Comparison of Thermodynamic Characteristics in Ordinary Quantum and Classical Approaches and Game Theory

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Abstract

We fix the temperature $T$ and consider mean energy and Boltzmann-Gibbs-Shannon entropy as two players of a game. As a result, basic formulas for the ordinary quantum mean energy and the Boltzmann-Gibbs-Shannon entropy are derived. We compare also the quantum and classical approaches without a demand for Planck’s constant being small. Important inequalities for statistical sum, quantum energy, quantum entropy, and their classical analogs follow.

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1 Introduction

In the theory of ordinary quantum equilibrium systems $[7,13]$ the statistical sum

$$Z_q(\beta, h) = \sum_{n=1}^{\infty} e^{-\beta E_n(h)}, \quad \beta = 1/kT$$

(1)

plays the main role. In formula (1) $k$ is the Boltzmann constant, $h$ is the Plank constant, and $E_n(h)$ are eigenvalues of the energy operator $L$ (see (16)) of the considered system. In the classical physics the integral

$$Z_c(\beta) = \int \int e^{-\beta H(p,q)} \, dp, \, dq$$

(2)

is the analog of the sum in (1). In formula (2) the function

$$H(p, q) = \frac{1}{2m} \sum_{j=1}^{N} p_j^2 + V(q)$$

(3)

is the classical Hamiltonian, $p$ are corresponding generalized momenta, $q$ are generalized coordinates, and $m$ is the mass of a particle. E. Wigner and J.G.
Kirkwood (see [11, Ch. 4]) showed that the quantum statistical sum \( Z_q(\beta, h) \) and the classical statistical sum \( Z_c(\beta) \) are connected by the relation

\[
\lim_{h \to 0} (2\pi h)^N Z_q(\beta, h) = Z_c(\beta),
\]

where \( N \) is the dimension of the corresponding coordinate space. Schrödinger equation is of great current interest (see, for instance, recent works [2, 5, 6, 12, 19, 23] and references therein). In particular, the comparison of the quantum and classical approaches without the demand for \( h \) being small is of important scientific and methodological interest. For that, we consider the quantum mean energy

\[
E_q(\beta, h) = \sum_{n=1}^{\infty} E_n(h)e^{-\beta E_n(h)}/Z_q(\beta, h)
\]

and the classical mean energy

\[
E_c(\beta) = \int \int H(p, q)e^{-\beta H(p, q)} dp dq/Z_c(\beta)
\]

of the same system. In the present paper we shall discuss the following conjectures.

Conjecture 1.1 The inequality

\[
(2\pi h)^N Z_q(\beta, h) \leq Z_c(\beta)
\]

is true for all \( h > 0 \) and \( \beta > 0 \).

Conjecture 1.2 The inequality

\[
E_q(\beta, h) \geq E_c(\beta)
\]

is true for all \( h > 0 \) and \( \beta > 0 \).

Conjecture 1.3 The following asymptotic equalities

\[
(2\pi h)^N Z_q(\beta, h) \sim Z_c(\beta), \quad \beta \to +0,
\]

\[
E_q(\beta, h) \sim E_c(\beta), \quad \beta \to +0
\]

are valid.

It is essential that the limits, which are considered in (4) and (9), are different. Note also that \( \beta = k/T \), which means that the relation \( \beta \to +0 \) is equivalent to \( T \to +\infty \).

We proved (see [20, 21]) that in important special cases (one-dimensional potential well and harmonic oscillator) relations (7)-(10) are true. In the present paper we consider a much more general case.

In Section 5 we consider the quantum energy \( E \) and the entropy \( S \) together. One could repeat a statement from [24, p. vii]: "... virtually nothing more
basically than energy and entropy deserves the qualification of pillars of modern physics. The connection between E and S we interpret in terms of game theory. The necessity of the game theory approach can be explained in the following way. According to the second law of thermodynamics, physical system in equilibrium has the maximal entropy among all the states with the same energy. So, a problem of the conditional extremum appears, but the corresponding equation for the Lagrange multiplier is transcendental and very complicated. Therefore, another argumentation is needed to find the basic Gibbs formulas (see [7, 13]).

In our approach we consider another extremal problem. For that purpose we fix the Lagrange multiplier \( \beta = k/T \) (not energy), that is, we fix the temperature and introduce the compromise function \( F = -\beta E_q(\beta, h) + S_q(\beta, h) \). Then the mean energy \( E_q(\beta, h) \) and the entropy \( S_q(\beta, h) \) are two players of a game and the compromise result is the extremum point of \( F \). The obtained results have an interesting intersection with the results from game theory, namely, the transition from the classical (determined strategy) to quantum (probabilistic strategy) mechanics leads to a gain for both players. Basic formulas for the quantum energy and for the entropy follow from this result.

2 General case, statistical sum

We use measure and integration connected with Wiener processes (see [11, 15, 22]). With the help of these notions we formulate the important D. Ray’s results [17].

**Theorem 2.1** (D. Ray [17]) Let \( \Omega \) be an open set in \( \mathbb{R}^N \) such that at each boundary point \( x \) of \( \Omega \) there is a sphere with the center at \( x \), some open sector of which is entirely outside the closure \( \overline{\Omega} \) of \( \Omega \).

Let \( \bar{V}(x) \) be a non-negative function, which is bounded on each bounded subset of \( \overline{\Omega} \) and satisfies a Lipschitz condition

\[
|\bar{V}(x') - \bar{V}(x)| \leq M(x)|x' - x|^{\alpha}, \quad 0 < \alpha \leq 1, \quad x', x \in \overline{\Omega}.
\] (11)

Suppose also that either \( \Omega \) is bounded or that

\[
\lim_{|x| \to \infty} V(x) = \infty, \quad x \in \Omega.
\] (12)

Then the differential operator

\[
\bar{L}u = -\frac{1}{2} \Delta u + \bar{V}(x)u
\] (13)

on \( L^2(\Omega) \), where \( u = 0 \) on the boundary, has a discrete spectrum \( \lambda_n > 0 \) and

\[
\sum_{n=1}^{\infty} e^{-t \lambda_n} \leq (2\pi t)^{-N/2} \int_{\overline{\Omega}} e^{-t \bar{V}(x)} dx, \quad t > 0.
\] (14)
D. Ray proved also the relation
\[
\sum_{n=1}^{\infty} e^{-t\lambda_n} \sim (2\pi t)^{-N/2} \int_{\Omega} e^{-t\bar{V}(x)} dx, \quad t \to 0.
\] (15)

**Remark 2.1** For the case $\Omega = \mathbb{R}^N$, the results similar to (14) and (15) were deduced in a number of papers (see the results and references in B. Simon’s book [22], Chapter 3).

The relation (15) can be interpreted as a weak form of M. Kac’s principle of imperceptibility of the boundary [11] in the case of equation (13). We note that our paper [18] is dedicated to a weak form of the Kac’s principle of imperceptibility of the boundary in the case of the stable processes. It is interesting that D. Ray’s results can be interpreted in a new way.

We shall show that inequalities (6) (Conjecture 1.1) and (8) (Conjecture 1.3) follow from (14) and (15), respectively. To do it let us consider the Schrödinger differential operator
\[
L\Psi = -\frac{\hbar^2}{2m} \Delta \Psi + V(x)\Psi
\] (16)
in an open subset $\Omega$ of the $N$-dimensional Euclidean space $\mathbb{R}^N$. Assume that
\[
\Psi|_\Gamma = 0,
\] (17)
where $\Gamma$ is the boundary of $\Omega$. Taking into account the relation $\lambda_n = \frac{\hbar^2}{2m} E_n$ we see that in the case (16) inequality (14) has the form
\[
\sum_{n} e^{-t\frac{\hbar^2}{2m} E_n} \leq (2\pi t)^{-N/2} \int_{\Omega} e^{-t\frac{\hbar^2}{2m} V(x)} dx, \quad t > 0.
\] (18)

From (2), where the integral in $p$ is taken over $\mathbb{R}^N$, and from (3), we obtain
\[
Z_c(\beta) = (2\pi m / \beta)^{N/2} \int_{\mathbb{R}^N} e^{-\beta V(x)} dx.
\] (19)

Putting $t = \frac{\hbar^2}{m} \beta$ and taking into account (11), we write (18) in the form
\[
(2\pi \hbar)^N Z_q(\beta, h) \leq Z_c(\beta), \quad \beta = k/T.
\] (20)

In the same way we deduce from (15) that
\[
(2\pi \hbar)^N Z_q(\beta, h) \sim Z_c(\beta), \quad \beta = k/T \to 0.
\] (21)

So we proved the following assertion.

**Theorem 2.2** Let the conditions of Theorem 2.1 be fulfilled. Then relations (7) and (9) are true.

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Corollary 2.1 Let the conditions of Theorem 2.1 be fulfilled. If
\[ \int_{\Omega} e^{-\beta V(x)} dx < \infty, \]  
then
\[ \sum_{n=1}^{\infty} e^{-\beta E_n} < \infty. \]

Example 2.1 (Potential well.) If $\Omega$ is bounded and $V(x) = 0$, then according to (19) we have
\[ Z_c(\beta) = \frac{(2\pi m/\beta)^{N/2}}{\text{vol}(\Omega)}, \]  
where "vol" means volume.

3 General case, mean energy

The following assertion confirms partially Conjecture 1.2.

Theorem 3.1 Let the conditions of Theorem 2.1 be fulfilled and
\[ E_q(\beta, h) < \infty, \quad E_c(\beta) < \infty. \]  
Then the inequality
\[ \int_{+\tau}^{\beta} (E_q(\gamma, h) - E_c(\gamma)) d\gamma \geq 0, \quad \beta > 0 \]  
is true.

Proof. Using relations (1), (5) and (2), (6) we have
\[ E_q(\beta, h) = -\frac{\partial Z_q(\beta, h)}{\partial \beta}/Z_q(\beta, h), \quad E_c(\beta) = -\frac{\partial Z_c(\beta)}{\partial \beta}/Z_c(\beta). \]  
Formulas (27) imply that
\[ \int_{\tau}^{\beta} (E_q(\gamma, h) - E_c(\gamma)) d\gamma = \log \left( \frac{Z_c(\gamma)/((2\pi h)^N Z_q(\gamma, h))}{\gamma} \right), \]  
where $0 < \tau < \beta$. According to (20), (21), and (28) we obtain
\[ \int_{+\tau}^{\beta} [E_q(\gamma, h) - E_c(\gamma)] d\gamma = \log \left( \frac{Z_c(\beta)/((2\pi h)^N Z_q(\beta, h))}{\gamma} \right) \geq 0. \]  
The theorem is proved. □

Example 3.1 (Potential well.) If $\Omega$ is bounded and $V(x) = 0$, then according to (24) and (27) we have
\[ E_c(\beta) = N/2\beta. \]  

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4 General case, Boltzmann-Gibbs-Shannon entropy

The entropy of a quantum system is defined by the relation (see [7, 13]):

\[ S_q = - \sum_{n=1}^{\infty} P_n \log P_n, \quad (31) \]

where

\[ P_n(\beta, h) = e^{-\beta E_n(h)} / Z_q(\beta, h). \quad (32) \]

The entropy is one of the fundamental notions in quantum mechanics (see some recent results, discussions, and references in [3,4,14,24–26]). It follows from (1), (5), and (31), (32) that

\[ S_q(\beta, h) = \beta E_q(\beta, h) + \log Z_q(\beta, h). \quad (33) \]

The classical definition of the entropy has the form (see [13, Ch. 1]):

\[ S_c(\beta, h) = \beta E_c(\beta) + \log Z_c(\beta) - N \log (2\pi h). \quad (34) \]

Note that (34) contains a regularizing term \(-N \log (2\pi h)\).

Example 4.1 Now, we consider the case

\[ E_n(h) = \phi(h) E_n, \quad E_n > 0, \quad (35) \]

where \(E_n\) does not depend on \(h\), \(\phi(h)\) is a monotonically increasing function and \(\phi(+0) = 0\). In this case formula (33) takes the form

\[ S_q(\beta, h) = -\lambda \Phi'(\lambda) / \Phi(\lambda) + \log \Phi(\lambda), \quad (36) \]

where \(\lambda = \phi(h)\beta\) and

\[ \Phi(\lambda) = \sum_{n=1}^{\infty} e^{-\lambda E_n}. \quad (37) \]

Lemma 4.1 The function

\[ \Psi(\lambda) = -\lambda \Phi'(\lambda) / \Phi(\lambda) + \log \Phi(\lambda) \quad (38) \]

is a monotonically decreasing function.

Proof. According to (37) and (38) the inequality

\[ \Psi'(\lambda) = -\lambda \sum_{n>m} (E_n - E_m)^2 e^{-\lambda(E_n+E_m)} / \Phi^2(\lambda) < 0 \quad (39) \]

is true. The lemma is proved. \(\square\)

Using Lemma 4.1 we obtain the following statement.
Theorem 4.1 Let conditions (35) be fulfilled. Then the entropy \( S_q(\beta, h) \) is a monotonically decreasing function with respect to \( \beta \) and with respect to \( h \).

Example 4.2 (Potential well.) Consider the spectral problem

\[
-\frac{\hbar^2}{2m} \Delta u = Eu, \quad u_\Gamma = 0
\]

in an \( N \)-dimensional domain \( \Omega \) with the boundary \( \Gamma \). It is easy to see that condition (35) is fulfilled for this problem and \( \phi(h) = h^2 \). Hence, the assertions of Theorem 4.1 are true in the case of the potential well.

Example 4.3 (Homogeneous potential.) We suppose that the non-negative potential \( V(x) \) is a homogeneous function, that is,

\[
V(hx) = h^\nu V(x), \quad h > 0, \quad \nu > 0, \quad x \in \mathbb{R}^N.
\]

Remark 4.1 The function

\[
V(r) = r^\nu, \quad r = \left( \sum_{k=1}^{N} x_k^2 \right)^{1/2}, \quad \nu > 0
\]

satisfies condition (41).

Using substitution \( x = h^\alpha y \) we rewrite the equation

\[
-\frac{h^2}{2m} \Delta u(x) + V(x)u(x) = Eu(x)
\]

in the form

\[
-\frac{h^{2-2\alpha}}{2m} \Delta \tilde{u}(y) + h^{\alpha \nu} V(y)\tilde{u}(y) = E\tilde{u}(y).
\]

We note that \( 2-2\alpha = \alpha \nu \) if \( \alpha = 2/(2+\nu) \). In this case (35) holds and

\[
\phi(h) = h^{2\nu/(2+\nu)}.
\]

Hence, the assertions of Theorem 4.1 are true in the case of homogeneous potentials.

Relations (1) and (5) imply the assertion.

Proposition 4.1 Let a potential \( V(r) \) have the form (42). Then we have

\[
\frac{d}{dh} \left( h^N Z_q(\beta, h) \right) = h^{N-1} Z_q(\beta, h) \left( N - \alpha \beta E_q(\beta, h) \right).
\]

By some direct calculations we get another proposition.

Proposition 4.2 Let a potential \( V(r) \) have the form (42). Then we have

\[
E_c(\beta) = \frac{N}{\alpha \beta}.
\]
From Propositions 4.1 and 4.2 we obtain the statement below.

**Proposition 4.3** Let a potential \( V(r) \) have the form (42). Then the relations

\[
E_q(\beta, h) > E_c(\beta) \quad \text{and} \quad \frac{d}{dh} (h^N Z_q(\beta, h)) < 0
\]

are equivalent.

In addition to Conjecture 1.1 we formulate the following conjecture.

**Conjecture 4.1** The function \( h^N Z_q(\beta, h) \) is monotonically decreasing with respect to \( h \).

If (42) holds, Proposition 4.3 shows that Conjectures 1.1 and 4.1 are equivalent.

**Remark 4.2** In particular, our considerations could be used to treat an old problem by A. Wehrl. In his paper [26] he wrote: "It is usually claimed that in the limit \( h \to 0 \) the quantum-mechanical expression tends toward the classical one, however, a rigorous proof of this is nowhere to be found in the literature". Assuming that

\[
E_q(\beta, h) \to E_c(\beta), \quad h \to 0,
\]

\[
(2\pi h)^N Z_q(\beta, h) \to Z_c(\beta), \quad h \to 0,
\]

and using (4.3) and (4.4) we get

\[
S_q(\beta, h) = S_c(\beta, h) + o(1), \quad h \to 0.
\]

The present paper contains conditions for relations (49) and (50) to hold.

## 5 Connection between energy and entropy, game theory point of view

Let the eigenvalues \( E_n \) of the energy operator \( L \) be given. Consider the mean energy \( E = \sum_n E_n P_n \) and the entropy \( S = -\sum_n P_n \log P_n \). Here \( P_n \) are the corresponding probabilities, that is, \( \sum_n P_n = 1 \). Hence \( P_n \) can be represented in the following form \( P_n = p_n / Z \), where \( Z = \sum_n p_n \). Our aim is to find the probabilities \( P_n \). For that purpose we consider the function

\[
F = \lambda E + S,
\]

where \( \lambda = -\beta = -1/kT \) (see (1)).

**Fundamental Principle.** The function \( F \) defines the game between the mean energy \( E_q \) and the entropy \( S_q \).
To find the stationary point of $F$ we calculate

$$\frac{\partial F}{\partial p_k} = \lambda \left( E_k/Z - \sum_{n=1}^{\infty} E_n p_n / Z^2 \right) - (\log p_k) / Z + \sum_{n=1}^{\infty} p_n \log p_n / Z^2. \quad (53)$$

It follows from (53) that the point

$$p_n = e^{\lambda E_n}, \quad n = 1, 2, \ldots \quad (54)$$

is a stationary point. Moreover, the stationary point is unique up to a scalar multiple. Without loss of generality this multiple can be fixed as in (54).

**Corollary 5.1** The basic formulas (5), (31), and (32) are immediate from (54).

By direct calculation we get in the stationary point (54) the equalities

$$\frac{\partial^2 F}{\partial p_k^2} = -Z_k / (p_k Z^2) < 0, \quad Z_k := \sum_{j \neq k} p_j; \quad \frac{\partial^2 F}{\partial p_k \partial p_j} = 1 / Z^2 > 0, \quad j \neq k. \quad (55)$$

Relations (55) imply the following assertion.

**Corollary 5.2** The stationary point (54) is a maximum of the function $F$.

**Proof.** We use the following result (see [16, Ch.7, Problem 7]):

$$\det \begin{bmatrix} r_1 & a & a & \ldots & a \\ b & r_2 & a & \ldots & a \\ b & b & r_3 & \ldots & a \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ b & b & b & \ldots & r_k \end{bmatrix} = \frac{af(b) - bf(a)}{a - b}, \quad (56)$$

where

$$f(x) = (r_1 - x)(r_2 - x)\ldots(r_k - x). \quad (57)$$

In the case that $a = b$, the equality below is easily derived from (56):

$$\det \begin{bmatrix} r_1 & a & a & \ldots & a \\ a & r_2 & a & \ldots & a \\ a & a & r_3 & \ldots & a \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ a & b & a & \ldots & r_k \end{bmatrix} = -af'(a) + f(a). \quad (58)$$

Using (55) and (58) we calculate the Hessian $H_k(F)$ in the stationary point:

$$H_k(F) = Z^{-2k}[-f'(1) + f(1)], \quad (59)$$

where $f$ is given by (57) and $r_n = -Z_n / p_n$. Rewrite (59) in the form

$$H_k(F) = (-Z)^{-k} \left( 1 - \left( \sum_{n=1}^{k} p_n / Z \right) / \prod_{n=1}^{k} p_n \right)$$
to see that the relation \( \text{sgn} \left( H_k(F) \right) = (-1)^k \) is true. Hence, the corollary is proved. \( \square \)

Note that the basic relations (54) are obtained by solving a new extremal problem. Namely, in the introduced function \( F \) the parameter \( \lambda \) is fixed instead of the energy \( E \), which is usually fixed.

**Remark 5.1** In the game theory the transition from deterministic to probabilistic strategy leads to a gain for players. The transition from classical to quantum mechanics leads to a gain for both players (energy and entropy) too (see [3] and Theorem 4.4).

### 6 Conclusion

For small values of \( h \) the relation between quantum and classical statistical sums was deduced by E. Wigner and J.G. Kirkwood. However, the comparison of the quantum and classical approaches for energy, statistical sum and entropy without the demand of \( h \) being small is of essential scientific and methodological interest. In our paper we obtain some general results and discuss some conjectures connected with the formulated problem.

In particular, general and rigorous results on relations between ordinary quantum and classical statistical sums (see Theorem 2.2) could be derived from an important work by D. Ray [17] on the spectra of Schrödinger operators. Furthermore, our approach allows to treat an old entropy problem by A. Wehrl (see Remark 4.2). We introduce also the function, the extremum point of which gives the well-known Gibbs formulas. The results of the paper intersect with some ideas of game theory (see, e.g., [10]): the transition from classical (determined strategy) to quantum mechanics (probabilistic strategy) leads to a gain for both players. However, we stress that the connection between energy and entropy is a new type of a game, where the players do not have a freedom to choose their strategy.

Our note could be considered as an input into the important discussion on the deterministic and probabilistic aspects of quantum theory (see [1][8][9], and references therein). As the next step it would be fruitful to consider also the possibility to generalize our conjectures and results for the case of nonextensive statistical mechanics [23].

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