
UNIFORMLY SUITABLE ESTIMATION FOR THERMODYNAMIC VALUES

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The operator method and the cumulant expansion are used for the approximate calculation of partition functions and free energy in quantum statistics. It is shown for some model systems that the zeroth approximation of the method interpolates these values with rather good accuracy in the entire range of both the Hamiltonian parameters and temperature. The proposed method allows one to calculate also the corrections to the zeroth approximation.

1 Introduction

An important contribution of Professor Hagen Kleinert and his research group concerns the development of non-perturbative methods for quantum field theory and quantum statistics [1]. His analysis of this problem is based mainly on the functional formulation of quantum mechanics. The Green function and the density matrix are the main objects in such an approach and that allows one to calculate the observable physical values directly, without an intermediate calculation of the energy spectrum for all stationary states of the system. Unfortunately, this great advantage of the method is rather restricted for the non-perturbative theories because of the difficulties when calculating the path integrals with non-quadratic action.

On the other hand, the operator method (OM) can be used for the non-perturbative solution of the Schrödinger equation [2]. It permits one to find the uniformly fitted interpolation and convergent series for eigenvalues of quite complicated Hamiltonians. But this approach is rather difficult for

calculations in quantum statistics, where the physical values are defined by the energy spectrum as a whole.

The purpose of the present work is to generalize the OM for the calculation of thermodynamic values in quantum statistics. Namely, we will show that the application of OM for the eigenvalues together with the cumulant expansion [3] for the summation on the quantum numbers of the system permits us to calculate the uniformly suitable estimation for the partition function and free energy and to find the second-order corrections for them in the entire range of temperature and Hamiltonian parameters.

2 Formulation of the Problem

First we want to define more precisely what we mean under “uniformly suitable estimation” (USE). Let us consider some physical variable with eigenvalues $F_n(\lambda)$ depending on the quantum number n and the physical parameter λ . Let us also take the function $F_n^{(0)}(\lambda)$ as the USE for $F_n(\lambda)$ with the following inequality being fulfilled in the entire range of variation of n and λ :

$$\left| \frac{F_n^{(0)}(\lambda) - F_n(\lambda)}{F_n(\lambda)} \right| \leq \xi^{(0)}. \quad (1)$$

Here the parameter $\xi^{(0)} < 1$ is supposed to be independent on the values n, λ and defines the accuracy of USE. In principle, we also suppose that there is a method for calculating a sequence of the functions $F_n^{(s)}(\lambda)$ corresponding to the decreasing sequence of the parameters $\xi^{(s)}$; $s = 0, 1, 2, \dots$, so that

$$\lim_{s \rightarrow \infty} F_n^{(s)}(\lambda) = F_n(\lambda). \quad (2)$$

It seems that the definition in Eq. (1) is not constructive because the exact values $F_n(\lambda)$ are unknown. However, there are several possibilities to estimate the value $\xi^{(0)}$. In particular, one can compare the asymptotic series for $F_n(\lambda)$ in different limiting cases of the parameter or the quantum number with the corresponding expansions of the function $F_n^{(0)}(\lambda)$. Besides, the difference between $F_n^{(1)}(\lambda)$ and $F_n^{(0)}(\lambda)$ can also be considered as an estimation for $\xi^{(0)}$. As an example, we mention the USE for the eigenvalues of the Hamiltonian for various physical systems calculated on the basis of the OM [1,4,5].

Let us consider from this point of view the thermodynamic perturbation theory in the Schrödinger representation of quantum statistics. Usually it is formulated for the free energy of the system [6] and the leading terms are the

following

$$F(\lambda, \beta) = F_0 + \lambda \sum_n V_{nn} w_n + \lambda^2 \sum_n \sum_{m \neq n} \frac{|V_{mn}|^2 w_n}{E_n^{(0)} - E_m^{(0)}} + \frac{1}{2} \beta \lambda^2 \left[\left(\sum_n V_{nn} w_n \right)^2 - \sum_n V_{nn}^2 w_n \right] + \dots \quad (3)$$

Here we have introduced $\beta = 1/k_B T$, where T is the temperature and k the Boltzmann constant; F, F_0 are the exact and approximate free energies respectively; $E_n^{(0)}$ are the eigenvalues of the unperturbed Hamiltonian and V_{mn} are the matrix elements of the perturbation operator with the following form of the total Hamiltonian

$$H = H_0 + \lambda V, \quad (4)$$

and $w_n = \exp[\beta(F_0 - E_n^{(0)})]$ is the unperturbed density matrix.

With any fixed number of terms, these series do not yield the free energy in the whole range of the temperature and the perturbation parameter even for the simplest cases. Let us illustrate this by means of the model Hamiltonian used in Ref. [7] for the analysis of convergence of usual perturbation series

$$\begin{aligned} H &= H_0 + \lambda V = \frac{1}{2}(\hat{p}^2 + x^2) + \lambda x^2, \\ E_n^{(0)} &= n + \frac{1}{2}, \quad F_0 = \frac{1}{\beta} \ln [2 \sinh(\beta/2)], \\ V_{mn} &= \left(n + \frac{1}{2} \right) \delta_{m,n} + \frac{1}{2} \left[\sqrt{(n+1)(n+2)} \delta_{m,n+2} \right. \\ &\quad \left. + \sqrt{n(n-1)} \delta_{m,n-2} \right], \end{aligned} \quad (5)$$

with $\delta_{m,n}$ being the Kronecker symbol.

Certainly, the exact free energy is well known for this model ($F = \ln [2 \sinh(\beta/2 \sqrt{1+2\lambda})] / \beta$) but if we use these matrix elements in formula (3), rather simple calculations lead to the following result

$$F(\lambda, \beta) = \frac{1}{\beta} \ln [2 \sinh \beta/2] + \frac{\lambda}{2} \coth \beta/2 - \frac{\lambda^2}{8} \left[1 + \coth \beta/2 + \frac{1}{2 \sinh^2 \beta/2} (1 + 2\beta) \right] + \dots \quad (6)$$

It is evident that this series does not satisfy the USE criterions in the plane of both parameters. In the low-temperature limit ($\beta \rightarrow \infty$), formula (6) leads to the power series of λ for the ground-state energy and this series diverges in the range of $\lambda > 1/2$ because of a singular point of the exact eigenvalue [7] in the complex plane of λ . When the temperature increases ($\beta \rightarrow 0$), the second-order correction becomes singular ($\sim -\lambda^2/4\beta^2$), although the exact free energy has no similar singularity.

So, instead of Eq. (3), our objective is to formulate another regular method which permits to find the USE for the free energy of the quantum system with an arbitrary energy spectrum $E(n)$.

3 Cumulant Expansion for the Quantum Partition Function

The partition function of some quantum system,

$$Z(\beta) = \sum_{n=0}^{\infty} \exp[-\beta E(n)], \quad (7)$$

can be represented in the operator form. Let us introduce the basic set of the state vectors as the eigenfunctions of the excitation number operator

$$\hat{n}|n\rangle = \hat{a}^+ \hat{a}|n\rangle = n|n\rangle, \quad (8)$$

with the creation \hat{a}^+ and annihilation \hat{a} operators, corresponding to the harmonic oscillator with arbitrary frequency ω .

Then, we can write

$$Z(\beta) = \langle v | \exp[-\beta E(\hat{n}) + v\hat{n} - \ln N(v)] | v \rangle. \quad (9)$$

Here $|v\rangle$ is the normalized state vector depending on the arbitrary parameter v having the physical meaning of the inverse temperature:

$$|v\rangle = \sqrt{N(v)} \sum_{n=0}^{\infty} e^{-vn} |n\rangle, \quad N(v) = 1 - e^{-v}. \quad (10)$$

Let us remind that the cumulant expansion is valid for an arbitrary exponential operator when averaging any normalized state vector [3],

$$\langle \exp(\hat{A}) \rangle = \exp \left[\sum_{n=1}^{\infty} \frac{K_n}{n!} \right], \quad (11)$$

where the cumulants K_n are expressed in terms of the moments of the operator \hat{A} . This expansion is the strict one and every cumulant corresponds to the partial summation of usual power series. The first few terms in Eq. (11) are [3]

$$\begin{aligned} K_1 &= \langle \hat{A} \rangle, \\ K_2 &= \langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2, \\ K_3 &= \langle \hat{A}^3 \rangle - 3\langle \hat{A} \rangle \langle \hat{A}^2 \rangle + 2\langle \hat{A} \rangle^3. \end{aligned} \quad (12)$$

If we apply now two terms of the cumulant expansion to the partition function, the representation (9) can be transformed as

$$\begin{aligned} Z(\beta) \simeq \tilde{Z}(\beta, v) &= \exp \left[\langle v | \hat{R} | v \rangle - \ln N(v) + \frac{1}{2} \left(\langle v | \hat{R}^2 | v \rangle - \langle v | \hat{R} | v \rangle^2 \right) \right], \\ \hat{R} &= -\beta E(\hat{n}) + v \hat{n}. \end{aligned} \quad (13)$$

A further analytical consideration is possible if we suppose that the fluctuation of the number of excitations with respect to its averaged value is limited in the entire range of the temperature; the self-consistency of this assumption will be tested by the final result. Then all values in formula (13) can be expanded in the series of this fluctuation and the following result can be obtained up to second order:

$$\begin{aligned} \tilde{Z}(\beta, v) \simeq \exp \left\{ -\beta E(\bar{n}) + v\bar{n} - \ln N(v) \right. \\ \left. - \frac{\bar{n}(\bar{n}+1)}{2} [\beta E''(\bar{n}) + \beta^2 E(\bar{n})E''(\bar{n}) + (\beta E'(\bar{n}) - v)^2] \right\}. \end{aligned} \quad (14)$$

Here the value \bar{n} has the physical meaning of the averaged number of excitations and it is defined by the formula

$$\bar{n} = \frac{e^{-v}}{1 - e^{-v}}, \quad e^{-v} = \frac{\bar{n}}{\bar{n} + 1}. \quad (15)$$

A more convenient way is to consider the value \bar{n} as the variational parameter instead of v and to find $\bar{n} = \bar{n}(\beta)$ from the minimum condition for the free energy calculated in the zeroth order of the cumulant expansion. In that way the following expansion can be obtained with the desired accuracy:

$$F(\beta) = -\frac{1}{\beta} \ln Z(\beta) = F^{(0)} + \Delta F + \dots,$$

$$F^{(0)} = E(\bar{n}) - \frac{1}{\beta} [(\bar{n} + 1) \ln(\bar{n} + 1) - \bar{n} \ln \bar{n}], \quad (16)$$

$$\Delta F = \frac{\bar{n}(\bar{n} + 1)}{2} E''(\bar{n}) [1 + \beta E(\bar{n})].$$

The value $\bar{n}(\beta)$ in the formula (16) should be calculated as the solution of the equation

$$\beta E'(\bar{n}) = \ln \frac{\bar{n} + 1}{\bar{n}}. \quad (17)$$

The formulas (16) and (17) define the USE for the free energy of the quantum system with known energy spectrum. They can be generalized for systems with several degrees of freedom.

4 Operator Method for the Estimation of the Eigenvalues

In order to make the above result in practice more effective, it should be supplemented by some uniformly suitable estimation for the eigenvalues considered as a function of quantum numbers and parameters of the Hamiltonian \hat{H} of the system. For this purpose we use the zeroth approximation of the OM [2] when the same operators \hat{a}, \hat{a}^+ , used in formula (8), are introduced to \hat{H} by means of the canonical transformation for the operators of coordinate and momentum

$$\hat{x} = \frac{1}{\sqrt{2\omega}}(\hat{a} + \hat{a}^+), \quad \hat{p} = -i\sqrt{\frac{\omega}{2}}(\hat{a} - \hat{a}^+), \quad (18)$$

with the frequency ω considered as variational parameter.

Then one has to select, in the total Hamiltonian, that part \hat{H}_0 which is diagonal with respect to the excitation number operator $\hat{n} = \hat{a}^+ \hat{a}$:

$$\hat{H} = \hat{H}_0(\hat{n}) + \hat{H}_1, \quad [\hat{H}_0, \hat{n}] = 0. \quad (19)$$

Thus the OM zeroth approximation for the energy levels of the system is defined as the evident eigenvalues of the operator

$$\hat{H}_0|n\rangle = E^{(0)}(n, \omega_n)|n\rangle. \quad (20)$$

The frequency parameters ω_n are the solutions of the variational equations for every quantum number

$$\frac{\partial E^{(0)}(n, \omega_n)}{\partial \omega_n} = 0. \quad (21)$$

As shown for a number of physical systems [2,4,5], the function $E^{(0)}(n, \omega_n)$ defines the USE for the exact energy spectrum with rather good accuracy. Thus, Eqs. (20) and (21), together with (16) and (17), permit us to calculate the USE for the quantum free energy as the solution of the system of algebraic equations.

In order to illustrate how this method works, let us consider the Hamiltonian corresponding to the problem of the anharmonic oscillator,

$$\hat{H} = \frac{1}{2}(\hat{p}^2 + \hat{x}^2) + \mu\hat{x}^2 + \lambda\hat{x}^4. \quad (22)$$

In this case the transformation (18) leads to the function

$$E^{(0)}(n, \omega_n) = \frac{2n+1}{4} \left[\omega_n + \frac{1}{\omega_n}(1+2\mu) \right] + \frac{3\lambda}{4\omega_n^2}(2n^2+2n+1). \quad (23)$$

The parameter ω_n is the solution of the cubic equation

$$\omega_n^3 - \omega_n(1+2\mu) - \frac{6\lambda(2n^2+2n+1)}{2n+1} = 0. \quad (24)$$

Then Eq. (17) for the averaged number of the excitations, i.e. the saddle point for the partition function, reads

$$\frac{\beta}{2} \left[\frac{1}{\omega_{\bar{n}}}(\omega_{\bar{n}}^2 + 1 + 2\mu) + \frac{3\lambda}{\omega_{\bar{n}}^2}(2\bar{n} + 1) \right] = \ln \frac{\bar{n} + 1}{\bar{n}}, \quad (25)$$

and the free energy takes the following form:

$$F^{(0)}(\beta, \lambda, \mu) = \frac{1}{4}\bar{n} \left(\omega_{\bar{n}} - \frac{1+2\mu}{\omega_{\bar{n}}} \right) + \frac{1}{8} \left(\omega_{\bar{n}} + \frac{1+2\mu}{\omega_{\bar{n}}} \right) - \frac{3\lambda}{2\omega_{\bar{n}}^2}\bar{n}(2\bar{n}+1) - \frac{1}{\beta} \ln \bar{n}. \quad (26)$$

In this work, we restrict ourselves to analytical calculations only. Let us consider some limiting cases for the solutions of equations (22) to (24). If, for example, the anharmonic parameter λ is zero, equations (22) and (23) lead to the exact values

$$\omega_n = \sqrt{1+2\mu}, \quad E^{(0)}(n, \omega_n) = E_n = \sqrt{1+2\mu} \left(n + \frac{1}{2} \right). \quad (27)$$

Eq. (24) has also the analytical solution

$$\bar{n} = \frac{e^{-\nu}}{1 - e^{-\nu}}, \quad \nu = \beta\sqrt{1+2\mu}. \quad (28)$$

When substituting this value, Eq. (16) transforms to the expression

$$F = \frac{1}{\beta} \ln [2 \sinh (\beta / 2 \sqrt{1+2 \mu})], \quad (29)$$

which coincides with the exact one as distinct from the usual thermodynamic perturbation theory.

Let us consider also the limiting cases of low ($\beta \rightarrow \infty$) and high ($\beta \rightarrow 0$) temperature. Using these conditions one can simplify the formulae (17) and (22) to (26) to the following form. In the case of $\beta \rightarrow \infty$ and thus

$$\bar{n} \simeq e^{-\beta \nu_0} \ll 1,$$

we have

$$\begin{aligned} \omega_0^3 - \omega_0(1+2\mu) - 6\lambda &= 0, \\ E(n, \omega_n) = E(0, \omega_0) &= \frac{1}{8} \left(3\omega_0 + \frac{1+2\mu}{\omega_0} \right) \simeq F^{(0)}, \\ \nu_0 = E'(0, \omega_0) &= \frac{1}{4} \left(3\omega_0 + \frac{1+2\mu}{\omega_0} \right), \\ \Delta F \simeq \frac{1}{2} \bar{n} \frac{3\lambda}{\omega_0^2} \beta E(0, \omega_0) &\simeq \frac{1}{32} \left(\omega_0 - \frac{1+2\mu}{\omega_0} \right) \left(3\omega_0 + \frac{1+2\mu}{\omega_0} \right) \beta e^{-\beta \nu_0}, \\ \left| \frac{\Delta F}{F^{(0)}} \right| &= \frac{1}{4} \left| \left(\omega_0 - \frac{1+2\mu}{\omega_0} \right) \right| \beta e^{\beta \nu_0} \ll 1. \end{aligned}$$

In the opposite case of high temperature $\beta \rightarrow 0$ and

$$\bar{n} = \left(\frac{36}{\lambda} \right)^{1/4} \left(\frac{3}{4\beta} \right)^{3/4} \gg 1,$$

we obtain, leaving only the major \bar{n} part in Eq. (24) and neglecting the term proportional to $\omega_{\bar{n}}$,

$$\begin{aligned} \omega_{\bar{n}} &\simeq (6\lambda\bar{n})^{1/3}, \\ \bar{E} = E(\bar{n}, (6\lambda\bar{n})^{1/3}) &\simeq \frac{9}{2} \left(\frac{\lambda}{36} \right)^{1/3} \bar{n}^{4/3}, \\ F^{(0)} &\simeq \bar{E} - \frac{1}{\beta} \left[\bar{n} \ln \frac{\bar{n}+1}{\bar{n}} + \ln \bar{n} \right] \simeq \frac{3}{4\beta} \ln \beta, \\ \Delta F &\simeq \frac{\bar{n}^2}{2} E''(1 + \beta E) \simeq \frac{7}{24\beta}, \end{aligned}$$

$$\left| \frac{\Delta F}{F^{(0)}} \right| \simeq \frac{7}{18|\ln \beta|} \ll 1.$$

So, the second-order corrections are small in both limiting cases. That means that the system of algebraic equations (22) to (26) defines the USE for the anharmonic oscillator.

Finally, the proposed method can be generalized to quantum systems with many internal degrees of freedom. This permits to consider analytically the thermodynamic characteristics of real molecular gases.

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