left(\frac{I_1(x)}{I_0(x)} \right)^2 \right] \right\}. \quad (53)$$

Let us now consider the hindered rotator with the modulated cosine potential. First we write the full partition function according to Eqs. (36) and (40):

$$\begin{aligned} Z &= Z_{cl} + Z(\hbar^2) \\ &= Z_f e^{-xI_0(x)} \left[1 + \varepsilon x \frac{I_2(x)}{I_0(x)} + \varepsilon^2 \frac{x^2}{4} \left(1 + \frac{I_4(x)}{I_0(x)} \right) \right] \\ &\quad - Z_f e^{-xI_0(x)} \frac{(\hbar\omega)^2\beta^2}{24} \left[\frac{I_1(x)}{I_0(x)} + \varepsilon x \left(\frac{3}{2} \frac{I_1(x)}{I_0(x)} + \frac{I_3(x)}{I_0(x)} \right) \right] \\ &= Z_f e^{-xI_0(x)} \left[1 + B_1 - \frac{(\hbar\omega)^2\beta^2}{24} B_2 \right] \end{aligned} \quad (54)$$

where B_1, B_2 are temporary abbreviations (notice that $I_0(x) \geq 1$, $x = \beta V_0/2$). The free energy now becomes:

$$F = -RT \ln(Z_f e^{-xI_0}) - RT \left\{ B_1 - \frac{(\hbar\omega)^2\beta^2}{24} B_2 - \frac{1}{2} \left(B_1^2 - \frac{\beta^2(\hbar\omega)^2}{12} B_1 B_2 \right) \right\}. \quad (55)$$

Here again we take the quantum corrections up to terms in \hbar^2 and consider the potential modulation correction up to terms in ε^2 in the semiclassical contribu-

tions and up to terms in ε within the quantum correction. With these approximations we get finally:

$$\begin{aligned}
 F = & -RT \ln Z_f - RT(\ln I_0(x) - x) \\
 & - RT \left[\varepsilon x \frac{I_2(x)}{I_0(x)} + \varepsilon^2 \frac{x^2}{4} \left(1 + \frac{I_4(x)}{I_0(x)} - 2 \left(\frac{I_1(x)}{I_0(x)} \right)^2 \right) \right] \\
 & + RT \frac{\beta^2 (\hbar \omega)^2}{24} \left[\frac{I_1(x)}{I_0(x)} + \varepsilon x \left(\frac{3}{2} \frac{I_1(x)}{I_0(x)} + \frac{I_3(x)}{I_0(x)} - \frac{I_1(x)I_2(x)}{I_0^2(x)} \right) \right]. \quad (56)
 \end{aligned}$$

The last line in this expression represents the quantum correction. The somewhat lengthy formulae for the other thermodynamic functions follow in the known way.

4. Discussion: hindered rotators and equilibrium and rate constants

Numerous papers are concerned with the quantum statistics and thermodynamics of free rotating molecules or free rotators within molecules, e.g. polymer molecules, see [7, 25, 26]. In his study on free internal rotation in molecular complexes Slanina [7] points out that in all probability there is no system having a zero barrier height. In this paper we succeed in formulating a complete quantum statistical theory of realistic hindered rotators from first principles, i.e. by use of the phase space formalism (Wigner formalism) of quantum statistics. We obtain relatively simple formulae for the partition function and the most important thermodynamic functions.

A basic question is to what extent it is possible to separate the hindered rotation of an internal rotator from the other degrees of freedom of a molecule. This question is of particular interest in the case of van der Waals or hydrogen-bonded molecular complexes or other floppy molecular systems. It was shown [27] that even in extremely floppy complexes with wide amplitude vibrational or torsional motion the quantum term values are very well fit by a rigid or semirigid rotator Hamiltonian, at least for a limited range of not too high temperatures. Therefore we expect our approach to give reliable contributions of internal rotators to the partition function and the thermodynamic functions of molecules and molecular complexes.

In many cases, in particular for the statistical calculation of equilibrium constants and rate constants of chemical reactions it is convenient to write down the thermodynamic functions without the contributions of the zero point energy (ground state energy E_0) of the molecular system considered. In that case it is sufficient to simply subtract this energy from the full expressions for the free energy F and the internal energy U . (The entropy S and the heat capacity C are independent from E_0). The zero point energy may be calculated within the Wigner formalism for the quantum mechanics (at $T = 0$ K) or by use of perturbation theory for a corresponding quantum mechanical anharmonic oscillator [11].

The formulae for the partition functions derived above – possibly without the terms containing the zero-point energy – directly yield the contributions of the internal rotators to the equilibrium constant of any homogeneous chemical reaction. As is well known [13] this equilibrium constant is given by the product or ratios of the total partition functions of the molecular systems involved. In

particular, in the important case of an isotopic exchange reaction the equilibrium constant is directly determined by the partition function ratio of the isotopic molecules considered.

Likewise the partition functions including that of an activated complex enter the formulae for the evaluation of rate constants of chemical reactions in the frame of the Eyring theory of absolute reaction rates. Again the isotopic effects in the kinetics of homogeneous chemical reactions are directly given by the corresponding partition function ratios [13].

The accuracy of the expressions for the partition function and the thermodynamic functions can be discussed by comparison with the tables of Pitzer and Gwinn [9] and Li and Pitzer [10], cf. [11, 13]. We conclude that for the most part of molecules and molecular complexes and in particular for the most interesting range of temperatures $T = 300 \cdots 700$ K our formulae have a completely sufficient accuracy of fractions of one per cent. Therefore, the contributions of hindered rotators to equilibrium and rate constants of chemical reactions including isotopic exchange reactions and isotopic kinetic effects can be calculated with a high reliability.

Our reasoning is found on Boltzmann quantum statistics. Slanina [7] remarks that at low temperatures Fermi–Dirac or Bose–Einstein statistics should be used. This remark certainly is incorrect because the molecules or molecular complexes carrying the rotators (e.g. CH_3) are localizable and thus distinguishable in the gaseous, liquid or solid state (their masses are high enough). The situation is here the same as in the case of nuclear magnetic resonance where spins – though being typical quantum objects – are nevertheless correctly treated with Boltzmann statistics.

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