Analytical Results for the Partition Function of a Generalized Anharmonic Oscillator

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The classical partition function, the semiclassical partition function in the Wigner-Kirkwood-perturbation approximation and the exact quantum statistical upper and lower bounds to the partition function for the general single and double well anharmonic oscillator with

$$\hat{H} = \hat{p}^2/2\,m + (m\,\omega^2/2)\,\hat{x}^2 + k_{2n}\,\hat{x}^{2n}, \quad n \geqq 2$$

and $\omega^2 \lesseqgtr 0$ are calculated by a simple integration. The quickly converging series is evaluated numerically for $n = 2$ and compared with numerical summations of Boltzmann-factors with eigenvalues from the literature. Matrix elements of $\exp(-\alpha x^{2n})$ in a harmonic oscillator basis are calculated as by-products.

1. Introduction

The Quantum Mechanics of Generalized Anharmonic Oscillators

Anharmonic oscillators are very important in the theory of elementary particles, of structural phase transitions in solid state physics and of molecular vibrational motions. Furthermore, a lot of work has been published recently in connection with the convergence of perturbation series. We shall take the opportunity to summerize some recent results.

1.1. Single well Oscillators

Oscillators with

$$\hat{H}_{2\mu}(k,\lambda) = -\frac{\mathrm{d}^2}{\mathrm{d}x^2} + k\hat{x}^2 + \lambda\hat{x}^{2\mu} \quad (k, \lambda > 0) \tag{1}$$

have been investigated by Hioe and Montroll [1] for $\mu = 2$, by Hioe, MacMillen and Montroll [2] for $\mu = 3, 4$ and by Banerjee [3] for $\mu = 2, 3, 4$ by using nonperturbative methods. For $\mu = 2$ the results of Hioe and Montroll are especially well suited for statistical calculations, as the eigenvalues for $\lambda \geqq 0,2$ are given in analytical form. The authors discuss the behaviour of solutions in different regimes of the quantum number n and the constants k and λ and give for the first eigenvalues for various constants tabulated eigenvalues. As these are important for low temperatures, the tables are useful for the low temperature approximation to the partition function (in the following abbreviated as PF). The calculation of higher eigenvalues, according to the same technique, is laborious and needs computation time for each combination of k, λ, μ.

1.2. Double well Oscillators

Few articles on the eigenvalues of double well oscillators have been published recently, though they have become very important in connection with "instantons" in quantum field theory. An interesting article on nonlinear contributions to the PF of a double well oscillator was published recently by Harrington [4].

Customarily eigenvalues for double well quartic oscillators have been calculated by matrix diagonalization. The Hamilton matrix was set up in a harmonic oscillator basis and diagonalized by appropriate techniques. For practical purposes results by Laane [5] are useful. He gave extended numerical tables for the first 17 eigenvalues for quartic single and double well anharmonic oscillators. Banerjee and Bhatnagar [6] generalized their nonperturbative methods to double well problems and calculated the first 5 eigenvalues for various k, λ very precisely. Twenty years ago Heilbronner, Rutishauser and Gerson [7] applied the numerical diagonalization technique to a double well oscillator with $\mu = 3$.

All these techniques suffer from the fact that for the calculation of the PF an (practically) infinite

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number of eigenvalues must be calculated to get the precise high temperature PF by summation of Boltzmann factors. We propose, therefore, a simple analytical method for the classical PF, the semiclassical PF in the Wigner-Kirkwood approximation and the exact upper and lower bounds to the quantum mechanical PF for arbitrary combinations of k, λ, μ. The quickly converging series is evaluated for $k, \lambda, 2$ and compared with independent analytical and numerical results.

2. The Classical PF

Consider the Hamiltonian

$$\hat{H} = (\hat{p}^2/2m) + (m\omega^2/2)\hat{x}^2 + k_{2n}\hat{x}^{2n} \tag{2}$$

which can be easily translated into the form of (1). According to Landau-Lifshitz [8] the classical PF Z_c is after integration over momentum

$$Z_c = (mkT/2\pi)^{1/2}\hbar^{-1} \cdot \int_{-\infty}^{+\infty} \exp\left\{-\beta\left(\frac{m\omega^2}{2}x^2 + k_{2n}x^{2n}\right)\right\} dx \tag{3}$$

with $\beta = (kT)^{-1}$, $\omega^2 > 0$ or $\omega^2 < 0$ (double well).

A well known integral (Gröbner-Hofreiter [9], p. 67) which was already used previously [10] in connection with the semiclassical PF of generalized oscillators can be applied:

$$I(a; m; 2k) = \int_0^\infty e^{-ax^m} x^{2k}\, dx = m^{-1} a^{-(2k+1)/m} \Gamma[(2k+1)/m], \tag{4}$$

where $\Gamma[(2k+1)/m]$ is the Gamma-function, tabulated in Abramowitz-Stegun [11].

If the first term in the exponential is expanded, the series can be integrated leading to a quickly converging result:

$$Z_c = \left(\frac{mkT}{2\pi}\right)^{1/2}\hbar^{-1}\int_{-\infty}^{+\infty}\exp(-\beta k_{2n}x^{2n}) \cdot\left[\sum_{s=0}^{\infty}(s!)^{-1}(-\beta m\omega^2/2)^s x^{2s}\right]dx = \left(\frac{2mkT}{\pi}\right)^{1/2}\hbar^{-1} \cdot\left\{\sum_{s=0}^{\infty}(s!)^{-1}(-\beta m\omega^2/2)^s I(\beta k_{2n}; 2n; 2s)\right\}. \tag{5}$$

This result is exact for both single and double well oscillators. Using the quotient criterium, one can prove easily that the series is convergent.

3. The Semiclassical Wigner-Kirkwood PF

The Wigner-Kirkwood semiclassical perturbation expansion and its improvements have been discussed elsewhere [10]. It has already become a textbook subject and was treated in detail by Landau and Lifshitz ([8], p. 96) so that the final formulas can be written down:

$$Z_{sc} = (1 + \hbar^2\bar{\chi}_2)\int e^{-\beta E(p,q)}\, d\Gamma, \tag{6}$$

$$\bar{\chi}_2 = \int \chi_2 \exp[-\beta E(p,q)] \cdot d\Gamma / \{\int \exp[-\beta E(p,q)]\, d\Gamma\}, \tag{7}$$

$$\chi_2 = -\frac{\beta^3}{24}\sum_i m_i^{-1}\left(\frac{\partial U}{\partial q_i}\right)^2, \tag{8}$$

$$E(p,q) = \sum_i \frac{p_i^2}{2m_i} + U(q),$$

$$U(q) = \text{potential energy}, \tag{9}$$

$$m_i = \text{masses of particles } i,$$

$$p, q = \text{momentum and coordinate}.$$

The integration is performed over the phase space volume $d\Gamma$.

For the present model system the potential energy U and its derivative $(\partial U/\partial x)^2$ are

$$U = \frac{m\omega^2}{2}x^2 + k_{2n}x^{2n}, \tag{10}$$

$$\left(\frac{\partial U}{\partial x}\right)^2 = m^2\omega^4 x^2 + 4nm\omega^2 k_{2n}x^{2n} + 4n^2(k_{2n})^2 x^{4n-2}, \tag{11}$$

so that

$$\bar{\chi}_2 = -\frac{\beta^3}{24m}\int_{-\infty}^{+\infty}\exp(-\beta U) \cdot\{m^2\omega^4 x^2 + 4nm\omega^2 k_{2n}x^{2n} + 4n^2(k_{2n})^2 x^{4n-2}\}\, dx \Big/ \int_{-\infty}^{+\infty}\exp(-\beta U)\, dx. \tag{12}$$

The integrals are again of the type $I(a; m; 2k)$ so that the result can be written as

$$\bar{\chi}_2 = \left(\frac{-\beta^3}{mA_1}\right)(m^2\omega^4 A_2 + 4nm\omega^2 k_{2n}A_3 + 4n^2(k_{2n})^2 A_4), \tag{13}$$

where

$$A_1 = \sum_{s=0}^{\infty} (s!)^{-1} (-\beta m \omega^2/2)^s \cdot I(\beta k_{2n}; 2n; 2s), \tag{14}$$

$$A_2 = \sum_{s=0}^{\infty} (s!)^{-1} (-\beta m \omega^2/2)^s \cdot I(\beta k_{2n}; 2n; 2s+2), \tag{15}$$

$$A_3 = \sum_{s=0}^{\infty} (s!)^{-1} (-\beta m \omega^2/2)^s \cdot I(\beta k_{2n}; 2n; 2s+2n), \tag{16}$$

$$A_4 = \sum_{s=0}^{\infty} (s!)^{-1} (-\beta m \omega^2/2)^s \cdot I(\beta k_{2n}; 2n; 2s+4n-2). \tag{17}$$

It remains to show the convergence of the preceding series A_i, which will be done easily by the quotient criterium.

We consider the general series

$$A = \sum_{s=0}^{\infty} (s!)^{-1} (-\alpha)^s I(b; 2n; 2s+2w), \tag{18}$$

$$\alpha = (\beta m \omega^2/2), \quad b = \beta k_{2n},$$

$$w = \text{positive integer}. \tag{19}$$

The quotient criterium reads

$$\lim_{s\to\infty} \left| \frac{a_{s+1}}{a_s} \right| = \lim_{s\to\infty} \left| \frac{(-\alpha)}{s+1} b^{-(1/n)} \cdot \Gamma\left(\frac{2s+2w+3}{2n}\right) \left(\Gamma\left(\frac{2s+2w+1}{2n}\right)\right)^{-1} \right|, \tag{20}$$

the quotient of the Γ-functions can be re-written by the asymptotic series ([11], p. 257).

$$\frac{\Gamma(z+a)}{\Gamma(z+b)} \sim z^{a-b} \left(1 + \frac{(a-b)(a+b-1)}{2z} + \cdots\right) \tag{21}$$

for $z \to \infty$ with the final result

$$\lim_{s\to\infty} \left| \frac{a_{s+1}}{a_s} \right| = \lim_{s\to\infty} \left| \left(\frac{\alpha}{s+1}\right) b^{-(1/n)} \cdot s^{(1/n)} \left(\frac{1+w/s}{n}\right)^{1/n} \right| = 0. \tag{22}$$

The series is absolute convergent according to the Leibniz- and quotient criterium and contains as special case the classical partition function for $w = 0$. A worked out example for the quartic type single and double well anharmonic oscillator will be given subsequently.

4. Upper and Lower Bounds to the PF

4.1. Lower Bound

It was shown elsewhere [12] that the lower bound for anharmonic oscillators with polynomial anharmonicity can be evaluated including the frequency or the internuclear distance as variational parameters. For the general theory of variational techniques in quantum statistics, the excellent article by Girardeau and Mazo [13] should be consulted.

The lower (or Gibbs-Bogoliubov) bound is

$$Z \geqq \mathrm{Tr}\{\exp(-\beta \hat{H}_0) \exp(-\beta \langle \hat{H}_1 \rangle_0)\}, \tag{23}$$

where

$$\langle \hat{H}_1 \rangle_0 = \mathrm{Tr}\{\exp(-\beta \hat{H}_0) \hat{H}_1\} / \mathrm{Tr}\{\exp(-\beta \hat{H}_0)\} \tag{24}$$

and $\mathrm{Tr}\{\ \}$ is the sum over diagonal elements formed in an appropriate basis. In contrast to perturbation theory, $\hat{H}_1$ need not be small compared to $\hat{H}_0$. $\hat{H}$ is written as

$$\hat{H} = \hat{H}_0 + \hat{H}_1, \tag{25}$$

$$\hat{H}_0 = (\hat{p}^2/2m) + (m\omega^{*2}/2)\hat{x}^2, \tag{26}$$

$$\hat{H}_1 = m(\omega^2 - \omega^{*2})\hat{x}^2/2 + k_{2n}\hat{x}^{2n}, \tag{27}$$

where ω^* is introduced as variational parameter. Using the well known moment-generating function for the harmonic oscillator (Messiah [14], p. 449)

$$\mathrm{Tr}\{\exp(-\beta \hat{H}_0) \exp(\alpha \xi \hat{x})\} / \mathrm{Tr}\{\exp(-\beta \hat{H}_0)\} = \exp(\gamma^2 \xi^2 R/2), \tag{28}$$

where

$$\gamma = (\hbar/2m\omega)^{1/2}\alpha, \quad R = \coth(\beta \hbar \omega^*/2), \tag{29}$$

the moments are the thermal averages

$$\langle \hat{x}^{2n} \rangle_{\mathrm{th}} = \frac{(2n)!}{2^n n!} R^n (\hbar/2m\omega^*)^n. \tag{30}$$

It was already discussed [12] how to vary ω^* to get optimal results, some values will be given for comparison in Table 1.

4.2. The Upper Bound

It is more difficult to evaluate the upper (or Golden-Thompson) bound to the quantum PF as it is only in few cases possible to calculate traces over exponential operators

$$Z \leqq \mathrm{Tr}\{\exp(-\beta \hat{H}_0) \exp(-\beta \hat{H}_1)\}. \tag{31}$$

Table 1. Quantitative behaviour of various methods for the calculation of the anharmonic oscillator PF in reduced units $\varepsilon = \beta\hbar\omega$. Z_{LB}^{V} lower bound with variation, Z_{HM} "exact" PF from the Hioe-Montroll eigenvalues, Z_{SC} semiclassical PF Z_{UB}^{V} upper bound with variation, Z_C classical PF.

λ	ε	Z_{LB}^{V}	Z_{HM}	Z_{SC}	Z_{UB}	Z_C
0.1	0.2	3.3932	—*	3.4700	3.4728	3.4886
0.5	0.2	2.4889	2.5731	2.5718	2.5779	2.6008
1.0	0.2	2.1372	2.2153	2.2144	2.225	2.2495
10.0	0.2	1.2188	1.2664	1.2654	1.2827	1.3283
0.1	1.0	0.7980	—*	0.7954	0.8014	0.8576
0.5	1.0	0.6002	0.6086	0.6048	0.6219	0.6977
1.0	1.0	0.5077	0.5143	0.5080	0.5329	0.6203
10.0	1.0	0.2202	0.2270	0.1762	0.2997	0.3861
0.1	5.0	6.0800 (− 2)	—*	− 0.048	6.3404 (− 2)	0.1907
0.5	5.0	3.0000 (− 2)	3.1189 (− 2)	− 0.1391	4.2662 (− 2)	0.1715
1.0	5.0	1.7201 (− 2)	1.8057 (− 2)	− 0.2064	3.5875 (− 2)	0.1589
10.0	5.0	4.7033 (− 4)	5.3960 (− 4)	− 0.5708	2.0174 (− 2)	0.1087

* The "exact" PF can, according to Hioe-Montroll [1], be calculated for $\lambda \geqq 0.2$ using the analytic expressions for the eigenvalues, $(-n)$ means 10^{-n}.

Even for the single well quartic anharmonic oscillator fairly complicated techniques were necessary [12]. In the present case, however, the trace will be calculated easily for arbitrary $k_{2n}\hat{x}^{2n}$ by using a property of the density matrix. The thermal average of an operator $\hat{O}$ is

$$\langle \hat{O} \rangle_{th} = \mathrm{Tr}\{\exp(-\beta\hat{H})\,\hat{O}\} = \int_{-\infty}^{+\infty} \varrho(x, x; \beta)\,\hat{O}\,\mathrm{d}x; \tag{32}$$

$\varrho(x, x; \beta)$ is the unnormalized diagonal density matrix

$$\varrho(x,x;\beta) = \sum_{n=0}^{\infty} \exp(-\beta E_n)\,\psi_n^*(x)\,\psi_n(x), \tag{33}$$

where E_n, ψ_n are the eigenvalues and eigenfunctions of $\hat{H}$. Taking the same splitting of $\hat{H}$ as in 3.1, the upper bound is written as

$$Z \leqq \mathrm{Tr}\{\exp(-\beta\hat{H}_0)\exp(-\beta\hat{H}_1)\} = \int_{-\infty}^{+\infty} \varrho_0(x, x; \beta)\exp(-\beta\hat{H}_1)\,\mathrm{d}x, \tag{34}$$

where $\varrho_0(x, x; \beta)$ is the diagonal density matrix of the harmonic oscillator $\hat{H}_0$ [15]

$$\varrho_0(x, x; \beta) = A^* \exp(-Bx^2),$$
$$A^* = [m\omega^*/2\pi\hbar \sinh(\beta\hbar\omega^*)]^{1/2},$$
$$B^* = (m\omega^*/\hbar)\tanh(\beta\hbar\omega^*/2). \tag{35}$$

It remains to calculate the integral

$$Z_{UB} = A^* \int_{-\infty}^{+\infty} \exp(-\beta k_{2n} x^{2n}) \cdot \exp(Cx^2)\,\mathrm{d}x,$$

$$C = -(m\omega^*/\hbar)\tanh(\beta\hbar\omega^*/2) - \beta m(\omega^2 - \omega^{*2})/2, \tag{36}$$

which is exactly of the same form as (5).

$$Z \leqq Z_{UB} = 2A^* \left\{ \sum_{s=0}^{\infty} (s!)^{-1} C^s\, I(\beta k_{2n}; 2n; 2s) \right\}. \tag{37}$$

By numerical variation of ω^* an optimal value of Z_{UB} can be found, as it is impossible to find analytically the minimum of the series depending on ω^*.

5. Explicit Calculation of Z_C, Z_{SC}, Z_{LB}, Z_{UB} for the Single and Double well Quartic Oscillator

5.1. Calculation for the Single well Oscillator in Reduced Units

To agree in notation with a previous article [12] and with the results from the high precision nonperturbative results of Hioe and Montroll [1] the following substitutions are made.

$$\hat{H} = (\hat{p}^2/2m) + (m\omega^2/2)\hat{x}^2 + k_4\hat{x}^4 \equiv (\hat{p}^2/2m) + k_2\hat{x}^2 + k_4\hat{x}^4, \tag{38}$$

$$\hat{x} = (\hbar/m\omega)^{1/2}\hat{Q}, \tag{39}$$

$$\hat{p} = (m\hbar\omega)^{1/2}\hat{P}, \tag{40}$$

$$k_2 = (m\omega^2/2); \quad k_2\hat{x}^2 = (\hbar\omega/2)\hat{Q}^2, \tag{41}$$

$$k_4\hat{x}^4 = \hbar\omega\lambda\hat{Q}^4, \tag{42}$$

so that $\hat{H}$ reads

$$\hat{H} = (\hbar\omega/2)(\hat{P}^2 + \hat{Q}^2) + \lambda\hbar\omega\hat{Q}^4. \tag{43}$$

With this Hamiltonian the various approximations can be written in reduced units $\varepsilon = \beta\hbar\omega$ as

$$Z_C = (\pi\varepsilon/2)^{-1/2} A_1 , \tag{44}$$

$$Z_{SC} = (1 + \hbar^2 \bar{\chi}_2) Z_C , \tag{45}$$

$$\hbar^2 \bar{\chi}_2 = -(\varepsilon^3/24 A_1) \cdot (A_2 + 8\lambda A_3 + 16\lambda^2 A_4) , \tag{46}$$

$$A_1 = (a^{-1/4}/4)\{\Gamma(1/4)[1 + (b^2/8a) + (5b^4/384a^2) + \cdots] - (b/a^{1/2})\Gamma(3/4)[1 + (b^2/8a) + (21b^4/1920a^2) + \cdots]\} , \tag{47}$$

$$A_2 = (a^{-3/4}/4)\{\Gamma(3/4)[1 + (3b^2/8a) + (21b^4/384a^2) + \cdots] - (b/4a^{1/2})\Gamma(1/4)[1 + (5b^2/24\,a) + (9b^4/384a^2) + \cdots]\} , \tag{48}$$

$$A_3 = (a^{-5/4}/4)\{(\Gamma(1/4)/4)[1 + (5b^2/8a) + (45b^4/384a^2) + \cdots] - (3b/4a^{1/2})\Gamma(3/4)[1 + (7b^2/24a) + (77b^4/1920a^2) + \cdots]\} , \tag{49}$$

$$A_4 = (a^{-7/4}/4)\{(3\Gamma(3/4)/4)[1 + (7b^2/8a) + (77b^4/384a^2) + \cdots] - (5b/16a^{1/2})\Gamma(1/4)[1 + (9b^2/24a) + (117b^4/1920a^2) + \cdots]\} , \tag{50}$$

$$a = \varepsilon\lambda ; \quad b = (\varepsilon/2) .$$

The series expansions A_i will also be needed in the subsequent calculations with nonreduced units. We, therefore, specify the constants a and b for each case separately.

Upper and lower bounds to the PF Z^V_{UB} and Z^L_{UB} including a variational parameter ω^* are

$$Z^V_{UB} = [2\omega^*/(\pi\omega \sinh(\beta\hbar\omega^*))]^{1/2} \cdot \sum_{s=0}^{\infty} \frac{(-C^*)^s}{s!} I(\varepsilon\lambda; 4; 2s) = [2\omega^*/(\pi\omega \sinh(\beta\hbar\omega^*))]^{1/2} A_1 , \tag{51}$$

where the constants in A_1 are for the upper bound Z^V_{UB}

$$a = \varepsilon\lambda ; \quad b = (\varepsilon/2)(1 - K^2) + K \tanh(\beta\hbar\omega^*/2) , \quad K = (\omega/\omega^*) . \tag{52}$$

The lower bound is

$$Z^V_{LB} = Z_0^* \exp\{-\beta\hbar R(\omega^2 - \omega^{*2})/(4\omega^*) - 3\varepsilon\lambda R^2\omega^2/(4\omega^{*2})\} , \quad Z_0^* = [2\sinh(\beta\hbar\omega^*/2)]^{-1} . \tag{53}$$

Results are given in Table 1, in contrast to previous calculations, where tables of parabolic cylinder functions are needed, the present calculations are elementary.

5.2. Z_C, Z_{SC}, Z^V_{UB}, Z^V_{LB} *in Nonreduced Units*

Following the customary notation in the theory of large amplitude motions, k_2 is written with positive sign for the single well and with negative sign for the double well oscillator. It is:

$$Z_C = (2m/\beta\pi\hbar^2)^{1/2} A_1 , \tag{54}$$

$$Z_{SC} = (1 + \hbar^2 \bar{\chi}_2) Z_C , \tag{55}$$

$$\hbar^2 \bar{\chi}_2 = -(\hbar^2\beta^3/24 m A_1)[4(k_2)^2 A_2 + 16 k_2 k_4 A_3 + 16(k_4)^2 A_4] , \tag{56}$$

where in the A_i the constants a and b are $a = \beta k_4$; $b = \beta k_2$.

The upper bound including variation of the frequency is

$$Z^V_{UB} = [2m\omega^*/\pi\hbar \sinh(\beta\hbar\omega^*)]^{1/2} A_1 \tag{57}$$

with constants

$$a = \beta k_4 , \quad b = \beta(k_2 - m\omega^{*2}/2) - (m\omega^*/\hbar)\tanh(\beta\hbar\omega^*/2) .$$

The lower bound with variation of the frequency is according to Section 4.1

$$Z^V_{LB} = Z_0^* \exp\{-\beta[R(\hbar/2m\omega^*) \cdot (k_2 - m\omega^{*2}/2) + 3R^2(\hbar/2m\omega^*)^2 k_4]\} , \tag{58}$$

$$R = \coth(\beta\hbar\omega^*/2) , \quad Z_0^* = [2\sinh(\beta\hbar\omega^*/2)] .$$

These formulas are valid for both single and double well oscillators, but for the latter case the energy zero must be increased to the top of the barrier to avoid negative potential energies.

For some double well oscillators covering low, intermediate and high barriers we give some numerical results.

Table 2. Molecular constants for ring puckering. 1. Chemical compound, 2. Quartic force constant in 10^5 [cm^{-1} Å^{-4}], 3. Quartic force constant in 10^{22} [Jm^{-4}], 4. Quadratic force constant in 10^3 [cm^{-1} Å^{-2}], 5. Quadratic force constant in 10^1 [Jm^{-2}], 6. Reduced mass in 10^{-27} [kg], 7. Barrier height $(k_2)^2/4\,k_4$ in 10^{-21} [J], 8. Reference.

	1	2	3	4	5	6	7	8
[1]		7.16	14.22	− 6.58	− 1.31	158.9	0.30	[21]
[2]		10.02	19.90	− 18.34	− 3.64	186.0	1.66	[22]
[3]		12.34	24.51	− 33.85	− 6.72	257.4	4.61	[23]
[4]		3.85	7.65	− 26.06	− 5.18	190.9	8.73	[24]

Table 3 shows detailed results for the low barrier double well oscillator, trimethylenoxid. This example was chosen as Laane's [5] tables give only the first seventeen eigenvalues and as it is possible to give a good estimation of the influence of the higher levels from the analytical eigenvalues for the quartic oscillator (1) with $k=0$ [1]

$$E_n = \lambda^{1/3}(1.3765074)\,[(n+1/2) + 0.0265(n+1/2)^{-1} + \cdots]^{4/3}. \quad (59)$$

Table 3. Comparison of different methods for the PF of oxetan [21]. T Temperature in K, Z^{V}_{LB} lower bound with variation, Z^{*}_{N} numerical PF, corrigated with quartic oscillator eigenvalues E_n ($n > 17$), Z_{SC} semiclassical PF, Z^{V}_{UB} upper bound with variation, Z_C classical PF.

T	Z^{V}_{LB}	Z^{*}_{N}	Z_{SC}	Z^{V}_{UB}	Z_C
50	0.39	0.56	0.51	0.71	0.70
100	0.90	1.10	1.09	1.19	1.19
500	3.26	3.74	3.73	3.76	3.76
1000	5.90	6.16	6.15	6.17	6.17

Table 4. Comparison of different methods for the PF at 1000 K. [N] number of the compound in Table 2, Z^{V}_{LB} lower bound with variation, Z_N numerical PF from Laane's tables, Z_{SC} semiclassical PF, Z^{V}_{UB} upper bound with variation, Z_C classical PF.

[N]	Z^{V}_{LB}	Z_N	Z_{SC}	Z^{V}_{UB}	Z_C
[1]	5.77	6.07	6.15	6.17	6.17
[2]	5.89	6.43	6.55	6.55	6.57
[3]	5.75	7.20	7.45	7.47	7.47
[4]	6.55	7.70	8.36	8.31	8.38

The agreement is very good, even at fairly low temperatures.

Table 4 shows a comparison of the PF at 1000 K for the model molecules calculated by different techniques. The numerical PF from Laane's eigenvalues is evidently too low, but the calculation of higher eigenvalues by matrix diagonalization or by the WKB-technique is cumbersome and will not present new insights. Despite this deficiency the agreement of the semiclassical and upper bound results are very good, so that one can conclude that the high temperature behaviour is well described by the analytical techniques of the text.

5.3. Alternative Techniques

For the quartic type anharmonic oscillator the classical and semiclassical PF can be calculated by an analytical technique, which unfortunately cannot be generalized for $n > 2$. A defining integral for parabolic cylinder functions [11] or a similar representation in terms of hypergeometric functions [16] can be used. As the parabolic cylinder functions are tabulated, the first representation seems to be more convenient.

From the integral (Abramowitz-Stegun [11], p. 687)

$$\int_0^\infty z^{2\nu-1}\exp(-az^4 - sz^2)\,dz = (\tfrac{1}{2})\,(2a)^{-\nu/2}\,\Gamma(\nu)\exp(s^2/8a) \cdot D_{-\nu}[s\,(2a)^{-1/2}] \quad (60)$$

follows

$$Z_c^{\text{exact}} = (2\pi\varepsilon)^{-1/2}(2\varepsilon\lambda)^{-1/4}\Gamma(1/2) \cdot \exp(\varepsilon/32\lambda) D_{-1/2}[\varepsilon(8\varepsilon\lambda)^{-1/2}], \quad (61)$$

where $D_{-1/2}(z)$ is the parabolic cylinder function of order $(-1/2)$ which can also be expressed in terms of modified Besselfunctions $K_{1/4}(z)$ or by hypergeometric functions. Tabulated values [11] are used after a five point Lagrange interpolation. The results agree with the present series calculations to four significant figures. For the double well oscillator the same formulas can be used, but instead of tables for the $D_{-\nu}(x)$ related tables $V(a, x)$ are applied ([11], p. 702),

$$V(a,x) = (1/\pi)\Gamma(\tfrac{1}{2}+a) \cdot \{\sin(\pi a) D_{-a-1/2}(x) + D_{-a-1/2}(-x)\}, \quad (62)$$

which allow the calculation of $D_{-\nu}(-x)$. The calculations for the double well oscillator were not performed in the above mentioned article [12].

6. A By-product: Generalized Matrix Elements of the Harmonic Oscillator

The technique of the present article can be used to calculate matrix elements of $\exp\{-k_{2n}x^{2n}\}$ in a harmonic oscillator basis. For $n=1$ a large variety of methods is known, ranging from direct integration by a Laplace-type integral to various disentangling techniques of Gauß-type exponential operators. For $n=2$ a defining integral of parabolic cylinder functions (see also (60)) was used in the calculation of eigenvalues of a generalized double well problem [17]. Matrix elements of the above mentioned type have also found interest in connection with integral transforms [18], [19] and Borel-summation of diverging series [20]. If we go back to the Q-representation of the harmonic oscillator, the problem reduces to calculating matrix elements

$$M_{nm} = \int_{-\infty}^{+\infty} u_n(Q) \exp\{-K_{2n}Q^{2n}\} u_m(Q)\, dQ, \quad (63)$$

where the eigenfunction $u_n(Q)$ is

$$u_n(Q) = (\pi^{1/2}2^n n!)^{-1/2}\exp\{-Q^2/2\} H_n(Q) = N_n \exp(-Q^2/2) H_n(Q), \quad (64)$$

and $H_n(Q)$ are the Hermite-polynomials.

One sees that M_{nm} is of the same type as (4) so that the final result is written in terms of an auxiliary integral

$$M_{2k}^* = \int_{-\infty}^{+\infty} \exp\{-K_{2n}Q^{2n} - Q^2\} Q^{2k}\, dQ = 2\sum_{s=0}^{\infty}(-1)^s (s!)^{-1} I(K_{2n}, 2n, 2s+2k). \quad (65)$$

For example, M_{13} is

$$M_{13} = N_1 N_3 \int_{-\infty}^{+\infty} \exp\{-K_{2n}Q^{2n} - Q^2\} \cdot (16\,Q^4 - 24\,Q^2)\, dQ = 8 N_1 N_3 (2 M_4^* - 3 M_2^*). \quad (66)$$

As by a suitable combination of various exponentials a symmetrically or asymmetrically structured anharmonic oscillator well can be formed, eigenvalues of such model potentials will be interesting for applications to disordered systems. Another application, which will be tested, is a more flexible variational wavefunction for the calculation of anharmonic oscillator eigenvalues.

7. Conclusion and Discussion

In a previous article fairly complicated mathematical techniques were used to derive analytical results for the single well quartic anharmonic oscillator. The present article simplifies the mathematics allowing the analytical calculation of the upper and lower bounds to the quantum PF, and the classical and arbitrary order semiclassical Wigner-Kirkwood PF for all single and double well x^{2n}-quadratic anharmonic oscillators. A further advantage is that from the present series solutions it is easy to derive thermodynamic functions H, S, C_v ... by simple differentiations according to the temperature.

We conclude that the problem of calculating the PF of fairly complicated quantum mechanical systems needing either advanced mathematics or computer time for matrix diagonalization or numerical solution of the Schrödinger equation for the eigenvalues can be treated by simple mathematics in a simple way.

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