Functional integral approach: A third formulation of quantum statistical mechanics

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Quantum statistical mechanics has developed primarily through two approaches, pioneered by Gibbs and Feynman, respectively. In Gibbs' method one calculates partition functions from phase-space integrations or sums over stationary states. Alternatively, in Feynman's approach, the focus is on the path-integral formulation. The Hubbard-Stratonovich transformation leads to a functional-integral formulation for calculating partition functions. We outline here the functional integral approach to quantum statistical mechanics, including generalizations and improvements to Hubbard's formulation. We show how the dimensionality of the integrals is reduced exactly, how the problem of assuming an unknown canonical transformation is avoided, how the reality of the partition function in the complex representation is guaranteed, and how the extremum conditions are simplified. This formulation can be applied to general systems, including superconductors.

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I. INTRODUCTION

In 1959 Hubbard [1] developed a functional-integral approach (FIA) to calculate the grand partition function of statistical mechanics. This approach is the third general approach to many-body statistical mechanics, and it gives rise to many interesting approximation schemes for many-body physics. The first two approaches to many-body quantum statistical mechanics are the configuration integral or sum over stationary states approach that goes back to Gibbs and the path-integral approach of Feynman.

The FIA has not been developed as fully as the first two approaches to statistical mechanics because of mathematical complexities and difficulties in generalizing the fundamental formulation. These matters are addressed in this paper after we first review Hubbard's functional-integral method.

A. Hubbard's method

Hubbard's approach was based on the Stratonovich identity [2]:

$$\int_{-\infty}^{\infty} \exp[-\pi x^2 - 2\sqrt{\pi} x \hat{A}]dx = e^{\hat{A}^2}. \tag{1}$$

Using this identity, the partition function can be transformed exactly from a many-body partition function to a functional integral over single-particle problems in a fictitious "time"-dependent external field. Begin with the usual definition of the partition function

$$\Xi = \mathrm{Tr}[e^{(\mu\hat{N}-\hat{H})/k_BT}], \tag{2}$$

where the Hamiltonian, $\hat{H}$, can be written in terms of a single-particle operator, $\hat{H}_0$, and a many-body term, $\hat{V}$:

$$\hat{H} = \hat{H}_0 + \hat{V},$$

$$\hat{V} = \frac{1}{2}\sum_{i,j;k,l} V_{i,j;k,l}\hat{a}_i^+\hat{a}_j\hat{a}_k^+\hat{a}_l. \tag{3}$$

Using the following notation

$$\beta \equiv \frac{1}{k_BT}, \quad \gamma \equiv (i,j), \hat{\xi}_{i,j} \equiv \hat{\xi}_\gamma \equiv \hat{a}_i^+\hat{a}_j,$$

$$\hat{K} \equiv \beta\sum_i \epsilon_i\hat{a}_i^+\hat{a}_i, \quad \hat{N} \equiv \sum_i \hat{a}_i^+\hat{a}_i, \tag{4}$$

then

$$\hat{V} = \frac{1}{2}\sum_{\gamma,\delta} V_{\gamma,\delta}\hat{\xi}_\gamma\hat{\xi}_\delta, \tag{5}$$

where the Hermitian property of the Hamiltonian ensures that $V^*_{\gamma,\delta} = V_{\delta,\gamma}$. Assuming that one can diagonalize $\hat{V}$ by a canonical transformation $\hat{S}$,

$$(\hat{S}^+\hat{V}\hat{S})_{\nu,\nu'} = \lambda_\nu\delta_{\nu,\nu'}, \tag{6}$$

then

$$\hat{V} = \frac{1}{2}\sum_\nu \lambda_\nu\hat{\rho}_\nu^2, \tag{7}$$

where

$$\hat{\rho}_{k,l} = \sum_{i,j} S_{i,j;k,l}\hat{a}_i^+\hat{a}_j \equiv \hat{\rho}_\nu. \tag{8}$$

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Making use of the ordering label technique of Feynman [3] and the Stratonovich identity of Eq. (1), Hubbard obtained

$$\Xi=\int e^{-L[x_{\nu,s}]}\prod_{\nu,s} dx_{\nu,s}, \tag{9}$$

where

$$L[x_{\nu,s}]=\pi\sum_{\nu,s} x_{\nu,s}^2+\beta f[x_{\nu,s}], \tag{10}$$

and f is the thermodynamic potential of an ideal gas moving in a time-dependent external field:

$$e^{-\beta f[x_{\nu,s}]}=\mathrm{Tr}\left[\exp\left(\hat{\nu}-\hat{K}_s-2\sqrt{\pi}\sum_{\nu,s}\sqrt{-\lambda_\nu}x_{\nu,s}\hat{\rho}_{\nu,s}\right)\right]. \tag{11}$$

B. Difficulties

There are some interesting problems with this formulation as it stands:

(i) It is difficult, and not always possible, to obtain the canonical transformation operator $\hat{S}$.

(ii) Even knowing $\hat{S}$, the operators $\hat{\rho}_\nu\equiv\hat{\rho}_{k,l}$ are still very complicated.

(iii) Is there a way to proceed without explicit forms for $\hat{S}$ and $\hat{\rho}_{k,l}$?

(iv) Can we reduce the dimensionality of the integrals?

(v) How can we simplify the extremum conditions of the Lagrangian for the method of steepest descents?

(vi) How can we generalize the functional-integral formulation of quantum statistical mechanics to include superconductivity?

These problems are discussed below. Previous applications of the functional-integral approach include the Anderson model [4], the Kondo effect [5], valence fluctuations, and the Hubbard model [6–18]. In the previous work, many approximation methods (e.g., static approximation, random phase approximation, independent harmonic approximation, quartic approximation, systematic diagrammatic analysis, single cross approximation, the time-domain approach, etc.) have been developed. The results of the FIA [14,16] have been compared with those of renormalization-group theory [19]. The present paper focuses only on the general problem of the formulation of a practical functional-integral approach.

II. AN OPERATOR IDENTITY

In order to generalize and improve the Hubbard theory, we start from the following operator identity:

Identity: When linear operators $\hat{A}$ and $\hat{B}$ commute, one has [12]

$$e^{\pm\hat{A}\hat{B}}=\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dy\,\exp[-\pi|z|^2-\sqrt{\pi}(\hat{A}z\pm\hat{B}z^*)], \tag{12}$$

where

$$z=x+iy. \tag{13}$$

(i) When $\hat{A}$ and $\hat{B}$ commute and are Hermitian, then $\hat{A}$ and $\hat{B}$ possess a common complete orthonormal set of eigenfunctions that can be taken as the representation basis. The identity can then be proven with c numbers.

(ii) Often (in fact, for the general case in statistical mechanics) $\hat{A}$ and $\hat{B}$ are not Hermitian. Nevertheless, since $\hat{A}$ and $\hat{B}$ commute by hypothesis, one can expand $\exp[-\sqrt{\pi}(\hat{A}z\pm\hat{B}z^*)]$ in a power series in x and y, and carry out the integration to prove the operator identity.

The Stratonovich identity, Eq. (1), is a special case of this operator identity, Eq. (12), when $\hat{A}=\hat{B}$.

III. FUNCTIONAL-INTEGRAL FORMULATION OF QUANTUM STATISTICAL MECHANICS

To have a practical functional-integral formulation, we need to reduce the dimensionality of the integrals and avoid the unknown transformation $\hat{S}$ and operator $\hat{\rho}_{k,l}$. Therefore, we prove the following general theorem without explicit use of $\hat{S}$ or $\hat{\rho}_{k,l}$.

Theorem. A general statistical equilibrium problem with Hamiltonian of the form $\hat{H}=\hat{H}_0+\hat{H}_{\mathrm{int}}$, where

$$\hat{H}_0=\sum_{k,k',\sigma}\left(I_{k,k'}+\frac{1}{2}U_0\delta_{k,k'}\right)\hat{a}^+_{k,\sigma}\hat{a}_{k',\sigma},$$

$$\hat{H}_{\mathrm{int}}=\pm\frac{1}{2V}\sum_q\sum_{k,\sigma}\sum_{k',\sigma'}U(q)\hat{a}^+_{k'+q,\sigma'}\hat{a}^+_{k-q,\sigma}a_{k,\sigma}\hat{a}_{k',\sigma'}, \tag{14}$$

can be transformed exactly into a problem of an ideal gas moving in a fictitious complex time-dependent external field. The price to be paid is the introduction of a functional integral. [Note that U_0 is the potential at the origin and $U(q)$ is taken to be positive, with the sign introduced explicitly by $\pm$.]

Proof. We first write

$$\hat{H}_{\mathrm{int}}=\pm\sum_q\hat{A}_q\hat{B}_q, \tag{15}$$

where

$$\hat{A}_q=\hat{B}_q^+=\sum_{k,\sigma}\sqrt{\frac{U(q)}{2V}}\hat{a}^+_{k+q,\sigma}\hat{a}_{k,\sigma}. \tag{16}$$

Introducing the Feynman-Dyson expansion and the time-ordering operator $\hat{T}$, we can write the grand partition function as

$$\Xi=\mathrm{Tr}[\hat{T}e^{\beta(\mu\hat{N}-\hat{H}_0)}e^{-\int_0^\beta\hat{H}_{\mathrm{int}}(\tau)d\tau}], \tag{17}$$

where $\hat{H}_{\mathrm{int}}(\tau)$ is the interaction representation form.

Now, using the Fourier expansion for an operator $\hat{O}(\tau)$,

$$\hat{O}(\tau)=\sum_{\nu=-\infty}^{\infty}\hat{O}^{\nu}e^{-2\pi i\nu\tau/\beta}, \tag{18}$$

where

$$\hat{O}^{\nu}=\frac{1}{\beta}\int_{0}^{\beta}\hat{O}(\tau)e^{2\pi i\nu\tau/\beta}d\tau, \tag{19}$$

we have

$$\int_{0}^{\beta}\hat{H}_{\rm int}(\tau)d\tau=\pm\beta\sum_{q}\sum_{\nu=-\infty}^{\infty}\hat{A}_{q}^{\nu}\hat{B}_{q}^{-\nu}. \tag{20}$$

Then applying the operator identity of Eq. (12), one obtains

$$\begin{aligned}\Xi=&\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\left(\prod_{q}\prod_{\nu=-\infty}^{\infty}dx_{q}^{-\nu}dy_{q}^{-\nu}\right)\\&\times\exp\left[-\pi\sum_{q,\nu}|z_{q}^{-\nu}|^{2}\right]\mathrm{Tr}\left[\hat{T}\exp\left\{\beta(\mu\hat{N}-\hat{H}_{0})\right.\right.\\&\left.\left.-\sqrt{\pi\beta}\sum_{q,\nu}[\hat{A}_{q}^{\nu}z_{q}^{-\nu}\mp\hat{B}_{q}^{-\nu}(z_{q}^{-\nu})^{*}]\right\}\right].\end{aligned} \tag{21}$$

Now return to the time domain where

$$\sum_{q,\nu}|z_{q}^{-\nu}|^{2}=\frac{1}{\beta}\sum_{q}\int_{0}^{\beta}|z_{q}(\tau)|^{2}d\tau,$$

and

$$\sum_{q,\nu}\hat{A}_{q}^{\nu}z_{q}^{-\nu}=\frac{1}{\beta}\sum_{q}\int_{0}^{\beta}\hat{A}_{q}(\tau)z_{q}(\tau)d\tau. \tag{22}$$

Since $\hat{A}_{q}^{+}=\hat{B}_{q}$, one has $\hat{B}_{q}^{-\nu}=(\hat{A}_{q}^{\nu})^{+}$. Then

$$\sum_{q,\nu}\hat{B}_{q}^{-\nu}(z_{q}^{-\nu})^{*}=\frac{1}{\beta}\sum_{q}\left[\int_{0}^{\beta}\hat{A}_{q}(\tau)z_{q}(\tau)d\tau\right]^{+}. \tag{23}$$

Now write

$$\tilde{U}(\tau)=\sqrt{\pi/\beta}\sum_{q}\{\hat{A}_{q}(\tau)z_{q}(\tau)\mp[\hat{A}_{q}(\tau)z_{q}(\tau)]^{+}\},$$

and

$$\hat{H}_{\lambda}(\tau)=\hat{H}_{0}+\lambda\tilde{U}(\tau). \tag{24}$$

Then we define

$$\Xi_{\lambda}(z)=\mathrm{Tr}[\hat{T}e^{\beta\mu\hat{N}-\int_{0}^{\beta}\hat{H}_{\lambda}(\tau)d\tau}], \tag{25}$$

which allows one to write, using Eq. (21),

$$\Xi=\int Dz\exp\left[-\frac{\pi}{\beta}\int_{0}^{\beta}\sum_{q}|z_{q}(\tau)|^{2}d\tau\right]\Xi_{1}(z)\equiv\langle\Xi_{\lambda}\rangle_{\lambda=1}. \tag{26}$$

$\hat{A}_{q}(\tau)$ is a quadratic form, and $\hat{H}_{\lambda}(\tau)$ is like the Hamiltonian of an ideal gas moving in an external field, $z_{q}(\tau)$, as is evident on rewriting $\tilde{U}$ in the form

$$\begin{aligned}\tilde{U}=&\sqrt{\frac{\pi}{\beta}}\sum_{q}\sqrt{\frac{U(q)}{2V}}\sum_{k,\sigma}\{\hat{a}_{k+q,\sigma}^{+}(\tau)\hat{a}_{k,\sigma}(\tau)z_{q}(\tau)\\&\mp\hat{a}_{k,\sigma}^{+}(\tau)\hat{a}_{k+q,\sigma}(\tau)z_{q}^{*}(\tau)\}.\end{aligned} \tag{27}$$

So the theorem is proven.

Comparing this approach with Hubbard's theory, we see the following advantages of this formulation:

(i) It avoids the difficulties of finding the canonical transformation $S_{i,j;k,l}$ and $\hat{\rho}_{k,l}=\Sigma_{i,j}S_{i,j;k,l}\hat{a}_{i}^{+}\hat{a}_{j}$.

(ii) The dimensionality of the integrals here is much less than in the Hubbard formulation, because in our formulation the functional integral is expressed as $\int\Pi_{q}dx_{q}(\tau)\,dy_{q}(\tau)$, whereas in the Hubbard formulation it is expressed as $\int\Pi_{i}\Pi_{j}dx_{i,j}(\tau)$. This reduction of dimensionality is important in applying the theory.

(iii) In the BCS theory of superconductivity, $V=-\Sigma_{k,k'}V_{k,k'}c_{k,\uparrow}^{+}c_{-k,\downarrow}^{+}c_{-k',\downarrow}c_{k',\uparrow}$, which cannot be diagonalized in the form of Eq. (7) to apply the Stratonovich identity. But using the operator identity Eq. (12), which only needs $\hat{A}_{q}=\hat{B}_{q}^{+}$ and their commutativity under the $\hat{T}$ operator, the present FIA can also be applied to the theory of superconductivity.

IV. PROPERTIES OF THE PARTITION FUNCTION

Only real partition functions are physically meaningful. Furthermore, within a single-phase region, the partition function must be analytic and positive. Positivity of Ξ is a necessary condition for reality of the thermodynamic variables. Analyticity ensures that the thermodynamic variables and their derivatives do not have any singular points, which would be associated with a phase transition.

However, physical systems do undergo phase transitions, and physical systems that are experimentally realizable are not single phase systems. The most interesting theoretical model systems also include phase-transition points. At such points the partition function, in the thermodynamic limit, can go to zero [20] or contain some more subtle nonanalyticity.

In this section we explore these properties of the partition function in the functional-integral approach.

A. Reality and method of steepest descents

We note that $\tilde{U}$ is Hermitian or anti-Hermitian as the two-body interaction is attractive or repulsive: $\tilde{U}^{+}=\mp\tilde{U}$ according to $\pm$ in $\hat{H}_{\rm int}$. When $\hat{H}_{\lambda}$ is Hermitian, $\Xi_{\lambda}(z)$ and hence Ξ, are manifestly real.

On the other hand, when $\hat{H}_{\lambda}$ is non-Hermitian, Ξ_{λ} can be complex valued. We prove here that Ξ is nevertheless always real.

Take $\tilde{U}^{+}=-\tilde{U}$ by hypothesis. Then to take the complex conjugate Ξ^{*}, we take $\tilde{U}\rightarrow\tilde{U}^{+}=-\tilde{U}$, and the rest of the operators are Hermitian. By symmetry we have

$$\tilde{U} \to -\tilde{U},$$

when

$$z_q(\tau) \to -z_q(\tau). \tag{28}$$

Since definite integrals are invariant under transformations of (dummy) integration variables, it is easy to prove that all the imaginary parts of the expression for Ξ_λ cancel exactly:

$$\Xi = \Xi^* = \langle \Xi_\lambda \rangle_{\lambda=1} = \langle \mathrm{Re}(\Xi_\lambda) \rangle_{\lambda=1} \equiv \langle \tilde{\Xi}_1 \rangle. \tag{29}$$

For convenience, we have defined $\tilde{\Xi}_1$ as follows:

$$\tilde{\Xi}_1 \equiv \mathrm{Re}(\Xi_\lambda)|_{\lambda=1} = \mathrm{Tr}\left\{ \hat{T} e^{\beta(\mu\hat{N}-\hat{H}_0)} \cosh\left[\int_0^\beta \tilde{U}(\tau) d\tau \right] \right\}$$
$$= \mathrm{Tr}\left\{ \hat{T} e^{\beta(\mu\hat{N}-\hat{H}_0)} \cos\left[\int_0^\beta \tilde{U}_0(\tau) d\tau \right] \right\}, \tag{30}$$

where $\tilde{U}_0 \equiv -i\tilde{U}$ is Hermitian. This definition of $\tilde{\Xi}_1$ differs from that in the Hubbard theory, and here $\tilde{\Xi}_1$ is manifestly real.

As long as the Lagrangian L has an extremum, one can use the method of steepest descents. So we write

$$\Xi = \int Dz \; e^{-L[z(\tau)]}, \tag{31}$$

where

$$L[z(\tau)] = \frac{\pi}{\beta} \sum_q |z_q(\tau)|^2 - \ln(\tilde{\Xi}_1[z(\tau)]). \tag{32}$$

L has an extremum at the point $\{x^0_{q,s}, y^0_{q,s}\}$ where

$$\left(\frac{\partial L}{\partial x_{q,s}} \right)_0 = 0, \quad \left(\frac{\partial L}{\partial y_{q,s}} \right)_0 = 0, \tag{33}$$

with s now standing in for the time variable. We expand the Lagrangian L in the vicinity of the extremum, and define a matrix L_2 with matrix elements

$$(L_2)_{q,s;q',s'} = \frac{1}{2\pi} \left(\frac{\partial^2 L}{\partial z_{q,s} \partial z_{q',s'}} \right). \tag{34}$$

Considering a suitable canonical transformation and the invariance of the determinant under canonical transformations, the functional-integral calculation can now be carried out. The method of steepest descents gives the following expression for the partition function:

$$\ln \Xi = -\frac{\pi}{\beta} \sum_q |z^0_q|^2 + \ln \tilde{\Xi}_1[z^0_q] + \frac{1}{2} \ln \det[L_2]_0 . \tag{35}$$

B. Positivity and analyticity of the partition function

We expect nonanalytic points, possible zeros, and possible singularities in the partition function at phase-transition points. $\tilde{\Xi}_1$, while real, can be negative when $\tilde{U}$ is anti-Hermitian. This is so because we can write $\tilde{U}(\tau) \equiv i\tilde{U}_0(\tau)$ where $\tilde{U}_0(\tau)$ is Hermitian. Then Eq. (30) can be rewritten as

$$\tilde{\Xi}_1 = \mathrm{Tr}\left\{ \hat{T} e^{\beta(\mu\hat{N}-\hat{H}_0)} \cos\left[\int_0^\beta \tilde{U}_0(\tau) d\tau \right] \right\}. \tag{36}$$

The cosine function, of course, allows $\tilde{\Xi}_1$ to be negative.

Since $\tilde{\Xi}_1$ appears as the argument of a logarithm in Eq. (32), $L[z(\tau)]$ can be complex, allowing Ξ to become zero. Furthermore, even when $\tilde{U}$ is Hermitian, Ξ could have singular points or other nonanalytic points. It is, in fact, the richness of the theory, that certainly includes the possibility of phase transitions, that allows these possibly troublesome points.

In most cases, even when $\tilde{U}$ is anti-Hermitian, Ξ will be positive definite as guaranteed by two factors: First, the Gaussian factor $\exp[-\pi\Sigma_{q,\nu}|z_q^{-\nu}|^2]$, which is maximum at the zero point, and decreases quickly at large $z_q^{-\nu}$. Second, the cosine function is positive in the first quadrant. At large argument, the cosine function oscillates quickly and mostly cancels, while the amplitude of the integrand is decaying very quickly anyway due to the Gaussian factor. These factors make $\tilde{\Xi}_1$ likely to be positive. As a rough estimate, since $\tilde{U}_0$ is linear in $z_q^{-\nu}$, we see from the Poisson formula that Ξ is positive:

$$\int_{-\infty}^{\infty} e^{-\pi x^2} \cos(\alpha x) dx = e^{-\alpha^2/4\pi} > 0. \tag{37}$$

It is interesting to see, however, that $\tilde{\Xi}_1$ may take negative values in the functional-integral approach, especially in the vicinity of a phase transition. In these cases, steepest descents in the complex domain could be used to study such a phase transition.

When the interaction is attractive, with no hard core, $\tilde{U}$ is Hermitian and Ξ_1 is positive definite. The same rough estimate as above, assuming a linear function $\tilde{U}(z)$, gives

$$\int_{-\infty}^{\infty} e^{-\pi x^2} \cosh(\alpha x) dx = e^{+(\alpha^2/4\pi)} > 1. \tag{38}$$

As expected, Ξ cannot have any zeros in this case. So how can models like BCS theory of superconductivity or Bose-Einstein condensation have a phase transition? All that is required for a phase transition is some nonanalytic point or singularity, not a zero in the partition function. A zero in the partition function is the case that was studied by Yang and Lee [20], but this is associated with a hard core in the interaction. In Bose-Einstein condensation, on the other hand

$$\ln \Xi = -\ln(1 - z e^{\epsilon_0/k_B T}) - \sum_{p \neq 0}^{\infty} \ln(1 - z e^{\epsilon_p/k_B T}), \tag{39}$$

which goes to $+\infty$ at the critical point. A similar argument is possible for BCS theory.

Although there is not yet a complete quantum theory of phase transitions, it appears that many cases are possible with different nonanalytic behaviors in the partition functions.

V. DISCUSSION

Starting from the operator identity Eq. (12), the general partition function can be expressed by a Gaussian average of an ideal gas partition function. [See Eqs. (24)–(26),(29), (30).] Compared with Hubbard's theory, our formulation possesses the following advantages:

(i) It avoids the necessity of diagonalizing $V_{i,j;k,l}$, finding the transformation $S_{i,j;k,l}$, and computing $\hat{\rho}_{k,l}$;

(ii) The dimensionality of the integrals is much less than in Hubbard's theory. For example, in Hubbard's theory for a fixed q one must evaluate all the integrals with respect to all $\{x_{q,k,\sigma}\}$. But in our formulation, one only has to carry out the integrations with respect to x_q and y_q.

(iii) In our general formulation, it is necessary to introduce a complex representation. $\widetilde{U}$ can be anti-Hermitian and Ξ_λ could in principle be complex. But we have proven that Ξ and $\tilde{\Xi}_1$ are always real. Reality is thus guaranteed for all partition functions. The expression for $\tilde{\Xi}_1$ is also interesting, even including the possibility of phase transitions.

(iv) The extremum condition and the method (approximation) of steepest descents are much simpler than in Hubbard's theory.

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