First online: December 1, 2021
Last modified: December 1, 2021
Katsunori Kubo, ASRC, JAEA

Variational principle for free energy

Lemma I

When A and B are Hermitian operators and $f(x)$ is a concave real-valued function,

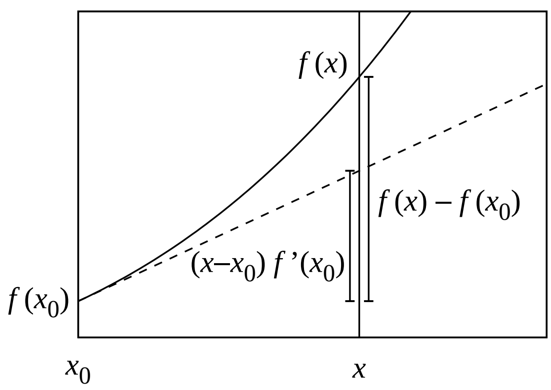
$$\mathrm{Tr}[f(B) - f(A) - (B - A)f'(A)] \geq 0. \tag{1}$$

Proof

When a_n and $|a_n\rangle$ are eigenvalues and eigenstates of A, b_n and $|b_n\rangle$ are eigenvalues and eigenstates of B and these eigenstates are normalized,

$$\begin{aligned} &\mathrm{Tr}[f(B) - f(A) - (B - A)f'(A)] \\ =& \sum_n \langle a_n|f(B) - f(a_n) - (B - a_n)f'(a_n)|a_n\rangle \\ =& \sum_{n,m} \langle a_n|f(B) - f(a_n) - (B - a_n)f'(a_n)|b_m\rangle\langle b_m|a_n\rangle \\ =& \sum_{n,m} |\langle a_n|b_m\rangle|^2[f(b_m) - f(a_n) - (b_m - a_n)f'(a_n)]. \end{aligned}$$

By assumption, $f(b_m) - f(a_n) - (b_m - a_n)f'(a_n) \geq 0$ (see the figure below) and (1) holds.



Lemma II

When all the eigenvalues a_n and b_n of Hermitian operators A and B satisfy $a_n > 0$, $b_n \geq 0$ and $\mathrm{Tr}A = \mathrm{Tr}B$,

$$\mathrm{Tr}B[\ln B - \ln A] \geq 0. \tag{2}$$

proof

When $f(x) = x \ln x$, $f'(x) = \ln x + 1$ and $f''(x) = 1/x$. Thus, $f(x)$ is a convex function for $x > 0$. Then, we substitute $f(x) = x \ln x$ into (1):

$$\begin{aligned}
&\mathrm{Tr}[B \ln B - A \ln A - (B - A)(\ln A + 1)] \\
&= \mathrm{Tr}[B \ln B - B \ln A - (B - A)] \\
&= \mathrm{Tr}[B \ln B - B \ln A] \\
&= \mathrm{Tr}B[\ln B - \ln A] \geq 0.
\end{aligned}$$

Bogoliubov-Feynman inequality

We consider

$$\begin{aligned}
A &= \frac{e^{-\beta H}}{\mathrm{Tr}\, e^{-\beta H}} = \frac{e^{-\beta H}}{e^{-\beta F}} = e^{\beta(F-H)}, \\
B &= \frac{e^{-\beta H_0}}{\mathrm{Tr}\, e^{-\beta H_0}} = \frac{e^{-\beta H_0}}{e^{-\beta F_0}} = e^{\beta(F_0-H_0)},
\end{aligned}$$

and definite $\mathrm{Tr}B[\cdots] = e^{\beta F_0}\, \mathrm{Tr}\, e^{-\beta H_0}[\cdots] = \langle \cdots \rangle_0$. Then, (2) becomes

$$\begin{aligned}
&\langle \ln B - \ln A \rangle_0 \\
&= \beta \langle (F_0 - H_0) - (F - H) \rangle_0 \\
&= \beta (F_0 - F + \langle H - H_0 \rangle_0) \geq 0.
\end{aligned}$$

Thus,

$$F_0 + \langle H - H_0 \rangle_0 \geq F. \tag{3}$$

If we choose a mean-field Hamiltonian H_0 that satisfies $\langle H \rangle_0 = \langle H_0 \rangle_0$, we obtain $F_0 \geq F$. In this way, a mean-field theory can be constructed as a variational theory of free energy.

Peierls inequality

We consider a normalized orthogonal basis $\{|n\rangle\}$ and

$$H_0 = \sum_n |n\rangle\langle n|H|n\rangle\langle n| \equiv \sum_n \bar{E}_n |n\rangle\langle n|.$$

For any operator A,

$$\langle A\rangle_0 = e^{\beta F_0}\,\mathrm{Tr}\,e^{-\beta H_0} A = e^{\beta F_0} \sum_n e^{-\beta \bar{E}_n} \langle n|A|n\rangle.$$

Since $\langle n|H_0|n\rangle = \langle n|H|n\rangle$, $\langle H_0\rangle_0 = \langle H\rangle_0$. Then, from (3),

$$F_0 = -k_{\mathrm{B}}T\ \ln \mathrm{Tr} e^{-\beta H_0} = -k_{\mathrm{B}}T\ \ln \sum_n e^{-\beta \bar{E}_n} \geq F.$$

References

[1] Kenn Kubo and Hidekazu Tanaka “Magnetism I” (Asakura Publishing, 2008) p. 213 [in Japanese].