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Steven M. Hornstein and William H. Miller

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## DISCLAIMER

QUANTUM CORRECTIONS (WITHIN THE CLASSICAL PATH APPROXIMATION)

TO THE BOLTZMANN DENSITY MATRIX

by

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ABSTRACT

A previously derived classical path approximation for diagonal matrix

elements of the Boltzmann density matrix (i.e., the particle density) is

expanded in a power series in $\hbar$ about the classical density. Comparing

term by term with Wigner's expansion of the exact quantum mechanical

density, one sees that the first quantum correction to the classical

density (which involves first and second derivatives of the potential

energy) is given correctly by the classical path approximation. Wigner's

expression for the second correction term, however, involves the first

four derivatives of the potential, and the classical path approximation

gives only the part of this term that involves the first three derivatives.

## I.  Introduction

Recent work has demonstrated the value of the classical path approxi-mation to quantum mechanical problems.  This classical-limit approach, in which the Feynman sum over all paths is replaced by a sum over only the classical path (or paths), has yielded accurate results in scattering problems[1] and quantum statistical mechanics.[2]

In this Letter we investigate in more detail a recently derived classical path approximation for the Boltzmann density matrix[2].  The particle density (i.e., the diagonal elements of the density matrix) given by this approximation was seen to be considerably more accurate than the ordinary classical density, being qualitatively correct (and reason-ably quantitative) even in the low temperature limit where the classical density is completely inadequate.  Furthermore, in regions where the potential energy function has only first and second non-vanishing derivatives, the classical path approximation was seen to give the exact quantum mechanical result for the density.

To gain more insight into the nature of the classical path approxi-mation and its level of accuracy, this paper systematically expands the classical-path density in a power series in $\hbar$, and explicit expressions are obtained for the first two "quantum correction" terms to the ordinary classical density.  Comparing with the exact quantum expressions for these correction terms obtained by Wigner[3], one sees that the first quantum correction to the classical density (which involves first and second derivatives of the potential) is given correctly by the classical path approximation.  The second correction term, however, involves the first four derivatives of the potential energy and the classical path

approximation gives only the part involving its first three derivatives.

## II. Expansion of the Classical Path Approximation

For a single particle in a one-dimensional potential well the particle density $\rho_\beta(x) \cong \langle x | e^{-\beta H} | x \rangle$ is given in the classical path approximation by[2] $(\beta \leq 1/kT)$

$$\rho_\beta(x) = D_\beta(x)^{-\frac{1}{2}} \exp[-\phi_\beta(x)] \tag{1}$$

where

$$\phi_\beta(x) = \beta V(x_0) + 2(2m/\hbar^2)^{\frac{1}{2}} \int_{x_0}^{x} dx' \, [V(x') - V(x_0)]^{\frac{1}{2}} \tag{2}$$

$$D_\beta(x) = 4\pi(\hbar^2/2m)^{\frac{1}{2}}[V(x_0) - V(x)] \int_{x_0}^{x} dx' \, [V(x') - V(x_0)]^{-\frac{3}{2}} . \tag{3}$$

The turning point $x_0$ is the function of $x$ and $\beta$ defined by the equation

$$\lambda^{\frac{1}{2}} = \int_{x_0}^{x} dx' \, [V(x') - V(x_0)]^{-\frac{1}{2}} , \tag{4}$$

where the "quantum parameter" (dimensions = length$^2$/energy) is

$$\lambda = \hbar^2 \beta^2 / 2m. \tag{5}$$

It is easy to show[2] that in the limit $\lambda \to 0$ Equations (1)-(4) reduce to the usual classical density

$$\rho_\beta^{CL}(x) = \left(\frac{2m}{\hbar^2}/4\pi\beta\right)^{\frac{1}{2}} \exp[-\beta V(x)]. \tag{6}$$

Here we wish to expand Equations (2)-(4) in a power series in $\lambda$ to obtain

Equation (1) in the form

$$\rho_\beta(x) = \rho_\beta^{CL}(x)[1 + \lambda C_1(x,\beta) + \lambda^2 C_2(x,\beta) + \dots]; \qquad (7)$$

i.e., the goal is to obtain explicit expressions for the "quantum correction" functions $C_k(x,\beta), k = 1,2,\dots$ .

The first step is to change variables of integration in Equations (2)-(4) from $x'$ to the dimensionless variable $z$, $x' = x_o + z \Delta x$, where $\Delta x \equiv x - x_o$; the limits of all the integrals then become 0 to 1. The integrands in Equations (2)-(4) are then expanded in a power series in $\Delta x$ and integrated term by term; Equation (4), for example, becomes

$$\lambda^{\frac{1}{2}} = 2(\Delta x/V')^{\frac{1}{2}} \left\{ 1 + \Delta x(5/12)(V''/V') + \Delta x^2[(43/160)(V''/V')^2 \right.$$
$$\left. - (11/60)(V'''/V')] + O(\Delta x^3) \right\} \quad , \qquad (4')$$

where $V' = V'(x)$, $V'' = V''(x)$, etc. Equation (4), a power series in $\Delta x$ for $\lambda$, can be inverted to obtain $\Delta x$ as a power series in $\lambda$:

$$\Delta x = (\lambda V'/4) \left\{ 1 - \lambda(5/24)V'' + \lambda^2[(61/1440)(V'')^2 + (11/480)V'V'''] \right.$$
$$\left. + O(\lambda^3) \right\} \qquad (8)$$

Inserting Equation (8) into the $\Delta x$-expansions of Equations (2) and (3) then gives a $\lambda$-expansion for these quantities:

$$\phi_\beta(x) = \beta[V - \lambda(V')^2/12 + \lambda^2(V')^2V''/60 + O(\lambda^3)] \qquad (2')$$

$$D_\beta(x) = 4\pi\beta(\hbar^2/2m) \left\{ 1 + \lambda V''/3 + \lambda^2[(V'')^2/30 - V'V'''/15] \right.$$
$$\left. + O(\lambda^3) \right\} , \qquad (3')$$

or

$$D_\beta(x)^{-\frac{1}{2}} = \left(\frac{2m}{\hbar^2}/4\pi\beta\right)^{\frac{1}{2}}\left\{1 - \lambda V''/6 + \lambda^2[(V'')^2/40 + V'V'''/30]\right. \\ \left. + O(\lambda^3)\right\} \, . \tag{3''}$$

Combining Equations (2') and (3'') in with Equation (1) gives the density in the form of Equation (7), where the first two quantum correction functions are identified as

$$c_1(x,\beta) = \beta[V'(x)]^2/12 - V''(x)/6 \tag{9}$$

$$c_2(x,\beta) = \beta^2[V'(x)]^4/288 - (11/360)\beta[V'(x)]^2V''(x) + [V''(x)]^2/40$$
$$+ V'(x)V'''(x)/30 \, . \tag{10}$$

Higher terms can be similarly generated.

The exact quantum expressions for these correction terms have been determined by Wigner[3], and one sees that Equation (9) for the first quantum correction is the same as Wigner's result. Wigner's expression for $c_2(x,\beta)$, however, is the same as that in Equation (10) but with the term $-V''''(x)/60\beta$ added to it.

## III. Discussion

Knowing from Wigner's work[3] that the first quantum correction to the classical density involves only first and second derivatives of the potential, one could have predicted beforehand that the classical path approximation would give the exact quantum result for this first correction term – for it has been noted above that the classical path approximation is exact (for all values of $\lambda$) if the potential has only first and second non-zero derivatives. Thus it is not surprising, too, that the part of the second correction term which involves the first two derivatives of the potential is given correctly. The surprising feature, which could not have been anticipated, is that the part of

$C_2(x,\beta)$ which involves the third derivative is also given correctly. The classical path approximation was seen not to be capable, however, of producing the fourth derivative term in the quantum expression for $C_2(x,\beta)$.

These observations are another example of the fact that the classical path approximation is not a high temperature (small $\beta$) approximation in the present statistical mechanical application, nor a short time approximation in scattering situations; rather it is an approximation that the potential energy is a slowly varying function. The second correction term $C_2(x,\beta)$, therefore, will be given quite accurately by Equation (10) if the fourth derivative of the potential is small compared to the three lower derivatives. This notion that the classical path approximation is basically an approximation of a slowly varying potential is also a well-known idea from ordinary WKB theory[4].

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# References

*   Alfred P. Sloan Fellow

1.  See, for example, W. H. Miller, J. Chem. Phys., 53, 1949; 3578 (1970); Chem. Phys. Letters, 7, 431 (1970); J. Chem. Phys., 54, 5386 (1971); 55, 3150 (1971).

2.  W. H. Miller, J. Chem. Phys., 55, 3146 (1971).

3.  E. P. Wigner, Phys. Rev., 40, 749 (1932).

4.  See, for example, L. I. Schiff, Quantum Mechanics, McGraw-Hill, New York, 1968, p. 271.