Classical pseudopotential for an equilibrium density matrix

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A variational procedure for an integral over a conditional Wiener measure is analyzed. This procedure yields a lower approximation of an equilibrium density matrix. A harmonic oscillator is considered as a trial system. The parameters which are varied are not only the frequency, as usual, but also the shift of the equilibrium position. The result is put in the form of an upper estimate of the pseudopotential, which is determined by a Gaussian transformation of the original potential. This new procedure leads to the correct Wigner correction for a diagonal element of the density matrix. For the energy of the ground state, it leads to a variational estimate by the Ritz method. An explicit analytic expression for the pseudopotential as a power series in the anharmonicity is derived for a system with one degree of freedom. The coefficients are expressed in terms of Legendre functions of the second kind, $Q_l(2n+1)$, where n is the mean occupation number for phonons of the trial system.

Methods for reducing quantum statistical calculations to the well-developed analytic and numerical procedures of classical statistical mechanics are finding progressively wider applications in the physics of the condensed state and field theory. The most important of these methods for continuous systems is the Feynman representation[1] of the equilibrium (temperature) density matrix by an integral over a conditional Wiener measure. The existing procedures for approximate evaluations of this integral outside perturbation theory (a Wigner expansion) involve a partition function and are based primarily on Feynman's variational principle,[1] with a harmonic oscillator being used as a model.

The Feynman-Kleinert variational procedure[2] is apparently the best developed of these methods. A similar method was proposed independently by Giachetti and Tognetti,[3,4] who also examined certain applications to nonlinear field models.[5–8] A partition function was also studied in Refs. 9 and 10.

A lower estimate of the quantum partition function was found in Refs. 2–9 as an effective classical statistical integral; the integral was approximated by an integral over closed paths with a fixed expectation value in terms of the evolution parameter.

The same results for the partition function are found through the use of the two-cumulant approximation of the path integral proposed in Ref. 11, combined with the method of steepest descent.[12] This mean value of the paths (a displacement parameter) is not fixed in the case of the density matrix of a system with one[13] or many[14] degrees of freedom in this procedure. It is instead varied. This situation leads, in particular, to an exact result for a harmonic oscillator in the correct Wigner correction for a diagonal element of the density matrix. The two-cumulant approximation, however, is heuristic in the sense that it leans on certain plausible qualitative physical considerations and is not controllable, since it contains an *a priori* estimate of the result.

In the present paper we eliminate the latter shortcoming.

We consider a nonrelativistic particle of mass m in a field with a potential $V(x)$. In a system of units with $\hbar = 1$ and $m = 1$, the exact equilibrium density matrix ρ_e can be represented[1] as a Feynman integral over a conditional Wiener measure:

$$\rho_e(x,\beta;x',0)=\int d_W x \exp\left\{-\int_0^\beta V[x(\beta_1)]\,d\beta_1\right\},$$
$$x(0)=x', \quad x(\beta)=x. \tag{1}$$

As a trial system (or reference system) we choose one which has the same mass and which has a potential $V_0(x)$ which also depends on adjustable parameters A. We write the density matrix in the classical Boltzmann form,

$$\rho \equiv \exp(-\beta W), \tag{2}$$

where $W(x,x';\beta)$ might be called a "classical pseudopotential" in this sense.

Now using Feynman's variational principle and the known[1] rules for taking an average over a Wiener process, we find a strict upper estimate of the pseudopotential W_e:

$$W_e \leqslant W = W_0 + \beta^{-1}\int_0^\beta d\beta_1 \int dx_1 v(x_1) p(x_1,\beta_1). \tag{3}$$

Here W_0 is the pseudopotential of the model, which is assumed known; $v = V - V_0$; and p is a conditional distribution of the intermediate coordinate x_1, given by

$$p(x_1,\beta_1;x,\beta;x',0)=\rho_0^{-1}(x,\beta;x',0) \times \rho_0(x,\beta;x_1,\beta_1)\rho_0(x_1,\beta_1;x',0). \tag{4}$$

According to (3), the best upper estimate W_1 is found by solving the variational problem

$$W_1 = \min_A W, \tag{5}$$

where A appears in a known way in all the functions which refer to the model and which have a subscript 0.

Equations (3)–(5) give a general solution. In practice, however, ρ_0 is known for only harmonic and singular oscillators (the latter represents a contraction of a multidimensional harmonic oscillator on a sphere).

As a model here we adopt

$$V_0=\Omega^2(x-x_0)^2/2 \tag{6}$$

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with the frequency Ω and the shift x_0 being used as adjustable parameters. In this case the distribution p is normal with a center Mx_1 given by

$$Mx_1=x_0+(\operatorname{ch}\varphi/\operatorname{ch} f)\xi+(\operatorname{sh}\varphi/\operatorname{sh} f)\eta \tag{7}$$

and with a dispersion Dx_1 given by

$$Dx_1=a^2[1-(\operatorname{ch}\varphi/\operatorname{ch} f)^2], \tag{8}$$

where

$$\xi=y-x_0, \quad y=(x+x')/2,$$
$$\eta=(x-x')/2, \quad f=\beta\Omega/2, \quad \varphi=(2\beta_1-\beta)\Omega/2, \tag{9}$$

and a^2 is the mean square displacement of the harmonic oscillator, given by

$$a^2=(2\Omega)^{-1}\operatorname{cth} f. \tag{10}$$

As a result we find

$$W_1(y,\eta;\beta)=\min_{\xi,\Omega} W(y,\eta;\beta;\xi,\Omega), \tag{11}$$

$$\begin{aligned} W=&(T/4)\,[1-2f\operatorname{cth}2f-2\ln(2f/\operatorname{sh}2f)]\\ &+T^2f[\operatorname{th}f(1-2f/\operatorname{sh}2f)\xi^2\\ &+\operatorname{cth}f(1+2f/\operatorname{sh}2f)\eta^2+2(\operatorname{th}f)\xi\eta]\\ &+U(y,\eta;\beta;\xi,\Omega). \end{aligned} \tag{12}$$

The smoothed potential U is found from the original potential V by means of a Gaussian transformation with parameters (7) and (8), followed by an integration over β_1 in accordance with (3) and (9).

For a diagonal element ($x'=y=x$, $\eta=0$) the smoothed potential allows an explicit analytic representation in series form:

$$U=\sum_{k,l=0}^{\infty} Q_{kl}V^{(2k+l)}(x)\,(4Tf\operatorname{th}f)^{-k}\frac{\xi^l}{k!\;l!}, \tag{13}$$

$$Q_{kl}=f^{-l}\sum_{m=0}^{k}\binom{k}{m}(-2)^{-m}Q_n(\operatorname{cth}f)\,(\operatorname{th}f)^n. \tag{14}$$

Here $n=k+l+m$, and Q_n is a Legendre function of the second kind.[15]

Series (13) is obviously a power series in the anharmonicity. This approach is particularly convenient in applications, e.g., in the theory of quantum crystals, in which V near a site is usually approximated by a polynomial. In this case, series (13) and (14) are truncated.

Let us consider the basic particular cases and limiting situations.

1) The harmonic oscillator. Here the exact result is found from the construction of the approximation.

2) The same comments apply to a first-order perturbation theory for a harmonic oscillator.

3) In the first order of a high-temperature (Wigner) expansion we find

$$W=V+\beta V'/12+\beta^2/24\min_{\xi,\Omega}[(\Omega^2\xi)^2-2V'(x)\,(\Omega^2\xi)]. \tag{15}$$

The optimum values of the adjustable frequency Ω and of the adjustable shift ξ satisfy the physically graphic equation

$$\Omega^2\xi=V'(x). \tag{16}$$

From (15) and (16) follows the correct first Wigner correction.[16]

4) In the low-temperature limit, we find a variational estimate by the Ritz method for the energy of the ground state on the basis of a trial Gaussian packet in accordance with the well-known result of Feynman and Kleinert.[2] Numerical calculations which they carried out demonstrate the high accuracy of this approximation even in the case of a pronounced anharmonicity.

The latter circumstance, combined with the result in (16), makes it possible to simplify the calculation procedure in a reasonable way. For this purpose we note that results 1)–3) do not depend on the choice of Ω. In case 3), the satisfaction of condition (16) is sufficient. Making use of this latitude, we choose Ω in accordance with the ground-state energy E_0. In other words, we find Ω from the low-temperature limit, (13):

$$E_0=\min_{\Omega}\left[\frac{\Omega}{4}+\left(\frac{\Omega}{\pi}\right)^{1/2}\int_{-\infty}^{\infty}V(x)\exp(-\Omega x^2)\,dx\right]. \tag{17}$$

We thus see that $\Omega=\Omega_0$ minimizes the ground-state energy in accordance with the Ritz variational principle.

We choose the shift ξ in accordance with (16) here. In other words, we choose it to result in the correct Wigner correction:

$$\xi=V'(x)/\Omega_0^2. \tag{18}$$

Both of the adjustable parameters are thus fixed unambiguously with the correct correspondence to the basic limiting cases. As a result we find the approximation

$$\begin{aligned} W_2(x,\beta)=&(T/4)\,[1-2f_0\operatorname{cth}2f_0-2\ln(2f_0/\operatorname{sh}2f_0)]\\ &+(4f_0\operatorname{cth}f_0)^{-1}\\ &\times(1-2f_0/\operatorname{sh}2f_0)\,[V'(x)]^2\\ &+\sum_{k,l=0}^{\infty}Q_{kl}V^{(2k+l)}(x)\,[V'(x)]^l\theta_f{}^k(\Omega_0^2)^{-k-l}/k!\;l!, \end{aligned} \tag{19}$$

where $f_0=\beta\Omega_0/2$, $\theta_f=(\Omega_0/2)\operatorname{coth}f_0$ is the energy of a harmonic oscillator, and the Q_{kl} are defined in (14).

All the parameters of approximation (19) are determined by the choice of the original potential V. This pronounced simplification of the calculations [a calculation from (14), (19) instead of a solution of variational problem (12) for each (x,β) configuration] is won at the cost of, in general, losing the extremal property of the approximant. However, all the most important qualities of cases 1)–4) of this approximant are preserved by construction.

We note in conclusion that the density matrix is a fundamental solution of the Bloch equation.[1] Several other equations of physical importance, e.g., the Fokker-Planck equation in the theory of Brownian motion and the diffusion equation in a medium with absorption (which may be random) are known to reduce to the Bloch equation. Conse-

quently, the method proposed here may also prove useful in the approximate solution of those other problems.

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