On the Validity of Certain Variational Principles for the Free Energy

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(Received October 8, 1984)

Some recently-published generalizations of the Peierls-Bogolyubov variational principle of statistical mechanics are shown to be defective.

Variational methods have long been popular tools in statistical mechanics in situations where either exact bounds to quantities of interest are required or where perturbational methods are not applicable, e.g., due to strong coupling. Probably the best-known variational method is the one due to Peierls and Bogolyubov, stating that the canonical free energy

\[ F: = -\beta^{-1} \log \text{Tr} \ e^{-\beta H} \]  

(1)

of a system described by the Hamiltonian \( H \) fulfills the inequality

\[ F \leq F_0 + \langle H - H_0 \rangle_\beta =: F_\beta. \]  

(2)

Here \( F_0 \) is the canonical free energy corresponding to some simplified Hamiltonian \( H_0 \) and \( \langle \cdot \rangle_\beta \) is the canonical average corresponding to \( H_0 \). Usually \( H_0 \) contains one or more variational parameters which are chosen such as to minimize the r.h.s. of (2).

In a recent paper published in this journal an improved version of (2) was suggested. However, it is shown below that the calculation in Ref. 2 contains a mistake invalidating the result. I shall also point out several errors seriously affecting the results of an earlier paper by the same author.

The starting point of many discussions of the variational principle (2), including is the inequality

\[ \text{Tr}(A \log A - A \log B) \geq \text{Tr}(A - B) \]  

(3)

for positive self-adjoint operators \( A \) and \( B \) such that both sides of (3) exist. Substituting for \( A \) the canonical density operator

\[ \rho_0 := e^{-\beta H_0}/\text{Tr} \ e^{-\beta H_0} \]  

(4)

corresponding to \( H_0 \) and for \( B \) the canonical density operator corresponding to \( H \), respectively, one arrives at (2). Using the same choice for \( B \), but leaving \( A \) unspecified, subject only to the normalization condition

\[ \text{Tr} \ A = 1 \]  

(5)

one gets

\[ F \leq \text{Tr} \left( AH + \frac{1}{\beta} A \log A \right). \]  

(6)

where the r.h.s. attains its minimum value for \( A = B \) and then yields the true free energy \( F \). The normalization condition \( \text{Tr} A = \text{Tr} B = 1 \) is obviously essential in going from (3) to either (2) or (6). Oguchi assumes that the Hamiltonian \( H_0 \) contains a variational parameter \( "a" \) distributed according to a probability density \( P(a) \) (to be determined later) and puts

\[ A := P(a) e^{-\beta H_0}/\text{Tr} e^{-\beta H_0} \]  

(7)

which requires the use of a modified trace operation in (3), namely

\[ \text{Tr} := \int da \ \text{Tr}. \]  

(8)

He then states that

\[ F \leq \int da \left[ \frac{1}{\beta} P(a) \log P(a) + P(a) F_\beta(a) \right] \]  

(9)

(making explicit that \( F_\beta \) depends on \( a \)). The \( P \log P \)-term in (9) has the appearance of an additional entropy which is intended to lower the Peierls-Bogolyubov bound to the free energy. Inequality (9), however, cannot be derived from (3), as I shall now demonstrate. Using (3) with the modified trace operation (8) and choosing

\[ B := Q(a) e^{-\beta H}/\text{Tr} e^{-\beta H} \]  

(10)

(with an arbitrary positive function \( Q(a) \)) and \( A \) according to (7), it is easy to obtain

\[ F \leq \int da P(a) F_\beta(a) \]

\[ + \frac{1}{\beta} \int da P(a) (\log P(a) - \log Q(a)) \]
Here $F_0(a_0)$ denotes the minimum value of $F_0(a)$ and the second inequality is obtained by employing the "classical analogue" of (3) and the principle that every function is greater than its minimum. This second inequality clearly states that the new upper bound on the free energy cannot be better (i.e., lower) than the Peierls-Bogolyubov bound, no matter how cleverly $P(a)$ and $Q(a)$ are chosen. There seems to be no choice of $Q(a)$ leading from (11) to (9); $Q(a)=1$ yields the $P \log P$-term of (9) correctly but leaves an additional term of unspecified magnitude due to the different normalizations of $P(a)$ and $Q(a)$. On the other hand, $P(a)=Q(a)$ cancels the $P \log P$-term as well as the normalization term and leaves only the original Peierls-Bogolyubov bound, weighted by $P(a)$. The error in Oguchi's derivation of (9) lies in the fact that he substitutes (7) in (6) and tacitly changes the "Tr" in (6) into "Tr". This, however, is illegal since the derivation of (6) from (3) rests on the assumption that $A$ and $B$ are normalized with respect to one and the same trace operation, namely "Tr". Suspending this assumption and starting from (3), as done above, shows that no advantage over the Peierls-Bogolyubov bound is obtained. As (9) is the central result of Ref. 2, the discussion may be closed at this point.

Next, we turn to some results of paper 3 in which upper and lower bounds to the free energy are derived from (3) or (6). For the derivation of the upper bounds Oguchi uses a modified form of the Peierls-Bogolyubov inequality (2) which is derived by substituting

$$A = e^{-\beta H} Y / \text{Tr} e^{-\beta H}$$

in (6) and requiring

$$Y > 0,$$

$$[H_0, Y] = 0,$$

$$\text{Tr} e^{-\beta H_0} Y = \text{Tr} e^{-\beta H_0}.$$

By these manipulations one may easily obtain

$$F \geq -\frac{1}{\beta} \log \text{Tr} e^{-\beta H_0} + \left\langle Y (H - H_0) + \frac{1}{\beta} Y \log Y \right\rangle,$$

where $\left\langle \right\rangle_0$ has the same meaning as in (2). It is, however, evident that (16) may be obtained from (2) by defining a new (temperature dependent) effective Hamiltonian

$$H'_0 := H_0 - \frac{1}{\beta} \log Y$$

and thus (16) cannot be considered a generalization of (2).

Finally an error in the lower bound to the free energy given in Theorem 4 of Ref. 3 is pointed out. This lower bound is derived by writing

$$H = \sum_{i=1}^{q} H_i$$

and using (6) together with the fact that the minimum value of a sum is greater than the sum of the minimal values of the individual terms. One obtains

$$F \geq \sum_{i=1}^{q} \min \left\{ \text{Tr} A H_i + \frac{1}{\beta q} \text{Tr} A \log A \right\}$$

where min means the minimum with respect to all positive operators $A$ of unit trace. Comparing this to (6) and taking into consideration the remarks following (6), one sees that the $i$-th term of the sum in (19) is nothing but the free energy corresponding to the Hamiltonian $H_i$ and the inverse temperature $q \beta$ and thus

$$F \geq -\frac{1}{\beta q} \sum_{i=1}^{q} \log \text{Tr} e^{-\beta q H_i},$$

which differs from the result given in Ref. 3 by a factor $q$ in the exponential. Finally I wish to give an explicit example showing the invalidity of Oguchi's lower bound to the free energy. Putting simply

$$H_i = H / q, \quad (i = 1, \cdots, q)$$

one concludes from Oguchi's formula that the free energy corresponding to $H$ is greater than the free energy corresponding to $H/q$, which is obviously wrong for any Hamiltonian having a negative ground-state energy. The well-known lower bound

$$E_\rho(H) \geq \sum_{i=1}^{q} E_\rho(H_i)$$

for the ground state energy of a Hamiltonian of the form (18) can only be derived from (20), but not from Oguchi's formula.

I am grateful to G. Kruhl for drawing my attention to Oguchi's work and to U. Brandt for a helpful discussion.

