

# Wigner Expansions for Partition Functions of Nonrelativistic and Relativistic Oscillator Systems

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## Abstract

The equilibrium quantum statistics of various anharmonic oscillator systems including relativistic systems is considered within the Wigner phase space formalism. For this purpose the Wigner series expansion for the partition function is generalised to include relativistic corrections. The new series for partition functions and all thermodynamic potentials yield quantum corrections in terms of powers of  $\hbar^2$  and relativistic corrections given by Kelvin functions (modified Hankel functions)  $K_\nu(mc^2/kT)$ . As applications are treated the symmetric Toda oscillator, isotonic and singular anharmonic oscillators and hindered rotators, i.e. oscillators with cosine potential.

## 1 Introduction

In recent years, the Wigner formalism as a phase space representation of quantum mechanics, quantum field theory and quantum statistics has found growing interest [1,2]. One of the main fields is the theory of anharmonic oscillator systems modelling various quantum systems, e.g. solitonic systems, quantum field theories, and transport processes in more complicated systems. The purpose of this paper is twofold,

1. to generalize the Wigner series expansion of equilibrium phase space quantum statistics in order to include special relativistic systems,
2. to show applicability and utility of the formalism by means of various examples.

Up to now a small number of papers on relativistic quantum theory in the Wigner formalism have appeared for equilibrium as well as for nonequilibrium systems. The topics treated for nonequilibrium processes range from multiparticle production and kinetic theory [3] to cosmology [4]. In the realm of relativistic phase space quantum mechanics there exist only a few papers. Janussis et al. [5] starting from the Dirac Hamiltonian introduce a Wigner function with  $4 \times 4$  spinor components. Ali [6] discusses the quantization of relativistic systems on phase space whereas Kim and Wigner [7] describe a covariant phase space representation for harmonic oscillators. A relativistic Fermi gas is treated in the frame work of the grand canonical ensemble by Greiner et al.

[8]. A pseudo-classical phase space description of the relativistic electron in terms of Grassmann variables was given in several versions [9]. There are also papers on relativistic quantum kinematics [10,11].

Over the years, fundamental problems regarding the correct description of simple systems such as the classical relativistic harmonic oscillator and its quantization have been treated in a number of publications, see f.i. [12-15]. Important papers on the covariance problem are [7,16]; a symplectic formulation of relativistic quantum mechanics has been given in [17,18]. We develop a Wigner formalism which is frame dependent. The focus of our attention is the comoving frame, i.e., we use the so-called synchronous gauge [19].

## 2 Relativistic Wigner Formalism

One of the advantages of the phase space methods of quantum statistics - Wigner-Weyl formalism [1], coherent state methods [20], Husimi transforms [21] or Bargmann representation [22] - is the possibility to evaluate exactly the partition function by means of a phase space integration. In practice it is convenient to expand the phase space integral into the Wigner series in powers of  $\hbar^2$  [23] as a basis of semiclassical quantum statistics.

The (non-relativistic) Wigner function  $f_W(q, p)$  can be defined as the Fourier transform of the off-diagonal elements of the density operator  $\langle q | \rho | q' \rangle$  (for systems without spin) [1]:

$$f_W(q, p) = \frac{1}{(2\pi\hbar)^f} \int dz \exp(ipz/\hbar) \langle q - \frac{z}{2} | \rho | q + \frac{z}{2} \rangle \quad (1)$$

Here  $f$  is the number of the degrees of freedom of the system considered. The density operator is given in the coordinate representation by

$$\langle q | \rho | q' \rangle = \sum_n \psi_n^*(q') w_n \psi_n(q) \quad (2)$$

with  $w_n = \exp(-\beta E_n)/Z$ , where  $\hat{H}\psi_n = E_n\psi_n$ ,  $\beta = 1/kT$ , and the partition function is

$$Z = \text{Tr} \exp(-\beta \hat{H}) = \sum_n \exp(-\beta E_n) \quad (3)$$

Within the frame of the Wigner formalism the partition function can be expressed as

$$Z = \iint dq dp \Omega_W(q, p; \beta) \quad , \quad (4)$$

where  $\Omega_W = (\exp(-\beta \hat{H}))_W$  is the Wigner equivalent of the operator  $\hat{\Omega} = \exp(-\beta \hat{H})$  defined as

$$\Omega_W(q, p; \beta) = \int dz \exp(ipz/\hbar) \langle q - \frac{z}{2} | \hat{\Omega} | q + \frac{z}{2} \rangle \quad (5)$$

The Bloch equation for the calculation of  $\Omega_W$  within the Wigner formalism reads

$$\frac{\partial \Omega_W(q, p; \beta)}{\partial \beta} = -H_W(q, p) \cos\left(\frac{\hbar}{2}\Lambda\right) \Omega_W(q, p; \beta) \quad , \quad (6)$$

here  $H_W(q, p)$  is the Wigner equivalent of the Hamiltonian  $\hat{H}$ , and  $\Lambda$  denotes the Poisson Bracket operator or symplectic differential operator

$$\Lambda = \frac{\partial \leftarrow}{\partial p} \frac{\partial \leftarrow}{\partial q} - \frac{\partial \leftarrow}{\partial q} \frac{\partial \leftarrow}{\partial p} \quad (7)$$

acting in (6) to the left and right hand sides. Up to now the formalism is completely exact. The partition function (4) can be calculated by means of a phase space integration without any knowledge of the energy levels of the system considered and without the necessity to sum up an infinite series of Boltzmann terms  $\exp(-\beta E_n)$ , the zero-point energy being already included.

In order to elucidate the principle of our formalism, we consider a system with a single degree of freedom characterized by a Hamiltonian  $\hat{H} = H_0(\hat{p}) + V(\hat{q})$  with

$$H_0(\hat{p}) = \sqrt{m^2 c^4 + \hat{p}^2 c^2} - mc^2 \quad (8)$$

and the potential energy  $V(q)$ . One has  $H_W(q, p) = H_0(p) + V(q)$ . The Wigner series [17] for the partition function  $Z$  is given by

$$Z = \frac{1}{2\pi\hbar} \iint dq dp \exp\{-\beta(H_0(p) + V(q))\} \sum_{n=0}^{+\infty} \hbar^{2n} \Phi_n(q, p; \beta) \quad (9)$$

with  $\Phi_0 = 1$ ,  $\Phi_n$ : n-th quantum correction. Solving the Bloch equation (6) for our relativistic quantum system yields

$$\Phi_1(q, p; \beta) = -\frac{1}{8}\beta^2 H_0'' V'' + \frac{1}{24}\beta^3 (H_0'' V'^2 + H_0'^2 V'') \quad (10)$$

where the primes denote differentiation with respect to the corresponding variables. We restrict ourselves to the first quantum correction.

We will evaluate (9) with (10), this approximative partition function is denoted by  $Z_{01}$ . We begin with the p-integration:

$$\begin{aligned} Z_{01}(k_{in}) &= Z_0(k_{in}) + Z_1(k_{in}) \quad (11) \\ \text{with } Z_0(k_{in}) &= \frac{1}{2\pi\hbar} \int e^{-\beta H_0(p)} dp \\ \text{and } Z_1(k_{in}) &= \frac{1}{2\pi\hbar} \int e^{-\beta H_0(p)} \hbar^2 \left[ -\frac{1}{8}\beta^2 H_0'' V'' + \frac{1}{24}\beta^3 (H_0'' V'^2 + H_0'^2 V'') \right] dp \end{aligned}$$

Substituting  $p/mc = \sinh u$  and using [43]

$$\int_0^{\infty} e^{b \cosh u} \cosh \nu u \, du = K_\nu(b) \quad (12)$$

where the  $K_\nu$  denote the Kelvin functions (modified Hankel functions) one gets

$$Z_0(k_{in}) = 2 \frac{1}{2\pi\hbar} e^{+\beta mc^2} mc K_1(\beta mc^2) \quad (13)$$

and after some algebra

$$\begin{aligned}
Z_{1(kin)} &= 2 \frac{1}{2\pi\hbar} e^{+\beta mc^2} c\hbar^2 \left[ -\frac{1}{8} \beta^2 V'' + \frac{1}{24} \beta^3 V'^2 \right] \times \\
&\times \left[ \frac{206}{128} K_1(\beta mc^2) - \frac{93}{128} K_3(\beta mc^2) + \frac{15}{128} K_5(\beta mc^2) \right] + \\
&+ 2 \frac{1}{2\pi\hbar} e^{+\beta mc^2} m c \hbar^2 \frac{1}{24} \beta^3 V'' c^2 \times \\
&\times \left[ -\frac{48}{128} K_1(\beta mc^2) + \frac{56}{128} K_3(\beta mc^2) - \frac{8}{128} K_5(\beta mc^2) \right]
\end{aligned} \tag{14}$$

where the series expansions

$$\left[ 1 + \frac{p^2}{m^2 c^2} \right]^{-3/2} = [1 + \sinh^2 u]^{-3/2} \simeq 1 - \frac{3}{2} \sinh^2 u + \frac{15}{8} \sinh^4 u \tag{15}$$

and

$$\frac{p^2}{m^2 c^2} \left[ 1 + \frac{p^2}{m^2 c^2} \right]^{-1} = \sinh^2 u [1 + \sinh^2 u]^{-1} \simeq \sinh^2 u - \sinh^4 u \tag{16}$$

have been used.

Now the integration over the momentum space is done, and (13), (14) represent, as a main result, the partition function up to the first quantum correction, proportional to  $\hbar^2$ , and relativistic corrections up to second and fourth order in  $p/mc$ . To proceed further one has to take into account the potential  $V(q)$  of the system considered. Then the full partition function (in our approximation) is given by

$$Z_{01} = Z_0 + Z_1 = \int dq \exp(-\beta V(q)) Z_{01(kin)}(q) \tag{17}$$

Here we only mention that with

$$K_1(z) \simeq \sqrt{\frac{\pi}{2z}} e^{-z}$$

in  $Z_{0(kin)}$  and

$$K_1(z) \simeq \sqrt{\frac{\pi}{2z}} e^{-z} \left( 1 + \frac{3}{8z} \right) , \quad K_3(z) = \sqrt{\frac{\pi}{2z}} e^{-z} \left( 1 + \frac{35}{8z} \right) , \quad K_5(z) = \sqrt{\frac{\pi}{2z}} e^{-z} \left( 1 + \frac{99}{8z} \right)$$

in  $Z_{1(kin)}$  the non-relativistic limit is reproduced correctly.

### 3 Toda oscillator

As a first example we choose the symmetric relativistic quantum Toda oscillator with the potential

$$V(q) = V_0 (\cosh aq - 1) \tag{18}$$

Its eigenvalues are not exactly known. If we compare (18) with the potential  $V(q) = m\omega_0^2 q^2 / 2$  of the harmonic oscillator we find

$$a = \sqrt{m\omega_0^2 / V_0} \tag{19}$$

where  $\omega_0$  is the (circular) frequency for harmonic (i.e. very small) oscillations. Toda molecules are discussed in [24], generalizations thereof in [25]. There exist a few papers on quantum statistics of toda chains [26] and Toda fields [27]. The non-relativistic phase space quantum statistics of the symmetric Toda oscillator with (18) is treated in [28]. The dynamics of non quantum relativistic Toda lattices is the topic of [29-31].

The part  $Z_0$  of (17) becomes

$$Z_0 = 2 \frac{1}{2\pi\hbar} e^{\beta mc^2} mc K_1(\beta mc^2) e^{\beta V_0} \frac{2}{a} K_0(\beta V_0) \quad (20)$$

and the part  $Z_1$  can be expressed as

$$\begin{aligned} Z_1 = & 2\hbar^2 \frac{1}{2\pi\hbar} c e^{\beta mc^2} K_1(\beta V_0) \beta^2 V_0 e^{\beta V_0} \times \\ & \times \left\{ -\frac{1}{6} \left[ \frac{206}{128} K_1(\beta mc^2) - \frac{93}{128} K_3(\beta mc^2) + \frac{15}{128} K_5(\beta mc^2) \right] + \right. \\ & \left. + \frac{mc^2\beta}{12} \left[ -\frac{48}{128} K_1(\beta mc^2) + \frac{56}{128} K_3(\beta mc^2) - \frac{8}{128} K_5(\beta mc^2) \right] \right\} \quad (21) \end{aligned}$$

The formulae (20) and (21) yield in the nonrelativistic limit  $kT \ll mc^2$  the correct partition function of [28]. The evaluation of higher order relativistic and quantum corrections is straight forward. From the Wigner series for the partition function, corresponding series expressions for the thermodynamic potentials follow in the well-known manner. These results are published in [32].

## 4 Isotonic or Singular Oscillator

Our next example is the quantum oscillator with the potential energy

$$V(q) = V_0 \left[ \frac{q}{a} - \frac{a}{q} \right]^2 \quad (22)$$

(normalized so that the potential minimum at  $q_{min} = a$  gives  $V(q_{min}) = 0$ ). This asymmetric anharmonic oscillator appears in the literature under various headings in two different interpretations:

1. isotonic oscillator [33-36], radial oscillator (with centripetal barrier) [37-39] or inverse quadratic oscillator [40],
2. singular oscillator [41] or nonpolynomial oscillator [42].

Interesting subject for oscillators of this type are the energy spectrum [38], canonical transformations [37], ladder operators and coherent states [34-36], phase space path integrals and the dynamics and symplectic groups [37,41]. The connection with three-dimensional potentials was discussed thoroughly [39]. Here we add the second quantum correction to the partition function:

$$Z(\hbar^4) = \frac{1}{\hbar} \sqrt{\frac{m}{2\pi\beta}} \int e^{-\beta V(q)} \frac{\hbar^4 \beta^3}{240m^2} Q(q) dq \quad (23)$$

where

$$Q(q) = -V^{(4)} + \beta(2V'V^{(3)} + \frac{3}{2}V''^2) - \frac{11}{6}\beta^2V''^2V'' + \frac{5}{24}\beta^3V''^4 \quad (24)$$

here is  $V' = \partial V(q)/\partial q$ ,  $V^{(3)} = V'''$ , and so forth. For the isotonic oscillator potential (22) all integrals to be calculated are of the type [43]:

$$\int_0^{\infty} x^{n-1} e^{-(Ax^2+Bq^{-2})} dx = \left[\frac{B}{A}\right]^{n/4} K_{n/2}(2\sqrt{AB}) \quad (25)$$

where the  $K$ -functions are again the modified Hankel functions (Kelvin functions) but here only of half integer index,  $n$  is an odd integer. These functions have a simple analytical shape, in particular one has

$$\begin{aligned} K_{\pm 1/2}(z) &= \sqrt{\frac{\pi}{2z}} e^{-z} \\ K_{\pm 3/2}(z) &= \sqrt{\frac{\pi}{2z}} e^{-z} \left(1 + \frac{1}{z}\right) \\ K_{\pm 5/2}(z) &= \sqrt{\frac{\pi}{2z}} e^{-z} \left(1 + \frac{3}{z} + \frac{3}{z^2}\right) \\ &\vdots \end{aligned} \quad (26)$$

In (25) one has for the isotonic oscillator

$$A = \beta V_0/a^2, \quad B = \beta V_0 a^2, \quad z = 2\sqrt{AB} = 2\beta V_0 \quad (27)$$

The exact classical (i.e. semiclassical) partition function becomes

$$Z_{cl} = kT/\hbar\omega \quad (28)$$

where

$$\omega = \sqrt{8V_0/ma^2} \quad (29)$$

is the classical (angular) frequency of our oscillator in the limit of very small (i.e. harmonic) oscillations. The partition function (28) is formally the same as the well-known expression for the classical harmonic oscillator with (angular) frequency  $\omega$ .

A simple but somewhat lengthy calculation then yields the first two terms of the partition function

$$Z = \frac{kT}{\hbar\omega} \left\{ 1 - \left[ \frac{1}{24} \left( \frac{\hbar\omega}{kT} \right)^2 \left( 1 + \frac{3kT}{8V_0} \right) \right] \right\} \quad (30)$$

where the expression in the square brackets being the famous  $\hbar^2/24$  quantum correction. The higher order quantum corrections can be calculated in a similar way using (25). Again all integrals lead only to the handy Kelvin functions with half-integer index. As is well known one gets the thermodynamic functions for a system of  $N$  oscillators from the partition function. The

(Helmholtz) free energy (here identical to the free enthalpy  $G$ ), the internal energy  $U$  (here identical to the enthalpy  $H$ ), the entropy  $S$  and the heat capacity  $C = \partial U / \partial T$  are given, respectively, by

$$\begin{aligned} F &= -NkT \ln Z \\ U &= NkT^2 \frac{\partial}{\partial T} \ln Z \\ S &= Nk(\ln Z + T \frac{\partial}{\partial T} \ln Z) \\ C &= Nk \frac{\partial}{\partial T} (T^2 \frac{\partial}{\partial T} \ln Z) \end{aligned} \quad (31)$$

Starting from (30) these functions can be written in the form of classical contribution plus quantum correction up to terms with  $\hbar^2$  using the series expansion of the logarithm function:

$$F = -NkT \left\{ \ln \frac{kT}{\hbar\omega} - \frac{1}{24} \left( \frac{\hbar\omega}{kT} \right)^2 \left( 1 + \frac{3kT}{8V_0} \right) \right\} \quad (32)$$

$$U = NkT \left\{ 1 + \frac{1}{12} \left( \frac{\hbar\omega}{kT} \right)^2 + \frac{1}{64} \frac{(\hbar\omega)^2}{V_0 kT} \right\} \quad (33)$$

$$S = Nk \ln \frac{kT}{\hbar\omega} + Nk \left\{ 1 + \frac{1}{24} \left( \frac{\hbar\omega}{kT} \right)^2 \right\} \quad (34)$$

$$C = Nk \left\{ 1 - \frac{1}{12} \left( \frac{\hbar\omega}{kT} \right)^2 \right\} \quad (35)$$

More detailed estimates show that these semiclassical expressions are of considerable accuracy for atomic oscillators above  $T = 100$  K, the errors being only a few percent and enlarging in the order  $F, U, S, C$ .

## 5 Hindered Rotators

The internal rotation of molecular groups (f.i. the methyl group) within molecules (f.i. ethane, polymers) or molecular complexes (f.i.  $C_3H_6OH_2$ ) is a topic of large interest since many years [44,45]. Related motions are the rotation of molecules adsorbed on solid surfaces [46,47] and the torsional oscillations of molecules or ions in the interior of molecular crystals [48,49]. 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 [50] or sometimes as (harmonic) torsional oscillators [51].

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 few number of papers on the quantum statistics of hindered rotators [52-56] whereas the literature on the quantum statistics of various types of anharmonic oscillators is abundant. The reason is that the Schrödinger equation for a hindered rotator is of the Mathieu-Hill type whose energy eigenvalues can be calculated only approximately. 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 [52,53]. Here, the Wigner formalism shows its advantages.

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

$$V(\phi) = \frac{1}{2}V_0(1 - \cos n\phi) \quad (36)$$

where  $n$  is the symmetry number (f.i.  $n = 3$  for the methyl group) or, more generally, by Fourier series [57]

$$V(\phi) = \frac{1}{2}V_0(1 - \sum_k a_k \cos kn\phi) \quad (37)$$

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

$$V(\phi) = \frac{1}{2}[V_3(1 - \cos 3\phi) - V_6 \cos 6\phi] \quad (38)$$

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  $V_6 \ll V_3$  (f.i.  $V_6/V_3 \approx 0.15$  for acetates) [57].

For a hindered rotator with a simple cosine potential the canonically conjugate coordinates are given by the rotation angle  $\phi$  and the angular momentum  $L$ , respectively; and the mass is to be replaced by the moment of inertia  $I$ .

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

$$\Omega = \sqrt{\frac{V_0}{2I}} n \quad (39)$$

With (36) the classical partition function is written as

$$Z_{cl} = \frac{\sqrt{2\pi I/\beta}}{hn} e^{-x} \int_0^{2\pi} e^{x \cos n\phi} d\phi \quad (40)$$

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

$$Z_{cl} = Z_f e^{-x} I_0(x) \quad (41)$$

where

$$Z_f = \frac{\sqrt{2\pi I/\beta}}{h} \frac{2\pi}{n} \quad (42)$$

is the classical partition function of a free internal rotator of symmetry number  $n$ , and  $I_0(x)$  is the modified Bessel function (or the Bessel function  $J_0(ix)$  of the purely imaginary argument  $ix$ ) of order zero [43].



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

$$Z(\hbar^2) = Z_f e^{-x} \frac{u^2}{2\pi} \int_0^{2\pi} e^{x \cos n\phi} \left( -\frac{1}{12} \cos n\phi + \frac{1}{24} x \sin^2 n\phi \right) d\phi \quad (43)$$

$$Z(\hbar^4) = Z_f e^{-x} \frac{u^4}{2\pi} \int_0^{2\pi} e^{x \cos n\phi} \left[ \frac{1}{240} \left( \frac{1}{x} \cos n\phi - 2 \sin^2 n\phi + \frac{3}{2} \cos^2 n\phi - \frac{11}{6} x \sin^2 n\phi \cos n\phi + \frac{5}{24} x^2 \sin^4 n\phi \right) \right] d\phi \quad (44)$$

All integrals in (43) and (44) can be expressed by Bessel functions  $J_\nu(z)$  of purely imaginary argument  $z = i\xi$ , where  $\nu$  is a positive integer index [43],

$$J_\nu(ix) = \frac{i^{-\nu}}{2\pi} \int_0^{2\pi} e^{ix \cos n\phi} \cos \nu n\phi d\phi \quad (45)$$

or by the modified Bessel functions

$$I_\nu(x) = i^{-\nu} J_\nu(ix) \quad (46)$$

One gets

$$Z(\hbar^2) = -Z_f e^{-x} \frac{1}{24} \beta^2 (\hbar\omega)^2 I_1(x) \quad (47)$$

$$Z(\hbar^4) = +Z_f e^{-x} \frac{1}{240} \beta^4 (\hbar\omega)^4 \left\{ -\frac{1}{\xi} I_1(x) + \frac{3}{2} [I_0(x) - \frac{1}{\xi} I_1(x)] - \frac{11}{24} \xi [I_1(x) - I_3(x)] + \frac{5}{8} I_2(x) \right\} \quad (48)$$

By means of the recursive relations [43]

$$I_{\nu-1}(x) - I_{\nu+1}(x) = 2\nu I_\nu(x)/x \quad (49)$$

we have finally the total partition function as a compact expression

$$Z = Z_f e^{-x} I_0(x) \left\{ 1 - \frac{\beta^2 (\hbar\omega)^2}{24} \frac{I_1(x)}{I_0(x)} + \frac{\beta^4 (\hbar\omega)^4}{5760} \left( 7 - \frac{2}{\xi} \frac{I_1(x)}{I_0(x)} \right) \right\} \quad (50)$$

The factor in curly brackets represents the quantum correction to the classical partition function (41).

In the case of a modulated cosine potential given by

$$V(\phi) = \frac{1}{2} V_0 (1 - \cos n\phi - \epsilon \cos 2n\phi) \quad (51)$$

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

$$Z_{cl} = Z_f e^{-\epsilon} \frac{1}{2\pi} \int_0^{2\pi} e^{x \cos n\phi} \left[ 1 + \sum_{\nu=1}^{\infty} \frac{x^\nu \epsilon^\nu}{\nu!} \cos^\nu 2n\phi \right] d\phi \quad (52)$$

With [43]

$$\cos^{2\mu-1} 2n\phi = \frac{1}{2^{2\mu-2}} \sum_{k=0}^{\mu-1} \binom{2\mu-1}{k} \cos(2\mu-2k-1)2n\phi \quad (53)$$

$$\cos^{2\mu} 2n\phi = \frac{1}{2^{2\mu}} \left\{ \sum_{k=0}^{\mu-1} 2 \binom{2\mu}{k} \cos 2(\mu-k)2n\phi + \binom{2\mu}{\mu} \right\} \quad (54)$$

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  $\epsilon$  or  $\epsilon^2$ . Therefore we use the approximation

$$Z_{cl} = Z_f e^{-\epsilon} \frac{1}{2\pi} \int_0^{2\pi} e^{x \cos n\phi} \left[ 1 + \epsilon x \cos 2n\phi + \epsilon^2 \frac{x^2}{2} \cos^2 2n\phi \right] d\phi \quad (55)$$

and get, by use of (45), after elementary transformations

$$Z = Z_f e^{-\epsilon} I_0(x) \left[ 1 + \epsilon x \frac{I_2(x)}{I_0(x)} + \epsilon^2 \frac{x^2}{4} \left( 1 + \frac{I_4(x)}{I_0(x)} \right) \right] \quad (56)$$

Comparing this expression with the classical partition function (41) without the potential proportional to  $\epsilon \cos 2n\phi$ , we identify the factor in square brackets in (56) as the potential modulation correction factor in  $Z_{cl}$ . With the help of the recursive relations (49) it is again possible to express the whole correction factor in terms of the Bessel functions  $I_0(\xi)$  and  $I_1(\xi)$  only.

We content ourselves with the first quantum correction  $Z(\hbar^2)$  and write

$$Z(\hbar^2) = Z_f e^{-\epsilon} \frac{1}{2\pi} \int_0^{2\pi} e^{x \cos n\phi} \left[ 1 + \epsilon R_1 + \epsilon^2 R_2 \right] \frac{\hbar^2 \beta^2}{12I} \left\{ -V'' + \frac{\beta}{2} V'^2 \right\} d\phi \quad (57)$$

where

$$R_1 = x \cos 2n\phi \quad (58)$$

$$R_2 = \frac{x^2}{2} \cos^2 2n\phi = \frac{x^2}{4} (1 + \cos 4n\phi) \quad (59)$$

$$V' = \frac{1}{2} V_0 (n \sin n\phi + \epsilon 2n \sin 2n\phi) \quad (60)$$

$$V'' = \frac{1}{2} V_0 (n^2 \cos n\phi + \epsilon 4n^2 \cos 2n\phi) \quad (61)$$

After somewhat lengthy calculations using elementary formulae for trigonometric functions of multiple arcs and (45), (46), one ends with

$$Z(\hbar^2) = -\frac{(\hbar\omega)^2\beta^2}{24} Z_f e^{-x} \{I_1(x) + \epsilon x \left(\frac{3}{2}I_1(x) + I_3(x)\right) - \epsilon^2 a\} \quad (62)$$

with

$$a = x(6I_0(x) - \frac{3}{2}I_1(x) + 4I_2(x) - I_3(x) - 2I_4(x)) + x^2(I_3(x) - I_5(x)) \quad (63)$$

This quantum correction again contains terms proportional to  $\epsilon$  and  $\epsilon^2$  due to the potential modulation. From now we neglect the term  $\epsilon^2 a$ . For the free energy of this simple hindered rotator we get:

$$F = F_{cl} + F(\hbar^2) \quad (64)$$

where

$$F_{cl} = -RT \ln Z_f - RT(\ln I_0(x) - x) \quad (65)$$

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

$$F(\hbar^2) = RT \frac{(\hbar\omega)^2\beta^2}{24} \frac{I_1(x)}{I_0(x)} \quad (66)$$

Now we come to the hindered rotator with the modulated cosine potential. First we write the full partition function according to (56)

$$\begin{aligned} Z &= Z_{cl} + Z(\hbar^2) \\ &= Z_f e^{-x} I_0(x) \left[ 1 + \epsilon x \frac{I_2(x)}{I_0(x)} + \epsilon^2 \frac{x^2}{4} \left( 1 + \frac{I_4(x)}{I_0(x)} \right) \right] - \\ &\quad - Z_f e^{-x} I_0(x) \frac{(\hbar\omega)^2\beta^2}{24} \left[ \frac{I_1(x)}{I_0(x)} + \epsilon x \left( \frac{3}{2} \frac{I_1(x)}{I_0(x)} + \frac{I_3(x)}{I_0(x)} \right) \right] \\ &= Z_f e^{-x} I_0(x) \left[ 1 + A - \frac{(\hbar\omega)^2\beta^2}{24} B \right] \end{aligned} \quad (67)$$

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

$$F = -RT \ln(Z_f e^{-x} I_0) - RT \left\{ A - \frac{(\hbar\omega)^2\beta^2}{24} B - \frac{1}{2} \left( A^2 - \frac{\beta^2(\hbar\omega)^2}{12} AB \right) \right\} \quad (68)$$

Here again we take the quantum correction up to terms in  $\hbar^2$  and consider the potential modulation correction up to terms in  $\epsilon^2$  in the semiclassical contributions and up to terms in  $\epsilon$  within the quantum correction. With these approximations we get finally:

$$\begin{aligned} F &= -RT \ln Z_f - RT(\ln I_0(x) - x) - RT \left[ \epsilon x \frac{I_2(x)}{I_0(x)} + \epsilon^2 \frac{x^2}{4} \left( 1 + \frac{I_4(x)}{I_0(x)} - 2 \left( \frac{I_1(x)}{I_0(x)} \right)^2 \right) \right] + \\ &\quad + RT \frac{\beta^2(\hbar\omega)^2}{24} \left[ \frac{I_1(x)}{I_0(x)} + \epsilon x \left( \frac{3}{2} \frac{I_1(x)}{I_0(x)} + \frac{I_3(x)}{I_0(x)} - \frac{I_1(x)I_2(x)}{I_0^2(x)} \right) \right] \end{aligned} \quad (69)$$

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