Path-integral approach to the Wigner–Kirkwood expansion

Petr Jizba\textsuperscript{1,*} and Václav Zatloukal\textsuperscript{2,†}

\textsuperscript{1,2}FNSPE, Czech Technical University in Prague, Břehová 7, 115 19 Praha 1, Czech Republic

\textsuperscript{1}ITP, Freie Universität in Berlin, Arnimallee 14, D-14195 Berlin, Germany

\textsuperscript{2}Max Planck Institute for the History of Science, Boltzmannstrasse 22, 14195 Berlin, Germany

We study the high-temperature behavior of quantum-mechanical path integrals. Starting from the Feynman–Kac formula, we derive a new functional representation of the Wigner–Kirkwood perturbation expansion for quantum Boltzmann densities. As shown by its applications to different potentials, the presented expansion turns out to be quite efficient in generating analytic form of the higher-order expansion coefficients. To put some flesh on the bare bones we apply the expansion to obtain basic thermodynamic functions of the one-dimensional anharmonic oscillator. Further salient issues, such as generalization to the Bloch density matrix and comparison with the more customary world-line formulation are discussed. The paper is accompanied by Mathematica code that generates higher order expansion terms for an arbitrary smooth local potential.

I. INTRODUCTION

The Wigner–Kirkwood (WK) expansion was originally presented in two seminal papers \cite{1, 2} and since its very inception it has had two important implications. On the one hand, it has been used for studying the equilibrium statistical mechanics of a nearly classical system of particles obeying Maxwell–Boltzmann statistics. WK expansion is in its essence an expansion of the quantum Boltzmann density in powers of Planck’s constant $\hbar$, or equivalently of the thermal de Broglie wavelength $\lambda = \hbar \sqrt{\beta/M}$, where $\beta$ is the inverse temperature and $M$ is the mass of a particle. On the other hand, it has paved a way for new alternative mathematical techniques and practical calculational schemes that are pertinent to the high-temperature regime in quantum systems.

In this paper, we pursue the study of the WK perturbation method by means of the path integral (PI) calculus. The relevance of the PI treatment in a high-temperature context is due to several reasons: PI’s allow to connect evolutionary equations (Bloch equation or Fokker–Planck equation) with the underlying stochastic analysis \cite{3, 4}, they are tailor-made for obtaining quasi-classical asymptotics \cite{5, 6}, they allow to utilize some powerful transformation techniques to simplify the original stochastic process \cite{5, 7}, etc. Besides, PI’s also provide an excellent tool for direct numerical simulations of the underlying stochastic dynamics including many-body systems \cite{8, 9}. One of the key advantages of the PI approach is, however, the fact that the techniques and methodologies used can efficiently bypass the explicit knowledge of the exact energy spectrum — the point that hindered earlier attempts to go beyond few leading orders.

\textsuperscript{*}Electronic address: p.jizba@fjfi.cvut.cz
\textsuperscript{†}Electronic address: v.zatloukal@fu-berlin.de
in the expansion (see, e.g., Refs. [10–14]). In particular, one can progress without relying on 
the explicit use of approximate expressions or interpolation formulas for the energy eigenvalues 
which are often difficult to judge due to lack of reliability in their error estimates.

The idea to use PI’s as a means of producing various WK-type expansions and related ther-
modynamic functions is clearly not new. Indeed, the first systematic discussions and analyzes 
of these issues emerged already during the early 1970’s. Among these belong the early attempts 
of PI treatments of the high-temperature behavior of partition functions for anharmonic oscilla-
tors [15–17] and gradient expansions of free energy [5]. These approaches belong in the class of 
the so-called analytic perturbation schemes which account for an explicit analytic expressions of 
the coefficient functions. For many practical purposes it is desirable to have explicit analytical 
expressions for coefficients in the WK perturbation expansion. This is so, for instance, when the 
symmetry (Lorentz, gauge, global) is supposed to be broken by quantum or thermal fluctuations. 
Though these issues are more pressing in quantum field theories, they have in recent two decades 
entered also in the realm of a few-body finite-temperature quantum mechanics. The catalyst 
has been theoretical investigations and ensuing state-of-the-arts experiments in condensed Bose 
gases, degenerate Fermi gases, quantum clusters or strongly coupled Coulomb systems. It is not 
only the zero-temperature regime that is of interest in these systems. Many issues revolve also 
around finite-temperature or “high”-temperature questions. These include, thermal and ther-
molectric transport of ultra-cold atomic gases [18, 19], hydrogen, helium, and hydrogen/helium 
mixtures and their astrophysical implications [20, 21], Lennard–Jones $^3$He and $^4$He gases [22], 
etc.

Apart from the aforementioned group of PI methods there are also various non-analytic meth-
ods among which the most prominent are computational methods, such as PI Monte Carlo and 
molecular dynamics simulations [23, 24], accompanied by a host of PI reweighted techniques [25]. 
Another important type of non-analytic method are the approximative schemes, to which be-
long variational approaches [5, 26, 27] and ergodic approximations [28]. Nice summaries of both 
analytic and non-analytic PI approaches can be found, e.g., in Refs. [5, 9].

A serious weakness of existent analytic WK expansions and their various disguises (be they 
based on PI’s or not), resides in their inability to progress very far with the expansion order. 
This makes it difficult to address thermodynamically relevant intermediate-temperature regions 
that is particularly pertinent in molecular and condensed matter chemistry (binding energies, 
self-dissociation phenomena, order-disorder transitions, etc.). The best analytic expansions are 
presently available within the framework of the world-line path integral method (known also 
as the string inspired method) [29]. In this approach the expansion coefficients are available 
up to order $O(\beta^2)$, subject to the actual interaction potential (cf. Refs. [29–31]). Other more 
conventional approaches, such as the recursive or non-recursive heat-kernel calculations [32, 33] 
or higher derivative expansions by Feynman diagrams [34–36], achieve at best the order $O(\beta^7)$. 
The key problem is a rapid escalation in the complexity of higher-order terms which is difficult 
to handle without some type of resummation. In the present paper we derive a new resummation 
formula that provides a rather simple and systematic way of deriving the coefficient functions. 
Its main advantages rely on both an analytic control of the high-temperature behavior, and on 
an accurate description over a wide temperature range via numerical calculations that can be 
simply carried out at the level of an undergraduate exercise.

The structure of the paper is as follows. To set the stage we recall in the next section some 
fundamentals of PI formulations of the Bloch density matrix and the ensuing partition function 
and Boltzmann density. With the help of the space-time transformation that transforms the 
Wiener-process sample paths to the Brownian-bridge sample paths we obtain the PI that repre-
sents a useful alternative to the original Feynman–Kac representation. Consequently we arrive 
at a new functional representation of the Boltzmann density which is more suitable for tackling 
the high-temperature regime than the genuine Wigner–Kirkwood formulation (see Sections II A, 
II B and III). While the method resembles in principle the Wentzel–Brillouin–Kramers (WKB)
solution for the transition amplitude, its details are quite different. In two associated subsections we examine some salient technical issues related to the low-order high-temperature expansion in one dimension. To illustrate the potency of our approach we consider in Section III the high-temperature expansion of the one-dimensional anharmonic oscillator. In particular, we perform the Boltzmann density and ensuing partition function expansions and compute the related thermodynamic quantities. The expansions obtained improve over the classic results of Schwarz [14] and Padé-approximation-based expansion of Gibson [37]. In Section IV we proceed by extending our expansion to the whole Bloch density matrix. The expansion thus obtained is compared with the more conventional Wick’s theorem based perturbation expansion based on the Onofri–Zuk Green’s functions. There we show that our prescription comprises substantially less (in fact, exponentially less) terms contributing to higher perturbation orders. Also the algebraic complexity of the coefficient functions involved is substantially lower in our approach. Various remarks and generalizations are proposed in the concluding section. For the reader’s convenience the paper is supplemented with two appendices which clarify some finer technical details. The paper is also accompanied by Mathematica code that generates the higher-order expansion terms for arbitrary smooth local potentials up to 18th order in $\beta$.

Let us add a final note. Most of the presented mathematical derivations are of a heuristic nature — as it should be expected from the mathematical analysis based on the path-integral calculus. For example, it is assumed throughout that the expansions such as (7) or (14) have meaning and represent, at least asymptotically, convergent series. Further, in a number of places, we assume that integration and summation may be interchanged. The basic purpose of this paper is to find explicit formulas for the coefficient functions $Q(m_1, \ldots, m_n)$, and in doing so to reveal the elaborate algebraic and combinatorial structure present in these functions. A more rigorous treatment of the aforementioned mathematical aspects is possible, but would involve different language and techniques than are employed in this paper.

II. WIGNER–KIRKWOOD EXPANSION

In this section we derive the Wigner–Kirkwood expansion by means of path-integral techniques. To this end we consider a $D$-dimensional non-relativistic quantum mechanical system described with the Hamiltonian

$$\hat{H} = \sum_{j=1}^{D} \frac{\hat{p}_j^2}{2M_j} + V(\hat{x}) ,$$

where $V(x)$ is a generic smooth potential, and $\hat{p}_j = -i\hbar \frac{\partial}{\partial x_j}$. We define the Gibbs operator $e^{-\beta \hat{H}}$, where $\beta = 1/(k_B T)$ is the inverse temperature, and $k_B$ the Boltzmann constant. The partition function $Z(\beta)$ is defined as the trace of the Bloch (or canonical) density matrix, i.e., in the position representation we have the formula

$$Z(\beta) = \int_{\mathbb{R}^D} dx \langle x | e^{-\beta \hat{H}} | x \rangle = \int_{\mathbb{R}^D} dx \ g(x, \beta) .$$

For brevity, we use here and throughout the convention $dx \equiv d^D x$. The un-normalized probability density $g(x, \beta)$ is also known as the Boltzmann density.

Matrix elements of the Bloch density matrix can be represented by the path integral as [5, 38]

$$\langle x_b | e^{-\beta \hat{H}} | x_a \rangle = \int_{x(0)=x_a}^{x(\beta \hbar)=x_b} Dx(\tau) \exp \left\{ -\frac{1}{\hbar} \int_0^{\beta \hbar} d\tau \left[ \sum_{j=1}^{D} \frac{M_j}{2} \dot{x}_j^2(\tau) + V(x(\tau)) \right] \right\} .$$

(3)
which can be viewed as the Wick-rotated quantum-mechanical transition amplitude. Indeed, if one changes the time \( \tau \) in \( i\tau \), one recovers the usual transition amplitude \( \langle x_b, \tau_b | x_a, \tau_a \rangle \) satisfying the Schrödinger equation with the Hamiltonian \( \hat{H} \) (cf. e.g. Refs. \([5, 6]\)). In the literature on stochastic processes is the path-integral representation of the Bloch density matrix also known as the Feynman–Kac formula \([39]\).

For the purpose of the density matrix computation, we shall primarily consider here only diagonal matrix elements, i.e., case when \( x_b = x_a \). We shall briefly return to the off-diagonal matrix elements in Section IV. To proceed we perform a change of space and time variables, \( x \to x_a + \Lambda \xi, \tau \to \beta \hbar s \), where \( \Lambda \) is a diagonal matrix \( \text{diag}(\lambda_1, \ldots, \lambda_D) \) with entries \( \lambda_j = \sqrt{\beta \hbar^2/M_j} \) (corresponding to the thermal de Broglie wavelength of the \( j \)th degree of freedom). The ensuing path integral

\[
\langle x_a | e^{-\beta H} | x_a \rangle = \frac{1}{\det \Lambda} \int_{\xi(0)=0}^{\xi(1)=0} D\xi(s) \exp \left\{ - \int_0^1 ds \left[ \frac{1}{2} \hat{\xi}^2(s) + \beta V(x_a + \Lambda \xi(s)) \right] \right\}, \tag{4}
\]

is formulated in terms of dimensionless time \( s \) and position \( \xi \). Note that the size of quantum fluctuations is now controlled by the parameters \( \lambda_j \), i.e., the only place (apart from the overall PI normalization factor) where the measure of quantum fluctuations — \( \hbar \) is present. Since \( \beta \) and \( \hbar^2 \) appear in (4) on the same footing, the small regime allows to treat in an unified manner both the semiclassical (small \( \hbar \)) and/or high-temperature (small \( \beta \)) approximations. By assuming small \( \Lambda \) the potential term can be Taylor-expanded as

\[
V(x_a + \Lambda \xi(s)) = V(x_a) + \sum_{m \neq 0} V^{(m)}(x_a) (\Lambda \xi(s))^m, \tag{5}
\]

where the \( D \)-dimensional index \( m = (m^1, \ldots, m^D) \) runs through all choices of \( m^j \)'s \( \in \{0, \ldots, \infty\} \) except for \( (m^1, \ldots, m^D) = (0, \ldots, 0) \). The multi-derivative \( (m) \) is defined through the identity

\[
V^{(m)}(x_a) = \frac{\partial^{m^1} V(x)}{\partial x^{m^1}} \bigg|_{x=x_a} = \frac{\partial^{m^1+\ldots+m^D} V(x)}{\partial x_{m^1} \ldots \partial x_{m^D}} \bigg|_{x=x_a}, \tag{6}
\]

with \( |m| = m^1 + \ldots + m^D \). Finally, the multi-factorial \( m! \equiv m^1! \ldots m^D! \), and the multi-power of a \( D \)-dimensional vector \( v \) is defined componentwise as \( v^m \equiv v_{m^1} \ldots v_{m^D} \). Expanding the exponential, followed by some rearrangement, allows to cast (4) in the form

\[
\langle x_a | e^{-\beta H} | x_a \rangle = \frac{1}{\det \Lambda} \sum_{n=0}^{\infty} (-\beta)^n \sum_{m_1,\ldots,m_n \neq 0} m! \prod_{j=1}^D \lambda_j^{m_j^1 + \ldots + m_j^D} \frac{V^{(m_1)}(x_a) \ldots V^{(m_n)}(x_a)}{m_1! \ldots m_n!} \hat{Q}. \tag{7}
\]

At this point, we have introduced the dimensionless quantity

\[
\hat{Q}(m_1, \ldots, m_n) = \frac{1}{m!} \int_0^1 ds_1 \ldots ds_n \int_{\xi(0)=0}^{\xi(1)=0} D\xi(s) \xi^{m_1}(s_1) \ldots \xi^{m_n}(s_n) \exp \left\{ - \int_0^1 ds \frac{1}{2} \hat{\xi}^2(s) \right\}, \tag{8}
\]

that does not depend on physical constants or parameters of the system. \( \hat{Q} \) is also manifestly symmetric under any permutation of its arguments. Let us stress that the \( n = 0 \) term in the expansion (7) equals 1.
In (8) we have denoted with $\langle \cdots \rangle$ the $|m_1| + \ldots + |m_n|$-point correlation function. It can be evaluated using diagrammatic approach based on the so-called Onofri–Zuk (or “world-line”) Green’s function [6, 29, 40, 41]

$$\Delta_{ij}(t, u) = -\frac{1}{2} \delta_{ij} \left[ |t - u| - (t + u - 2tu) \right].$$

We shall briefly sketch this approach in Sec. IV in connection with the off-diagonal density matrix elements. At any rate, procedure based on Green’s function (9) proves rather impractical when higher-order terms are to be calculated. Inasmuch as we shall follow a different route. To this end we rewrite expression (8) as a sum of $n!$ integrals over time-ordered sets $s_1 < \ldots < s_n$, slice the path integral at corresponding time instances, and replace the free-particle path integrals by more compact bra ket notation by virtue of (3). We obtain

$$Q(m_1, \ldots, m_n) = \frac{1}{n!} \sum_{\sigma \in S_n} Q(m_{\sigma(1)}, \ldots, m_{\sigma(n)}),$$

where the sum runs over all permutations of $n$ indices, and

$$Q(m_1, \ldots, m_n) = \int_{0 \leq s_1 < \ldots < s_n \leq 1} ds_1 \ldots ds_n \int_{\mathbb{R}^D} dy_1 \ldots dy_n \prod_{\nu = 0}^n \langle y_{\nu + 1} \rangle \exp \left[ -\sum_{\nu=0}^{n} s_{\nu+1} - s_{\nu} \frac{\dot{q}_\nu^2}{2} \right] |y_1\rangle \ldots |y_n\rangle.$$  \tag{11}

In the preceding we have defined $m_0 = 0$, $s_0 = 0$, $s_{n+1} = 1$, $y_0 = y_{n+1} = 0$, and the momentum $\dot{q} = (\dot{q}_1, \ldots, \dot{q}_D)$, conjugated to the (dimensionless) position operator $\hat{y} = (\hat{y}_1, \ldots, \hat{y}_D)$. Here and throughout we use the standard convention: $\dot{y}_j = -\frac{i}{\hbar} \frac{\partial}{\partial y_j}$ and $(y|q) = e^{i\hat{q}y}/(2\pi)^{D/2}$.

Combinatorial complexity can be reduced significantly by observing that for any function $F(m_1, \ldots, m_n)$ the following identity holds:

$$\sum_{m_1, \ldots, m_n \neq 0} \frac{1}{n!} \sum_{\sigma \in S_n} F(m_{\sigma(1)}, \ldots, m_{\sigma(n)}) = \sum_{m_1, \ldots, m_n \neq 0} F(m_1, \ldots, m_n).$$ \tag{12}

This statement is not trivial, since $F$ is not supposed to be invariant under permutations of the $m$’s. When applied to (7) for

$$F(m_{\sigma(1)}, \ldots, m_{\sigma(n)}) = \prod_{j=1}^D \lambda_{m_j}^{m_1 + \ldots + m_n} \frac{V(m_1)(x_1) \ldots V(m_n)(x_n)}{m_1! \ldots m_n!} Q(m_{\sigma(1)}, \ldots, m_{\sigma(n)}),$$ \tag{13}

the expansion can be then reduced to

$$\langle x_n | e^{-\beta H} | x_n \rangle = \frac{e^{-\beta V(x_n)}}{\text{det} \Lambda} \sum_{n=0}^{\infty} (\beta)^n \sum_{m_1, \ldots, m_n \neq 0} \prod_{j=1}^D \lambda_{m_j}^{m_1 + \ldots + m_n} \frac{V(m_1)(x_1) \ldots V(m_n)(x_n)}{m_1! \ldots m_n!} Q.$$ \tag{14}

This result is new. In addition, in Appendix we derive a new explicit expression for the coefficients $Q$ which proves to be very useful in the determination of the higher-order terms. In particular, there we show that

$$Q(m_1, \ldots, m_n) = K \int_{\mathbb{R}^D} \left( \frac{1}{2} \frac{\partial^2}{\partial q^{m_n}} \right) \left( \frac{1}{2} \frac{\partial^2}{\partial q^{m_1}} \right) \frac{1}{1 + \frac{q^2}{2}} \frac{1}{1 + \frac{q^2}{2}},$$ \tag{15}

where the multiplicative constant has the form

$$K = \frac{1}{\Gamma \left( n + 1 - \frac{\beta}{2} + \frac{|m_1| + \ldots + |m_n|}{2} \right)}.$$ \tag{16}
From Appendix B we can observe that the integral (15) suffers the infrared divergencies precisely in those instances when the $\Gamma$-function in $K$ has pole. Consequently, in practical applications one should appropriately regularize (e.g., via dimensional regularization) both $K$ and integral in (15) in order to resolve the indeterminate form of the product.

In passing we may note that because $Q$ is real, it must be equal to zero when $|m_1| + \ldots + |m_n|$ together with all partial sums $m_1 + \ldots + m_j$ ($j = 1, \ldots, D$) is an even number (cf. also Section IV and Appendix B). So the expansion of the density matrix (14) can be reorganized as an expansion in $\hbar^2$. This is emblematic of the Wigner–Kirkwood expansion [1] for systems with differentiable potentials. In the case of the non-differentiable potentials (cavities, billiards, etc.) the generalized derivative of Schwartz must be used instead [42].

Result (14) might be used for calculating higher-order terms beyond $\hbar^2$-correction (terms up to order $\hbar^6$ have been already determined in the literature [44]). Moreover, the structure of (14) clearly emphasizes that expansion is appropriate only when the involved thermal de Broglie wavelengths are much smaller than the typical length of variation of the potential.

A. Calculation of low-order terms in $D$ dimensions

In order to get further insight into structure of (14) we will now calculate first few terms in the expansion. To this end, we notice that a typical term in (15) has the generic structure

$$
\int_{\mathbb{R}^D} \frac{dq_1 dq_2 \ldots dq_D}{(2\pi)^D} \left( \frac{2\pi}{1 + \frac{q_1^2}{2}} \right)^{s-1} e^{-\sigma} \int_{\mathbb{R}^D} dq_2 \ldots dq_D e^{-\sigma \frac{q_2^2}{2}}
$$

$$
= \frac{\Gamma(s-\frac{D}{2} - |r|)}{(s-1)! (2\pi)^{D/2} r^!} \prod_{j=1}^D (2r_j)!^{1/2},
$$

where $r_1, \ldots, r_D, s \in \mathbb{N}$. If the power of any $q_j$ is odd, the above integral obviously vanishes. For the sake of simplicity, the discussion here will be restricted to the orders in $O(\beta^3)$, but it can be naturally extended to higher orders (cf. next section). At this level, we need to know (15) for $n = 1$ and $n = 2$.

Case $n = 1$: Here the lowest-order non-trivial contribution comes from $|m_1| = 2$, with $m_1^i = \delta_{ij}, m_1^k = \delta_{ik}$. After differentiating

$$
\frac{\partial^2}{\partial q_j \partial q_k} \frac{1}{1 + \frac{q_1^2}{2}} = -\frac{\delta_{jk}}{\left(1 + \frac{q_1^2}{2}\right)^2} + \frac{2q_j q_k}{\left(1 + \frac{q_1^2}{2}\right)^3},
$$

we can use the formulas (15) and (17) to find

$$
Q(m_1) = \frac{1}{(2\pi)^{D/2}} \frac{\delta_{jk}}{6}.
$$

Case $n = 2$: Here the lowest-order non-trivial contribution comes from $|m_1| = |m_2| = 1$, with $m_1^i = \delta_{ij}, m_2^j = \delta_{ik}$. Consequently, we need to estimate

$$
\frac{\partial}{\partial q_k} \left( \frac{1}{1 + \frac{q_1^2}{2}} \frac{\partial}{\partial q_j} \frac{1}{1 + \frac{q_1^2}{2}} \right) = -\frac{\delta_{jk}}{\left(1 + \frac{q_1^2}{2}\right)^2} + \frac{3q_j q_k}{\left(1 + \frac{q_1^2}{2}\right)^3},
$$

where $Q$ is real, it must be equal to zero when $|m_1| + \ldots + |m_n|$ together with all partial sums $m_1 + \ldots + m_j$ ($j = 1, \ldots, D$) is an even number (cf. also Section IV and Appendix B). So the expansion of the density matrix (14) can be reorganized as an expansion in $\hbar^2$. This is emblematic of the Wigner–Kirkwood expansion [1] for systems with differentiable potentials. In the case of the non-differentiable potentials (cavities, billiards, etc.) the generalized derivative of Schwartz must be used instead [42].

Result (14) might be used for calculating higher-order terms beyond $\hbar^2$-correction (terms up to order $\hbar^6$ have been already determined in the literature [44]). Moreover, the structure of (14) clearly emphasizes that expansion is appropriate only when the involved thermal de Broglie wavelengths are much smaller than the typical length of variation of the potential.

A. Calculation of low-order terms in $D$ dimensions

In order to get further insight into structure of (14) we will now calculate first few terms in the expansion. To this end, we notice that a typical term in (15) has the generic structure

$$
\int_{\mathbb{R}^D} \frac{dq_1 dq_2 \ldots dq_D}{(2\pi)^D} \left( \frac{2\pi}{1 + \frac{q_1^2}{2}} \right)^{s-1} e^{-\sigma} \int_{\mathbb{R}^D} dq_2 \ldots dq_D e^{-\sigma \frac{q_2^2}{2}}
$$

$$
= \frac{\Gamma(s-\frac{D}{2} - |r|)}{(s-1)! (2\pi)^{D/2} r^!} \prod_{j=1}^D (2r_j)!^{1/2},
$$

where $r_1, \ldots, r_D, s \in \mathbb{N}$. If the power of any $q_j$ is odd, the above integral obviously vanishes. For the sake of simplicity, the discussion here will be restricted to the orders in $O(\beta^3)$, but it can be naturally extended to higher orders (cf. next section). At this level, we need to know (15) for $n = 1$ and $n = 2$.

Case $n = 1$: Here the lowest-order non-trivial contribution comes from $|m_1| = 2$, with $m_1^i = \delta_{ij}, m_1^k = \delta_{ik}$. After differentiating

$$
\frac{\partial^2}{\partial q_j \partial q_k} \frac{1}{1 + \frac{q_1^2}{2}} = -\frac{\delta_{jk}}{\left(1 + \frac{q_1^2}{2}\right)^2} + \frac{2q_j q_k}{\left(1 + \frac{q_1^2}{2}\right)^3},
$$

we can use the formulas (15) and (17) to find

$$
Q(m_1) = \frac{1}{(2\pi)^{D/2}} \frac{\delta_{jk}}{6}.
$$

Case $n = 2$: Here the lowest-order non-trivial contribution comes from $|m_1| = |m_2| = 1$, with $m_1^i = \delta_{ij}, m_2^j = \delta_{ik}$. Consequently, we need to estimate

$$
\frac{\partial}{\partial q_k} \left( \frac{1}{1 + \frac{q_1^2}{2}} \frac{\partial}{\partial q_j} \frac{1}{1 + \frac{q_1^2}{2}} \right) = -\frac{\delta_{jk}}{\left(1 + \frac{q_1^2}{2}\right)^2} + \frac{3q_j q_k}{\left(1 + \frac{q_1^2}{2}\right)^3},
$$

where
which gives

\[ Q(m_1, m_2) = \frac{1}{(2\pi)^{D/2}} \frac{\delta_{jk}}{24}. \]  

(21)

By gathering the results (19) and (21) together we can write the expansion (14) in the \( n = 2 \) approximation as

\[
\langle x_a | e^{-\beta \hat{H}} | x_a \rangle \sim \frac{e^{-\beta V(x_a)}}{(2\pi)^{D/2} \text{det} \Lambda} \left( 1 - \frac{\beta}{12} \sum_{j=1}^{D} \lambda_j^2 \frac{\partial^2 V(x_a)}{\partial x_j^2} + \frac{\beta^2}{24} \sum_{j,k=1}^{D} \lambda_j \lambda_k \frac{\partial V(x_a)}{\partial x_j} \frac{\partial V(x_a)}{\partial x_k} \right). 
\]

(22)

This agrees, for \( \lambda_j = \lambda \) (i.e., for equal-mass particles), with the usual low-order Wigner–Kirkwood expansion (see, e.g., Refs. [5, 45]).

### B. Expansion for \( D = 1 \)

Here we show that the form of the coefficients \( Q(m_1, \ldots, m_n) \) can be substantially simplified in 1-dimension \( (D = 1) \). It is rather interesting that the simplification basically involves only arithmetic operations. To see what is involved we denote

\[
I(m_1, \ldots, m_n|r, s) = \int_{\mathbb{R}} \frac{dq}{2\pi} \left( \frac{i^{m_n} \frac{\partial^{m_n}}{1 + \frac{q}{2} \frac{\partial q^{m_n}}{2}} \cdots i^{m_1} \frac{\partial^{m_1}}{1 + \frac{q}{2} \frac{\partial q^{m_1}}{2}} \right) \left( \frac{1}{1 + \sqrt{2} q} \right)^{r} \left( \frac{1}{1 - \sqrt{2} q} \right)^{s},
\]

(23)

so that (cf. Eq. (15)): \( Q(m_1, \ldots, m_n) = K(m_1, \ldots, m_n)I(m_1, \ldots, m_n|1,1) \). By the \( m_1 \)-fold differentiation of the last bracket we obtain the recurrence relation

\[
I(m_1, \ldots, m_n|r, s) = \frac{(-1)^{m_1}}{2m_1/2} m_1! \sum_{k_1=0}^{m_1} (-1)^{k_1} \binom{r-1+k_1}{r-1} \binom{s-1+m_1-k_1}{s-1} \times I(m_2, \ldots, m_n|r + 1 + k_1, s + 1 + m_1 - k_1),
\]

(24)

with the initial condition

\[
I(0|r, s) = \int_{\mathbb{R}} \frac{dq}{2\pi} \left( \frac{1}{1 + \sqrt{2} q} \right)^{r} \left( \frac{1}{1 - \sqrt{2} q} \right)^{s} = \frac{2^{3/2}}{2^{r+s}} \binom{r+s-2}{r-1}.
\]

(25)

The latter identity is a straightforward consequence of Cauchy’s integral theorem where the contour integration is taken at either the pole \( i\sqrt{2} \) or \(-i\sqrt{2}\). Repeated use of (24), with (25) as the last step, leads to an explicit form for \( Q(m_1, \ldots, m_n) \), namely

\[
Q = \frac{(m_1 + \ldots + m_n + n)!}{\sqrt{2\pi 2^{(m_1 + \ldots + m_n)/2}}} \sum_{\ell_1=0}^{m_1} \cdots \sum_{\ell_n=0}^{m_n} \prod_{k=1}^{n} \frac{(-1)^{\ell_k} \binom{m_k}{\ell_k}}{(\ell_1 + \ldots + \ell_k + k)(m_1 - \ell_1 + \ldots + m_k - \ell_k + k)}. \]

(26)

In deriving we have used the duplication formula [46]: \( \sqrt{\pi} 2^{1/2} \Gamma(2z) = \Gamma(z) \Gamma(z+1/2) \). Resulting one-dimensional expansion takes the form

\[
\langle x_a | e^{-\beta \hat{H}} | x_a \rangle = \frac{e^{-\beta V(x_a)}}{\lambda} \sum_{n=0}^{\infty} (-\beta)^n \sum_{m_1, \ldots, m_n=1}^{\infty} \lambda^{m_1 + \ldots + m_n} V^{(m_1)}(x_a) \ldots V^{(m_n)}(x_a) \frac{Q}{m_1! \ldots m_n!}.
\]

(27)
Apart from the initial constant term $\beta^0 \hbar^i$, the latter expansion contains terms proportional to $\beta^i (\hbar^2)^j$, where $i, j \in \mathbb{N}$ and $i/3 \leq j \leq i - 1$ (or, equivalently, $j + 1 \leq i \leq 3j$).

For the first few orders the coefficients of the expansion can be found rather straightforwardly. In Table I we list the coefficients of the series $e^{\beta V(x)} \sqrt{2\pi} \lambda \langle x | e^{-\beta \hat{H}} | x \rangle$. To order $\beta^8$ these can be obtained without any excessive hardship (for further comments see [47]). The higher orders in fixed $\beta$ can now be simply obtained by grouping terms with equal order of $\beta$ and performing a number of multi-differentiations for $V(x)$ which can be easily done with Maple or Mathematica.

To this end we supplement the paper with Mathematica code that allows to generate the higher-order expansion terms (up to 18th order) for arbitrary smooth local potentials.

### III. EXAMPLE: ANHARMONIC OSCILLATOR IN $D = 1$

In the previous section, we have seen in some detail how the coefficients functions in the Wigner–Kirkwood expansion can be resolved in an explicit form. The basic results there were the formulas (14)–(16). The expressions found are quite general, valid for any smooth potential and in $D = 1$ are analytically accessible up to order $\beta^{18}$. Nevertheless, for consistency reasons it is useful to examine a problem possessing an exact solution in which it is possible to find closed expressions for the expansion coefficients. The $D = 1$ harmonic oscillator provides us with just such an exactly solvable example. Rather than starting directly with a simple harmonic oscillator, it is instructive to start with an anharmonic oscillator first and then regain the harmonic oscillator solution in the limit of vanishing coupling constant (i.e., zero anharmonicity limit). In addition, the anharmonic oscillator, which can be regarded as a field theory in one dimension, has long served as a testing ground for new ideas for solving field theories and hence is bolstered by a large body of literature. In this respect it is a natural model which any new approximation scheme should address. For a definiteness we start with the anharmonic potential

$$V(x) = \frac{M^2}{2} \omega^2 x^2 + \frac{g}{4!} x^4,$$

for which the high-temperature expansion (27) yields

$$\langle x | e^{-\beta \hat{H}} | x \rangle = \exp \left[ -\beta \left( \frac{M^2}{2} \omega^2 x^2 + \frac{g}{4!} x^4 \right) \right] \left[ 1 - \frac{\beta^2 h^2 (gx^2 + 2M\omega^2)}{24M} \right. \right.
$$

$$+ \frac{\beta^3 \left( 5M x^2 \hbar^2 (gx^2 + 6M\omega^2)^2 - 18gh^4 \right)}{4320M^2} \left. \right] + \frac{\beta^4 h^4 \left( 17g^2 x^4 + 84gMx^2\omega^2 + 36M^2\omega^4 \right)}{5760M^2} + O(\beta^5).$$

The higher-order corrections can be explicitly obtained with the help of Table I (up to order $\beta^8$) or with the enclosed Mathematica code quoted in [47] (up to order $\beta^{18}$).

In the case of zero anharmonicity ($g = 0$), we can check our results against the exact solution of the harmonic oscillator problem. The expansion (29) reduces to

$$\langle x | e^{-\beta \hat{H}} | x \rangle_{g=0} = \exp \left( -\beta \frac{M^2}{2} \omega^2 x^2 \right) \left[ 1 - \frac{1}{12} \beta^2 \omega^2 h^2 + \frac{1}{24} \beta^3 Mx^2\omega^4 h^2 + \frac{1}{160} \beta^4 \omega^4 h^4 + O(\beta^5) \right],$$

(30)
which, indeed, coincides with the corresponding expansion of the well-known analytic form of the Bloch density matrix for harmonic oscillator (see, e.g., Refs. [5, 6])

$$\langle x \mid e^{-\beta H} \mid x \rangle_{g=0} = \frac{\exp \left(-\frac{\beta \omega^2 x^2}{2} \right)}{\sqrt{2\pi \lambda}} \sqrt{\frac{\beta \omega}{\sinh(\beta \omega)}} \exp \left[-\frac{M x^2 \omega}{\hbar} \left(\tanh\frac{\beta \omega}{2} + \frac{\beta \omega}{2}\right)\right]. \quad (31)$$

In passing we may note that the expansion of the single-particle partition function $Z(\beta)$ associated with (29) can be phrased in terms of the \textit{parabolic cylindrical function} and its derivatives.
which, after re-expansion, give

\[
Z(\beta) = \frac{1}{\sqrt{2\pi\lambda}} \sqrt{\frac{3}{2\beta g}} \left[ \Gamma \left( \frac{1}{4} \right) + \frac{\sqrt{2} \sqrt{7} M \omega^2 \Gamma \left( -\frac{3}{4} \right)}{2\sqrt{\beta}} + \frac{3\beta M^2 \omega^4 \Gamma \left( \frac{3}{4} \right)}{g} \right] - \frac{\beta^{3/2} (\Gamma \left( \frac{3}{4} \right) \left( g^2 \hbar^2 + 18 M^4 \omega^6 \right))}{4 \sqrt{6} (\sqrt{g})^{3/2} M} - \frac{\beta^2 \left( -\frac{1}{2} \right) \sqrt{\frac{2\pi}{\delta g}} \Gamma \left( \frac{1}{4} \right)}{128 g^2} + O \left( \beta^{5/2} \right). \tag{32}
\]

This, when combined with appropriate thermodynamic formulas, yields the following expressions for entropy \( S \), the heat capacity \( C_V \) and internal energy \( U \):

\[
\frac{S}{k_B} = \frac{1}{k_B} \left( \frac{\partial F}{\partial T} \right)_V = \log Z(\beta) - \frac{\beta}{Z(\beta)} \left( \frac{\partial Z(\beta)}{\partial \beta} \right)_V
= \frac{3}{4} + \log \left( \frac{2\Gamma \left( \frac{1}{4} \right)}{\lambda} \sqrt{\frac{6}{\pi^2 \beta g}} \right) - \frac{\sqrt{2} \sqrt{7} M \omega^2 \Gamma \left( \frac{1}{4} \right)}{2\sqrt{\Gamma} \left( \frac{1}{4} \right)} + \frac{\beta^{3/2} \left( \pi g^2 h^2 \Gamma \left( \frac{1}{4} \right) + 3 \sqrt{2} M^4 \omega^6 \Gamma \left( \frac{3}{4} \right) \right)}{\sqrt{3} g^{3/2} M \Gamma \left( \frac{3}{4} \right)} + O \left( \beta^2 \right),
\]

\[
\frac{C_V}{k_B} = \frac{1}{k_B} \left( \frac{\partial S}{\partial T} \right)_V = -\frac{\beta}{k_B} \left( \frac{\partial S}{\partial \beta} \right)_V
= \frac{3}{4} + \frac{\sqrt{2} \sqrt{7} M \omega^2 \Gamma \left( \frac{1}{4} \right)}{2\sqrt{\Gamma} \left( \frac{1}{4} \right)} - \frac{\beta^{3/2} \left( \sqrt{3} \pi g^2 h^2 \Gamma \left( \frac{1}{4} \right) + 3 \sqrt{2} M^4 \omega^6 \Gamma \left( \frac{3}{4} \right) \right)}{2 g^{3/2} \Gamma \left( \frac{3}{4} \right)} + O \left( \beta^2 \right),
\]

\[
U = -T^2 \left( \frac{\partial F/T}{\partial T} \right)_V = \frac{\partial F \beta}{\partial \beta}_V
= \frac{3}{4\beta} + \frac{\sqrt{2} \sqrt{7} M \omega^2 \Gamma \left( \frac{1}{4} \right)}{\sqrt{\beta} \sqrt{\pi} \left( \frac{1}{4} \right)} - \frac{3 M^2 \omega^4 \left( \Gamma \left( \frac{1}{4} \right)^2 - 4 \Gamma \left( \frac{1}{4} \right)^2 \right)}{4 g \Gamma \left( \frac{1}{4} \right)^2} + \frac{\sqrt{3} \pi g^2 h^2 \Gamma \left( \frac{1}{4} \right) + 15 \sqrt{2} M^4 \omega^6 \Gamma \left( \frac{3}{4} \right)}{320 g^{3/2} \Gamma \left( \frac{3}{4} \right)} + O \left( \beta \right). \tag{33}
\]

\[ F = -k_B T \log Z(\beta) \text{ is the Helmholtz free energy}. \] These expansions are not only in excellent agreement with the classic (spectral-theorem based) expansions of Schwarz [14] and Gibson [37] but they also go beyond these expansions by providing explicit forms for higher-order terms not present in Refs. [14, 37].
Unfortunately when $M$ in (28) is negative (i.e., we would have a double-well potential) the WK approach would fail. Indeed the WK expansion cannot accommodate non-perturbation effect such as multi-instanton contribution and ensuing tunneling, as by its very construction it is basically a perturbation expansion around a free solution. From this point of view a tunneling in a double well potential seems to be beyond reach in our expansion. Of course, tunneling could be included by considering some sort of a hybrid approach in which the “phase part” of the transition probability would be calculated via WKB (possibly including multi-instanton contribution), while the fluctuating factor would be evaluated perturbatively via WK method. One of the potential bonuses would be the fact that one could bypass the notorious problems with the Van Vleck determinant on caustics. Such a hybrid approach would, however, clearly go beyond the simple WK approach that is used in our paper. In our future investigation we will touch more upon this issue.

IV. OFF-DIAGONAL BLOCH DENSITY MATRIX ELEMENTS

So far, we have almost exclusively been dealing with the diagonal elements of the Bloch density matrix — Boltzmann density. This was well justified by expected applications in statistical physics, where typically only the partition function is required and hence only diagonal elements of the density matrix are relevant (of course, only as long as the Maxwell-Boltzmann statistics is considered). This is also the linchpin of the original Wigner–Kirkwood work.

Expansion and the formula for the Bloch density matrix (14) can be straightforwardly generalized beyond the original Wigner–Kirkwood analysis by considering the off-diagonal form of the density matrix (also called the heat kernel or euclidean Feynman amplitude). This would be particularly pertinent in cases, when one would like to incorporate the exchange effects that are a consequence of fermion or boson statistics or when the linear response theory would be in question. By following the same train of thought as in Sec. II we can phrase the path-integral representation of the full Bloch density matrix in terms sum over the Brownian bridge sample paths. The path transformation that transforms the Wiener process $\Omega_W = \{x(\cdot)\}$ to the Brownian bridge process $\Omega_{BB} = \{\xi(\cdot)\}$ is

$$x(\tau) = x_a(1 - s) + x_b s + \Lambda \xi(s).$$

(34)

Let us recall that the “Euclidean time” variable $\tau$ is connected with $s$ via the relation $\tau = \beta \hbar s$.

The Brownian bridge sample paths fulfill the Dirichlet boundary conditions $\xi(0) = \xi(1) = 0$.

With this the Feynman–Kac formula for the Bloch density matrix (3) acquires the form

$$\langle x_b | e^{-\beta H} | x_a \rangle = \exp \left\{ -\frac{1}{2} \left[ \Lambda^{-1} (x_b - x_a) \right]^2 \right\} \frac{1}{\det \Lambda} \times \int_{\xi(0)=0}^{\xi(1)=0} \mathcal{D}\xi(s) \exp \left\{ - \int_0^1 ds \left[ \frac{1}{2} \xi^2(s) + \beta V(x_a(1 - s) + x_b s + \Lambda \xi(s)) \right] \right\},$$

(35)

where the surface term in the action got canceled due to boundary conditions of the Brownian bridge. We can expand the potential $V(\ldots)$ around the free-particle classical solution as

$$V(x_a(1 - s) + x_b s + \Lambda \xi(s)) = V(x_a(1 - s) + x_b s) + \sum_{m\neq0} \frac{V^{(m)}(x_a(1 - s) + x_b s)}{m!} (\Lambda \xi(s))^m,$$

(36)
and write the density matrix in the form
\[
\langle x_b | e^{-\beta H} | x_a \rangle = \frac{\exp \left\{ -\frac{1}{\beta} [\mathcal{A}^{-1}(x_b - x_a)]^2 - \beta \bar{V}(x_b, x_a) \right\}}{\det \Lambda} \times \sum_{n=0}^{\infty} (-\beta)^n \sum_{m_1, \ldots, m_n \neq 0}^{D} \lambda_n^{m_1 + \ldots + m_n} \frac{\bar{V}(m_1)_s(x_b, x_a) \ldots \bar{V}(m_n)_s(x_b, x_a) * Q_{s_1 \ldots s_n}(t = 1)}{m_1! \ldots m_n!} .
\] (37)

In the previous we have introduced the abbreviations
\[
\bar{V}(x_b, x_a) = \int_0^1 ds \bar{V}(x_a(1 - s) + x_b s),
\]
\[
\bar{V}(m_1)_s(x_b, x_a) = V(m_x)(x_b - s_i(x_b - x_a)) .
\] (38)

The multi-dimensional convolution appearing in (37) is a straightforward extension of the one-dimensional convolution
\[
(X(s_i) * Y(s_i))(t) = (Y(s_i) * X(s_i))(t) = \int_0^t ds_i X(t - s_i)Y(s_i) .
\] (39)

It is the above definition of the convolution which dictates the (seemingly strangely appearing) form of the right-hand-side of (38). Sub-indices \(s_i\) appearing in \(Q\) in (37) just indicate the integration variables in the convolution. We see again, that the key object is the coefficient function \(Q\) (cf. Eq. (8)) or better the ensuing \((|m_1| + \ldots + |m_n|)\)-point correlator \(Q_{s_1 \ldots s_n}\)
\[
\int_{\xi(0)=0}^{\xi(1)=0} D\xi(s) \xi^{m_1}(s_1) \ldots \xi^{m_n}(s_n) \exp \left. \left[ - \int_0^1 ds \frac{1}{2} \dot{\xi}^2(s) \right] \right|_{j=0} = \frac{\delta^{(|m_1| + \ldots + |m_n|)}}{\delta j(s_1)^{m_1} \ldots \delta j(s_n)^{m_n}} \int_{\xi(0)=0}^{\xi(1)=0} D\xi(s) \exp \left. \left[ - \int_0^1 ds \frac{1}{2} \dot{\xi}^2(s) + \int_0^1 ds \dddot{j}(s) \cdot \xi(s) \right] \right|_{j=0} = \mathcal{N} \frac{1}{\delta j(s_1)^{m_1} \ldots \delta j(s_n)^{m_n}} \exp \left. \left[ \frac{1}{2} \int_0^1 dsdu j_i(s) \Delta_{ij}(s, u) j_j(u) \right] \right|_{j=0} .
\] (40)

The normalization constant \(\mathcal{N}\) denotes the path integral for a simple Brownian bridge. The summation convention is automatically utilized in the argument of the exponent on the last line. The Green function \(\Delta_{ij}(s, u)\) is chosen so that it satisfies the equations
\[
\frac{\partial^2}{\partial t^2} \Delta_{ij}(t, u) = -\delta_{ij} \delta(t - u) ,
\]
\[
\Delta_{ij}(0, u) = \Delta_{ij}(1, u) = 0 .
\] (41)

The solution is the world-line Green function of Onofri and Zuk [40, 41]
\[
\Delta_{ij}(s, u) = -\frac{1}{2} \delta_{ij} [t - u - (t + u - 2t)] .
\] (42)

As a result, we can write \(\bar{Q}(m_1, \ldots, m_n)\) in the form
\[
\bar{Q} = \mathcal{N} \int_0^1 ds_1 \ldots ds_n \delta^{(|m_1| + \ldots + |m_n|)} \frac{\delta j(s_1)^{m_1} \ldots \delta j(s_n)^{m_n}}{\delta j(s_1)^{m_1} \ldots \delta j(s_n)^{m_n}} \exp \left. \left[ \frac{1}{2} \int_0^1 dtdu j_i(t) \Delta_{ij}(t, u) j_j(u) \right] \right|_{j=0} .
\] (43)
The former can be further simplified with the help of Coleman’s identity:
\[
F(-i\partial/\partial x)G(x) = G(-i\partial/\partial y)F(y)e^{iyx}|_{y=0},
\]
which is valid for any (sufficiently smooth) functions \( F \) and \( G \). After some additional algebra one verifies that
\[
Q = \frac{\mathcal{N}i^{m_1+\ldots+m_n}}{n!} \exp \left[ -\frac{1}{2} \int_0^1 dtdu \frac{\delta}{\delta z_i(t)} \Delta_{ij}(t,u) \frac{\delta}{\delta z_j(u)} \right]
\times \int_0^1 ds_1 \ldots ds_n \left. z(s_1)^{m_1} \ldots z(s_n)^{m_n} \right|_{z=0}.
\]
(45)
For similar reasons as in ordinary quantum field theory, i.e., namely for the Wick theorem application, it might be convenient to formulate the \( Q \)-function in the Fourier picture. In this case the Fourier transform is discrete due to the Dirichlet boundary conditions for \( \xi \). In addition, when we periodically extend the shape of the potential \( V \) from the interval \( s \in [0, 1] \) to the whole \( \mathbb{R} \) and take the Fourier transform the calculations of (37) will substantially simplify due to the convolution theorem [42].

Form (45) indicates that \( Q \) can be calculated via Wick’s theorem with world-line Green’s functions (42), cf. also Refs [5, 29, 48, 49]. In fact, it is not difficult to list the corresponding Feynman-like diagrammatic rules for \( Q(m_1, \ldots, m_n) \). On the other hand, the number of terms involved in evaluating \( Q \) via (45) grows as \((2m-1)!! = (2m)!!/2^m m!\) where \( m = (|m_1| + \ldots + |m_n|) \) (see, for instance, Ref. [60]). This should be contrasted with (15) where the number of terms grows as (see Appendix B)
\[
\prod_{j=1}^{D} \left[ (m_1^j + \ldots + m_n^j)/2 + 1 \right].
\]
(46)
Our prescription comprises substantially less terms and this is even more pronounced at high values of \( m \)’s (i.e., at high derivative orders). In Appendix B we prove that the inequality
\[
(2m - 1)!! \geq \prod_{j=1}^{D} \left[ (m_1^j + \ldots + m_n^j)/2 + 1 \right].
\]
(47)
always holds whenever \( m \geq 2 \). There we also show that the number of terms is in our case exponentially lower than in Wick’s theorem based approaches.

Note, also that the number of \( s \)-integrations in (45) matches the perturbation order, i.e., \( n \), while the number of integrations in our formula (15) equals to the dimension of particles configuration space. In this respect, is the presented method less complex with the increasing perturbation order than other methods in use. As a matter of fact, with the method based on the world-line Green function, a complete calculation of all coefficients was achieved to order \( \mathcal{O}(\beta^{12}) \), see Ref. [50]. Closely related gradient expansion calculations (with the same order of precision) were performed in Ref. [51].

Finally, note that \( Q \) from (45) is non-zero only when \(|m_1| + \ldots + |m_n|\) together with all partial sums \( m_1^j + \ldots + m_n^j \) (\( j = 1, \ldots, D \)) is even. In fact, also all partial sums \( m_1^j + \ldots + m_n^j \) (\( j = 1, \ldots, D \)) must be zero. This fact was already pointed out in Sect. II in connection with the coefficient \( Q \). Again, the evenness is true only for smooth potentials. In the general case the space derivatives must be substituted with the generalized derivative of Schwartz [42] which can bring about also odd terms, i.e. odd powers of \( \hbar \). Also other non-analytical behaviour can emerge — e.g., it was shown in [43] that exchange contributions to the free energy of the jellium vanish exponentially fast with \( \hbar \) as a consequence of the Coulomb repulsion between identical charges which diverges at zero separation.
V. CONCLUSIONS AND PERSPECTIVES

In this paper we have presented a novel PI-based high-temperature expansions of the Boltzmann’s density $\rho(x, \beta)$ and partition function $Z(\beta)$. Ensuing generalizations to the full Bloch density matrix were also discussed and explicitly compared with the Onofri-Zuk world-line approach. It was found that our prescription comprises substantially less terms contributing to higher perturbation orders than the more conventional Wick’s theorem based perturbation expansions. Also the algebraic complexity of the coefficient functions involved is markedly lower in our approach.

The expansions obtained are valid for arbitrary number of particles and provide an analytic control of the high-temperature behavior. In addition, the implementation is sufficiently general for any system described by smooth potential energy functions. Because of its analytic form, the presented high-temperature expansion can be further conveniently used, e.g., to analyze the breakdown of symmetry, generate a gradient expansion for the free energy for a wide class of potentials, calculate ground-state energies, set up the extended Thomas–Fermi approximations or serve as the starting point for a numerical evaluation of various thermodynamical quantities (e.g., virial coefficients, specific heat or entropy). As a demonstration, we have briefly discussed the high-temperature thermodynamics of the anharmonic oscillator.

We would like to remark that the compactness of our form for the coefficient function $Q$ might be deceptive with regard to applications requiring the use of non-local potentials. In the genuine Wigner–Kirkwood method, the single-particle density is expressed as functional of the one-body potential $V(x)$. Though our treatment can accommodate also few-body potentials it is intrinsically formulated only for local potentials. Since non-local potentials are an integral part of statistical quantum theory, e.g. in cases when the exchange part of the Hartree–Fock self-consistent potential is considered, the corresponding generalization of Eqs. (15) and (37) to non-local potentials would be desirable. Situation is simple only for two-particle systems with potentials of the form $V(x_1, x_2) = V(x_1 - x_2)$. There the transformation to the center of mass frame allows to reduce the problem to a single-particle in an external potential $V(x)$. For other cases, the formula (15) for the coefficient functions $Q$ could be derived in the same spirit as in Section II but the appealing simplicity of $Q$ would be clearly lost.

The versatility of the method developed in this paper together with a renewed interest in the study of the high-temperature asymptotic expansions of the Bloch density matrix suggest several extensions of this work. A pertinent extension could address spin-dependent potentials, like the spin-orbit interaction whose interest in nuclear physics is well known. Also the case of momentum dependent terms which are relevant in charged particle systems interacting with electromagnetic field or in Brueckner’s theory used in nuclear physics, would be desirable to include. Important limitation of our method lies in the fact that our discussion was confined only to cases where Hamiltonians did not include fermionic degrees of freedom. Similarly as the original WK method also our approach is inherently formulated within the framework of Boltzmann statistics and so it does not incorporate the exchange effects (which are relevant, e.g., in a hot Fermionic plasma). There exist various generalizations of the WK formalism to include the effects of magnetic field [52], or exchange corrections (see, e.g., Refs. [53, 54]) and the corresponding extension of our approach in this direction would be also worth of pursuing particularly in view a naturalness with which PI’s handle fermionic particle systems [5]. All these aforementioned issues are currently under active investigation.

It appears worthwhile to stressed that the WK expansion is not the WKB expansion. For instance, the leading asymptotic behaviors are different; while the WK expansion starts with $\exp(-\beta V(x))$, the WKB starts with $\exp(-\beta S(x_{cl}, x))$ (here the action functional $S$ is evaluated along the classical solutions $x_{cl}$ with the boundary conditions $x(0) = x(h\beta) = x$). Even starting points for both these expansions were historically different. WK started with the Wigner transform approach to statistical physics [1, 2] while WKB (in PI’s) started with the expansion
(in terms of moments of Gaussian fluctuations) around classical trajectory [5, 6]. It is also clear that in the WK one does not organize the expansion in terms of orders of fluctuations around classical solution (as the WKB does). Naturally, both approaches share many common features and there is a bulk of the literature comparing both methods and their respective pros and cons. The interested reader can see, e.g., Refs. [55, 56].

Let us finally make a few comments concerning the low-temperature regime. It is clear that when the temperature decreases, the de Broglie wavelength increases, and the Wigner–Kirkwood perturbation expansion becomes unwarranted. This happens whenever the involved thermal de Broglie wavelength is comparable with a typical length over which the potential varies. So the low temperature expansion is normally beyond reach of the WK method. Nevertheless, with the high-temperature expansion at one’s disposal one can tackle also the low-temperature expansion (at least numerically) provided the sufficient number of the coefficient functions in the high-temperature series is available. To this end, one is free to employ some of the existent duality approaches. Among these, a particularly powerful is a nonperturbative approximation scheme called variational or optimized perturbation theory [5, 57–59]. There the basic idea is to combine the renormalization-group concept known as the principle of minimal sensitivity [59] with the techniques of perturbation theory and the variational principle to convert the divergent weak-coupling power series into a convergent strong-coupling power series (and vice versa).

Last but not least, recently Paulin et al. [28] employed the concept of the occupation time for Wiener processes to formulate the so-called ergodic local-time approximation to PI’s. The ergodic approximation is particularly well suited for the low-temperature regime. In high-temperature domain it performs less satisfactory since the non-trivial correlations between occupation times must be taken into account [28]. Finding the dictionary that would allow a simple passage between our and Paulin et al. approach in the high and intermediate-temperature regimes would be particularly desirable in light of a similar mathematical structure (namely Eq. (4) that both approaches share. Work along these lines is presently in progress.

Acknowledgments

We would like to acknowledge helpful feedbacks from J. Klauder, H. Kleinert and C. Schubert. This work was supported by GA ČR Grant No. P402/12/J077.

Appendix A: Simplification of coefficients \( Q(m_1, \ldots, m_n) \)

Here we employ a convenient trick that will allow us to can carry out the s-integrations in (11) explicitly. We first formally promote the upper limit of the s-integrations (i.e., 1) to a new variable \( s_{n+1} \), and Laplace-transform \( Q \) with respect to \( s_{n+1} \), i.e.

\[
\tilde{Q}(E) = \int_0^\infty ds_{n+1} e^{-Es_{n+1}} \int_{0<s_1<\ldots<s_n<s_{n+1}} ds_1 \ldots ds_n \int_{\mathbb{R}^D} dy_1 \ldots dy_n \times \prod_{\nu=0}^n \langle y_{\nu+1} | \exp \left[ -\frac{(s_{\nu+1} - s_{\nu}) \hat{q}^2}{2} \right] | y_{\nu} \rangle y_{\nu}^{m_{\nu}}. \tag{A1}
\]

Change of variables \( s'_\nu = s_{\nu+1} - s_{\nu}, \nu = 0, \ldots, n \), then leads to

\[
\tilde{Q}(E) = \int_0^\infty ds'_0 \ldots ds'_n \int_{\mathbb{R}^D} dy_1 \ldots dy_n \prod_{\nu=0}^n \langle y_{\nu+1} | \exp \left[ -s'_\nu \left( E + \frac{\hat{q}^2}{2} \right) \right] | y_{\nu} \rangle y_{\nu}^{m_{\nu}}. \tag{A2}
\]
The $s$-integrations can now be done easily,

\[ \tilde{Q}(E) = \int_{\mathbb{R}^D} dy_1 \ldots dy_n \prod_{\nu=0}^n \langle y_{\nu+1} | \frac{1}{E + \frac{\nu}{2}} | y_\nu \rangle y_\nu^{m_\nu}. \]  

(A3)

In order to further simplify (A3) we perform the re-scaling $y_\nu \rightarrow y_\nu / \sqrt{E}$, and use the fact that

\[ \mathcal{I} \langle y_{\nu+1} | \frac{1}{E + \frac{\nu}{2}} | y_\nu \rangle = \int_{\mathbb{R}^D} dq (2\pi)^D \frac{\exp \left( i q \frac{y_{\nu+1} - y_\nu}{\sqrt{E}} \right)}{E + \frac{\nu}{2}} \]  

\[ = q^{-\nu} \sqrt{E} E^{D/2-1} \langle y_{\nu+1} | \frac{1}{1 + \frac{\nu}{2}} | y_\nu \rangle. \]  

(A4)

This explicitly decouples $E$, giving rise to

\[ \tilde{Q}(E) = E^{D/2-n-1-\left(\sum_{m=1}^D m + \sum_{n=1}^D \frac{m}{2}\right)/2} \int_{\mathbb{R}^D} dy_1 \ldots dy_n \prod_{\nu=0}^n \langle y_{\nu+1} | \frac{1}{1 + \frac{\nu}{2}} | y_\nu \rangle y_\nu^{m_\nu}. \]  

(A5)

Now the inverse Laplace transform can be performed and evaluated at $s_{n+1} = 1$. With the help of the formula $\int_0^\infty ds s^\nu e^{-sE} = \Gamma(\nu + 1)E^{-\nu-1}$, we obtain

\[ Q = K \int_{\mathbb{R}^D} dy_1 \ldots dy_n \prod_{\nu=0}^n \langle y_{\nu+1} | \frac{1}{1 + \frac{\nu}{2}} | y_\nu \rangle y_\nu^{m_\nu}, \]  

(A6)

where the multiplicative factor

\[ K = \frac{1}{\Gamma \left( n + 1 - \frac{D}{2} - \sum_{m=1}^D m + \sum_{n=1}^D \frac{m}{2} \right) }. \]  

(A7)

In the second step we invoke a resolutions of unity $\int_{\mathbb{R}^D} dy_\nu | y_\nu \rangle \langle y_\nu | = \mathbb{I}$, which brings $Q$ to the form

\[ Q = K \langle y_{n+1} | \frac{1}{1 + \frac{\nu}{2}} \hat{y}_{m-n} \frac{1}{1 + \frac{\nu}{2}} \hat{y}_{m-n-1} \ldots \frac{1}{1 + \frac{\nu}{2}} \hat{y}_{m-1} \frac{1}{1 + \frac{\nu}{2}} | y_0 \rangle. \]  

(A8)

With the use of the algebraic identity

\[ [\hat{y}_j, \mathcal{F}(\hat{q})] = i \frac{\partial \mathcal{F}(\hat{q})}{\partial q_j} \bigg|_{q=q}, \]  

(A9)

and the fact that $\hat{y}_j | y_0 \rangle = 0$, ($j = 1, \ldots, D$) we can bring (A8) to the form (recall the definition $y_0 = y_{n+1} = 0$)

\[ Q = K \langle y_{n+1} | G(q) | y_0 \rangle = K \int_{\mathbb{R}^D} \frac{dq}{(2\pi)^D} G(q), \]  

(A10)

with $G(q)$ defined as

\[ G(q) = \left( \frac{1}{1 + \frac{\nu}{2}} \frac{\partial q_{m-n}}{\partial q_{m-n}} \right) \ldots \left( \frac{1}{1 + \frac{\nu}{2}} \frac{\partial q_{m-1}}{\partial q_{m-1}} \right) \frac{1}{1 + \frac{\nu}{2}}. \]  

(A11)
Note that we could arrive at the same conclusion by employing in (A6) the spectral expansion of the position operator (or better, its power) in both position and momentum representations, i.e.

\[ \hat{y}^m = \int_{\mathbb{R}^D} dq_n |q_n\rangle \langle y|^{im} \frac{\partial^{im}}{\partial q_n^m} |q_n\rangle. \]  

(A12)

Ensuing lack of one \( \delta \)-function then causes the residual \( q \)-integration in (A10).

**Appendix B: Structure of \( Q(m_1, \ldots, m_n) \)**

In this appendix we show that the number of terms involved in evaluating \( Q(m_1, \ldots, m_n) \) via (15) grows as (46). We start by observing that the function \( G(q) \) in (A11) can be written as a sum

\[ G(q) = \sum_{r,s} a_{r,s} q^r \left( 1 + \frac{q^2}{2} \right)^s, \]  

(B1)

with combinatorial factors \( a_{r,s} \) whose explicit form is not not relevant for the arguments to follow. The components of multi-index \( r \) satisfy \( 0 \leq r^j \leq m^j_1 + \ldots + m^j_n \) for all \( j = 1, \ldots, D \) since each differentiation \( \partial/\partial q_j \) can produce at most one power of \( q_j \).

The summation index \( s \) in (B1) is not independent variable but it is fully specified once \( r \) is known. To see this, consider an elementary differentiation step

\[ \frac{\partial}{\partial q^j} q^r \left( 1 + \frac{q^2}{2} \right)^s = \frac{r^j q^{r-e_j}}{\left( 1 + \frac{q^2}{2} \right)^s} \frac{sq^{r+e_j}}{\left( 1 + \frac{q^2}{2} \right)^{s+1}}, \]  

(B2)

where \( e^j_i = \delta_{ij} \), and define \( \Delta \) to be the difference between the degree of the polynomial in the denominator and the numerator. The derivative shifts \( \Delta \) from \( 2s - |r| \) to \( 2s - |r| + 1 \), and this is common to both terms on the right hand side. Hence, the nonzero terms in sum (B1) must satisfy the condition \( 2s - |r| = |m^j_1| + \ldots + |m^j_n| + 2n + 2 \). This is also evident on the dimensional ground.

We also note that due to (B2) \( r^j \) in (B1) has, for all \( j \), the same even parity as the total degree of differentiation \( m^j_1 + \ldots + m^j_n \) because otherwise the integral in (A10) would vanish. Altogether, we see that there are only

\[ \sum_{r,s} 1 = \prod_{j=1}^{D} \sum_{r^j=0}^{m^j_1+\ldots+m^j_n} 1 = \prod_{j=1}^{D} \left[ (m^j_1 + \ldots + m^j_n)/2 + 1 \right], \]  

(B3)

non-trivially contributing terms in (B1).

Let us close this appendix by proving the inequality (47). To this end we observe that one can write

\[ \frac{(2m - 1)!!}{2^m m!} = \frac{1}{\sqrt{\pi}} \Gamma \left[ 1/2 + \sum_{j=1}^{D} (m^j_1 + \ldots + m^j_n) \right] \prod_{j=1}^{D} 2^{m^j_1+\ldots+m^j_n} \geq \prod_{j=1}^{D} 2^{m^j_1+\ldots+m^j_n} \geq \prod_{j=1}^{D} \left[ 1 + (m^j_1 + \ldots + m^j_n)/2 \right]. \]  

(B4)
On the first line we have used the duplication formula [46]: \( \Gamma(z)\Gamma(z + 1/2) = \sqrt{\pi}\Gamma(2z)2^{1-2z}. \)

On the second line the use was made of the inequality \( \Gamma(1/2 + z) \geq \sqrt{\pi} \) (valid for \( z \geq 2 \)) and the convexity inequality \( 2z^2 - 1 \geq z \log 2 > z/2 \) (valid for \( z \geq 0 \)).

\[\begin{align*}
\text{(1)} & \quad E. Wigner, Phys. Rev. 40, 749 (1932). \\
\text{(2)} & \quad J.G. Kirkwood, Phys. Rev. 44, 31 (1933). \\
\text{(3)} & \quad B. Simon, Functional Integration and Quantum Physics, (Academic, New York, 1979). \\
\text{(4)} & \quad Z. Haba, Feynman Integral and Random Dynamics in Quantum Physics; A Probabilistic Approach to Quantum Dynamics, (Kluwer, London, 1999). \\
\text{(5)} & \quad H. Kleinert, Path Integrals in Quantum Mechanics, Statistics, Polymer Physics, and Financial Markets, 5-th edition, (World Scientific, London, 2009). \\
\text{(6)} & \quad J. Zinn-Justin, Statistical Mechanics: Algorithms and Computations, (Oxford University Press, Oxford, 2006) \\
\text{(7)} & \quad F.T. Hioe and E.W. Montroll, J. Math. Phys. 16, 1945 (1975). \\
\text{(8)} & \quad F.T. Hioe, D. Machiilien and E.W. Montroll, Phys. Rep. 43, 305 (1978). \\
\end{align*}\]
1971).
[43] B. Jancovici, Physica A, 91, 152 (1978).
[44] T. Kihara, Y. Midzuno and T. Shizume, J. Phys. Soc. Jpn. 10, 249 (1955).
[45] L.D. Landau, and E. Lifschitz, Statistical Physics, (Pergamon, Elmsford, 1980).
[46] I.S. Gradshteyn and I.M. Ryzhik, Table of Integrals, Series, and Products, 7-th edition, (Elsevier, New York, 2007).
[47] See supplementary material at [...] for Wolfram Mathematica notebook expansion1D.nb that implements the formulas (26) and (27), and allows to insert a specific (smooth) potential $V(x)$. The expansion up to order $\beta^{18}$ is available in the file expansion1D18orders.m, and is imported automatically into the .nb notebook.
[48] Z. Bern and D.A. Kosower, Phys. Rev. Lett. 66, 1669 (1991); Nucl. Phys. B 379, 451 (1992).
[49] M.J. Strassler, Nucl. Phys. B 385, 145 (1992).
[50] D. Fliegner, P. Haberl, M.G. Schmidt, C. Schubert, Ann. Phys. (N.Y.) 264, 51 (1998).
[51] D. Fliegner, M.G. Schmidt and C. Schubert, Z. Phys. C 64, 111 (1994).
[52] A. Alastuey and B. Jancovici, Physica A: Stat. Mech. 97, 349 (1979).
[53] L. Wang, Plasma Phys. Control. Fusion 29, 395 (1987).
[54] J. Caro, E. Ruiz Arriola and L.L. Salcedo, J. Phys. G 22, 981 (1996).
[55] T.A. Osborn and F.H. Molzahn, Phys. Rev. A34, 1696 (1986).
[56] M. Durand, P. Schuck and X. Viñas, Phys. Rev. A36, 1824 (1987).
[57] H. Kleinert, Phys. Lett. A 173, 332 (1993).
[58] C.M. Bender, K.A. Milton, M. Moshe, S.S. Pinsky and L.M. Simmons Jr., Phys. Rev. Lett. 58, 2615 (1987).
[59] P.M. Stevenson, Phys. Rev. D23, 2916 (1981).
[60] M. Blasone, P. Jizba and G. Vitiello, Quantum Field Theory and its Macroscopic Manifestations (Imperial College Press, London, 2011).