Quantum Mechanical Results Of The Matrix Elements Of The Boltzmann Operator Obtained From Series Representations

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(Dated: May 5, 2014)

Abstract

Recently developed series representations of the Boltzmann operator are used to obtain Quantum Mechanical results for the matrix elements, \( \langle x | \exp(-\beta \hat{H}) | x' \rangle \), of the imaginary time propagator. The calculations are done for two different potential surfaces: one of them is an Eckart Barrier and the other one is a double well potential surface. Numerical convergence of the series are investigated. Although the zeroth order term is sufficient at high temperatures, it does not lead to the correct saddle point structure at low temperatures where the tunneling is important. Nevertheless the series converges rapidly even at low temperatures. Some of the double well calculations are also done with the bare potential (without Gaussian averaging). Some equations of motion related with bare potentials are also derived. The use of the bare potential results in faster integrations of equations of motion. Although, it causes lower accuracy in the zeroth order approximation, the series show similar convergence properties both for Gaussian averaged calculations and the bare potential calculations. However, the series may not converge for bare potential calculations at low temperatures because of the low accuracy of zeroth order approximation. Interestingly, it is found that the number of saddle points of \( \langle x | \exp(-\beta \hat{H}) | x' \rangle \) increases as the temperature is lowered. An explanation of observed structures at low temperatures remains as a challenge. Besides, it has implications for the quantum instanton theory of reaction rates at very low temperatures.

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I. INTRODUCTION

Semiclassical theories are useful for the treatments of large dimensional systems because of their favorable scaling with the dimension of the system. They allow one to study systems that are very hard to treat with quantum mechanics due to exponential scaling of the sizes of bases with increasing number of dimensions in quantum mechanics. Besides, they offer advantages over classical methods by allowing one to include quantum effects such as interference and tunneling which cannot be described with classical methods.

Development of semiclassical propagators for studying dynamics of atomic and molecular systems dates back to pioneering works of Van Vleck [1] and Gutzwiller [2]. Van Vleck Propagator is obtained as a semiclassical approximation to path integral and it is exact for quadratic Hamiltonians. However, it has some drawbacks due to some difficulties related with its numerical implementation. Firstly, dynamics is formulated as a double ended boundary value problem, so that it is necessary to do nonlinear searches to find classical trajectories that satisfy the boundary conditions of the problem. Secondly, Van Vleck propagator has a prefactor that has singularities. These problems with the Van Vleck propagator is overcome by the development of initial value representation (IVR) methods. In the IVR, integration variable related with the end point of a coordinate is transformed to an initial momentum so that the dynamics problem is posed as an initial value problem in which the initial conditions of the problem are specified by the initial phase space points. Thus, it is not necessary to make nonlinear searches for finding classical paths connecting the end points. Besides, the IVR based propagators do not include prefactors that have singularities. In addition to its numerical advantages IVR also offers a more intuitive physical picture for dynamics.

History of IVR dates back to its use by Miller [3] and Markus [4] in studies of classical S-matrix calculations for collisions. Modern semiclassical propagators are based on the idea of using Gaussian wave packets suggested by Heller [5, 6] which is later refined by Herman and Kluk [7]. Since the work of Heller, many IVR based propagators are developed for real time dynamics. Several reviews about different aspects of the subject can be found in the literature [8–16].

The success of the IVR based methods in real time dynamics also motivated the development of semiclassical methods for imaginary time dynamics. Several methods has
been proposed for a semiclassical approximation of the imaginary time propagator [17–20]. Recently, Frantsuzov et. al. developed semiclassical approximation to imaginary time propagator [19, 20], named Time Evolving Gaussian Approximation (TEGA), which is based on an earlier method suggested by Hellsing et. al. [17]. Another approximation to imaginary time propagator is suggested by Pollak and Martin-Fierro [21]. In this method, named PSTEGA (Phase Space Time Evolving Gaussian Approximation), coherent states are used. Since the Gaussians that are used in the TEGA method can be considered as coherent states with zero momentum, PSTEGA method can be considered as a generalization of the TEGA method. Although the propagator involves phase space integration instead of configuration space integration, it is possible to integrate equations of motion in an efficient way. As shown in the appendix, the momentum degrees of freedom can be integrated implicitly so that matrix elements of the equilibrium density matrix can be evaluated with an expansion in configuration space as in the TEGA method. Besides, the PSTEGA method provides a new way of evaluating time correlation functions.

Although the IVR based semiclassical methods has been used successfully in many systems, the approximations involved in these calculations remained uncontrolled such that there was no way to estimate the errors in these calculations. This problem has been overcome by the development of correction operator formalism by Pollak and co-workers [22–27]. They have shown that the exact quantum mechanical propagator can be expanded in a series in which the zeroth order term is an approximation to the exact propagator. Then, the higher order terms are obtained from the zeroth order term in a recursive manner by using the correction operator. Therefore, it is possible obtain quantum mechanical results, at least in principle, starting with a semiclassical calculation.

In this paper, some equations of motion related with the PSTEGA calculations, in which bare potentials are used, are derived. In addition to that an efficient way of solving the PSTEGA equations of motion is shown. Then the TEGA and the PSTEGA methods are applied to two different systems one with an Eckart Barrier and another with a double well potential surface. Numerical convergence properties of the series are investigated and the accuracy of the results is checked with quantum mechanical calculations. In the calculations both the Gaussian averaging and the bare potential are used. The results show that the use of bare potential leads to lower accuracy in the zeroth order approximation. Nevertheless, calculations show similar convergence properties with the Gaussian averaged potential
calculations. The results show interesting structures at low temperatures.

In section II theory of the TEGA and PSTEGA methods are reviewed. Then, in section III calculations and results are presented. The paper ends with discussions and conclusions in section IV.

II. THEORY

The theory of the TEGA method as a semiclassical approximation is first developed by Frantsuzov and Mandelshtam \[19, 20\] based on an earlier method suggested by Hellsing et.al. \[17\]. Later, Shao and Pollak applied the Correction Operator formalism to the TEGA method and showed how it can be used to obtain quantum mechanical results for the matrix elements of the Boltzmann operator \[28\]. The theory of the PSTEGA method is developed by Pollak and Martin-Fierro \[21\]. In the following subsections, first the theory of the correction operator formalism and the series expansion of the thermal propagator will be given in a general manner. Then, the details of TEGA and PSTEGA methods will be given. Equations of motion for the PSTEGA calculation in which the bare potential is used will be given for the first time.

A. Preliminaries

Consider an $N$ dimensional system with the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2} + V(\hat{q}),$$

(1)

where $\hat{q}$ and $\hat{p}$ are $N$ dimensional vectors of mass weighted coordinate and momenta respectively satisfying the usual commutation relation $[\hat{q}_i, \hat{p}_j] = i\hbar\delta_{ij}$, and $V(\hat{q})$ is the potential surface of the system.

The thermal propagator $\hat{K}(\tau) \equiv \exp(-\tau\hat{H})$ is the solution of the imaginary time Schrödinger equation (or the Bloch equation),

$$\left(-\frac{\partial}{\partial \tau} - \hat{H}\right) \hat{K}(\tau) = 0,$$

(2)

at imaginary time $\tau$ with the initial condition $\hat{K}(0) = I$, where $I$ is the $N$ dimensional identity matrix.
If there exist a good approximation \( \hat{K}_0(\tau) \) for the exact propagator \( \hat{K}(\tau) \), then the correction operator \( \hat{C}(\tau) \) can be defined as follows:

\[
\hat{C}(\tau) = \left( -\frac{\partial}{\partial \tau} - \hat{H} \right) \hat{K}_0(\tau).
\] (3)

The differential equation above can be inverted to an integral equation by realizing that the exact propagator is the solution of the homogeneous equation (Bloch equation). The formal solution is given by,

\[
\hat{K}(\tau) = \hat{K}_0(\tau) + \int_0^\tau d\tau' \hat{K}(\tau - \tau') \hat{C}(\tau').
\] (4)

B. Series Representation Of The Thermal Propagator

Although equation (4) provides a formal solution, it is not very useful in that form since the exact propagator appears on both sides of the equation. On the other hand, if \( \hat{K}_0(\tau) \) is a good approximation to the exact propagator, \( \hat{K}(\tau) \), then it makes sense to expand the exact solution in a series where \( \hat{K}_0(\tau) \) is the leading order term of the series such that

\[
\hat{K}(\tau) = \sum_{i=0}^{\infty} \hat{K}_i(\tau).
\] (5)

By plugging the expansion above to equation (4), and assuming that \( \hat{K}_j \sim \hat{C}^j \), the following recursion relation is obtained for the higher order terms by equating the terms that are of the order of the same power of the correction operator:

\[
\hat{K}_{i+1}(\tau) = \int_0^\tau d\tau' \hat{K}_i(\tau - \tau') \hat{C}(\tau'), \; i \geq 0.
\] (6)

Thus, given an approximation, the exact thermal propagator can be obtained from that approximation recursively, by using a series in which the zeroth order term is the approximation.

C. Symmetric Form Of The Series Representation

The exact thermal propagator is Hermitian: \( \hat{K}(\tau) = \hat{K}(\tau)^\dagger \). However, both the TEGA and the PSTEGA approximations do not provide a hermitian representation for \( \hat{K}_0(\tau) \). Therefore, the series expansion that contains the TEGA or the PSTEGA approximations as the zeroth order term cannot give a Hermitian representation of the exact propagator.
This problem can be remedied as follows. In order to make every single term in the series expansion Hermitian, the equation below can be used:

$$\hat{K}(\tau) = \hat{K}(\tau/2)\hat{K}^\dagger(\tau/2). \quad (7)$$

Since $$(\hat{K}(\tau/2)\hat{K}(\tau/2)^\dagger)^\dagger = \hat{K}(\tau)\hat{K}(\tau/2)^\dagger$$, the use of this identity guarantees generation of a Hermitian representation of $\hat{K}(\tau)$ from any representation of $\hat{K}(\tau/2)$ regardless of whether that representation is Hermitian or not. Thus, by expanding all of the terms in equation (7) in a series as in equation (5), the following series expansion is obtained for $\hat{K}(\tau)$ in terms of the terms in the series expansion of $\hat{K}(\tau/2)$

$$\hat{K}(\tau) = \sum_j \hat{K}^{(j)}(\tau), \quad (8)$$

where

$$\hat{K}^{(j)}(\tau) = \sum_{i=j}^{i=j} \hat{K}_i(\tau/2)\hat{K}_{j-i}^\dagger(\tau/2). \quad (9)$$

It is clear that a representation of the term on the left hand side will be Hermitian regardless of whether the representations of the terms on the right hand side are Hermitian or not.

**D. Definitions Of Averaged Quantities**

Frantsuzov and Mandelshtam derived the equations of motion for the TEGA method variationally [20]. This method leads to the result that the potential and its derivatives should be Gaussian averaged. In the rest of the paper, the following notation is used for denoting the Gaussian averaging of a quantity $h(q)$:

$$\langle h(q) \rangle = \left( \frac{1}{\pi} \right)^{N/2} \frac{1}{\sqrt{\det(G(\tau))}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\mathbf{x} \times \exp\left(-((\mathbf{x} - \mathbf{q}(\tau))^T G(\tau)^{-1}(\mathbf{x} - \mathbf{q}(\tau)))h(\mathbf{x})\right), \quad (10)$$

where $\mathbf{q}(\tau)$ is an $N$ dimensional vector defining the center of the Gaussian and $G(\tau)$ is an $N \times N$ dimensional positive definite matrix defining the width of the Gaussian.

Shao and Pollak has shown that the equations of motion for the TEGA method can be derived by requiring that the method is exact for harmonic potentials [28], and the same idea is also used in the development of the PSTEGA method [21]. By using this idea of deriving equations of motion, Shao and Pollak suggested that the TEGA method can be generalized
for an arbitrary averaging function. Given a reasonable zeroth order approximation, the series representation will converge to the correct result. Consequently, Shao and Pollak suggested that the calculations can be done with the bare potential (without Gaussian averaging). Provided that this still gives a reasonable zeroth order approximation, one can obtain the exact propagator from that approximation via correction operator formalism. The use of the bare potential leads to faster integrations of equations of motion since the Gaussian averagings are not done.

E. Equations Of Motion For The TEGA

Matrix elements of the approximate solution of the Bloch equation in the TEGA is given by \[19, 20\],

\[
\langle x|\hat{K}_0(\tau)|q_0\rangle = \left(\frac{1}{2\pi}\right)^{N/2} \frac{1}{|\text{det}(G(\tau))|^{1/2}} \times \exp\left(-\frac{1}{2}((x - q(\tau))^T G(\tau)^{-1}(x - q(\tau))) + \gamma(\tau)\right). \tag{11}
\]

In the equation above, the \(N\) dimensional vector \(q = q(\tau)\) defines the center of the Gaussian, the \(N \times N\) dimensional positive definite matrix \(G = G(\tau)\) defines the width of the Gaussian, and the parameter \(\gamma = \gamma(\tau)\) is a real scale factor.

In order for this representation of the thermal propagator to satisfy the initial condition that \(\hat{K}(0) = I\), the following conditions should be imposed for small \(\tau\):

\[
q(\tau \simeq 0) = q_0, \quad G(\tau \simeq 0) = \hbar^2 \tau I, \quad \gamma(\tau \simeq 0) = -\tau V(q_0). \tag{12}
\]

If Gaussian averaging is used, the equations of motion for the three variables are \[20, 29\]:

\[
\frac{d}{d\tau} G(\tau) = -G(\tau)\langle \nabla \nabla^T V(q(\tau))\rangle G(\tau) + \hbar^2 I, \tag{13}
\]

\[
\frac{d}{d\tau} q(\tau) = -G(\tau)\langle \nabla V(q(\tau))\rangle, \tag{14}
\]

\[
\frac{d}{d\tau} \gamma(\tau) = -\frac{1}{4} \text{Tr}[\langle \nabla \nabla^T V(q(\tau))\rangle G(\tau) - \langle V(q(\tau))\rangle]. \tag{15}
\]

The use of the bare potential leads to the same equations of motion except that the potential and its derivatives are not Gaussian averaged. However, the coefficient \(-1/4\) in the equation of motion of the variable \(\gamma(\tau)\) becomes \(-1/2\) \[28\].
When equation (9) is used the matrix elements of each term in the series expansion of the Boltzmann operator can be calculated as follows:

$$
\langle x | \hat{K}^{(i)}(\tau) | x' \rangle = \sum_{i=0}^{i=j} \int dy \langle x | \hat{K}_i(\tau/2) | y \rangle \langle y | \hat{K}^\dagger_{j-i}(\tau/2) | x' \rangle.
$$
(16)

F. Equations Of Motion For The PSTEGA

In the PSTEGA method [21], the thermal propagator is represented in a coherent state basis whose coordinate state representation is given by

$$
\langle x | g(p, q, \tau) \rangle = \left( \frac{1}{\det(G(\tau))^{1/4}} \right) \exp \left( -\frac{1}{2}(x - q(\tau))^T G^{-1}(\tau)(x - q(\tau)) + i \frac{\hbar}{2} p^T(\tau)(x - q(\tau)) \right).
$$
(17)

In the equation above, $N$ dimensional vectors $q = q(\tau)$ and $p = p(\tau)$ are the position and momentum vectors respectively and the $N \times N$ dimensional positive definite matrix $G(\tau)$ is the width matrix. The matrix elements of the imaginary time propagator can be expanded in the coherent state basis as

$$
\langle x | \exp(-\tau \hat{H}) | x' \rangle = \int \frac{dp dq}{2\pi} \langle x | \exp(-\tau \hat{H}) | g(p, q, 0) \rangle \langle g(p, q, 0) | x' \rangle,
$$
(18)

and the mixed matrix elements of the thermal propagator are approximated as

$$
\langle x | \exp(-\tau \hat{H}) | g(p, q, 0) \rangle \simeq \langle x | \hat{K}_0(\tau) | g(p, q, 0) \rangle 
\equiv f(p, q, \tau) \langle x | g(p, q, \tau) \rangle.
$$
(19)

If the potential is Gaussian averaged, equations for the variables, $q$, $p$, $G$, and $f(\tau)$ are given by [21]

$$
\frac{\partial q(\tau)}{\partial \tau} = -G(\tau) \langle \nabla V(q(\tau)) \rangle, \quad q(0) = q_0,
$$
(20)

$$
\frac{\partial p(\tau)}{\partial \tau} = -\hbar^2 G(\tau)^{-1} p(\tau), \quad p(0) = p_0,
$$
(21)

$$
\frac{\partial G(\tau)}{\partial \tau} = -G(\tau) \langle \nabla \nabla^T V(q(\tau)) \rangle G(\tau) + \hbar^2 I,
$$
(22)

$$
f(\tau) = \exp \left( -\int_0^\tau d\tau' \left[ \frac{1}{2} p^T(\tau') p(\tau') + \langle V(q(\tau')) \rangle + \frac{\hbar^2}{4} \text{Tr}[G(\tau')^{-1}] - i \frac{\hbar}{\hbar} \frac{\partial q(\tau')}{\partial \tau'} \right] \right).
$$
(23)
As the way Pollak and Martin-Fierro have done [21], the equations of motion for the bare potential calculations can be derived by requiring that the method is exact for quadratic potentials. In this case \( f(\tau) \) is given by

\[
f(\tau) = \exp \left( -\int_0^\tau \mathrm{d}\tau' \left[ \frac{1}{2} p^T(\tau') p(\tau') + V(q(\tau')) \right] + \frac{\hbar}{4} \mathrm{Tr}[G(\tau')^{-1}] - \frac{i}{\hbar} p^T(\tau') \frac{\partial q(\tau')}{\partial \tau'} \right. \]
\[\left. + \frac{1}{4} \mathrm{Tr}[\nabla \nabla^T V(q(\tau')) G(\tau')] \right). \tag{24}
\]

Other equations will be the same except that the potential and its derivatives are not Gaussian averaged. In the PSTEGA approximation, initial width of the Gaussians is arbitrary.

In calculations, it is not necessary to make a propagation in phase space, since the equation of motion for \( p(\tau) \), equation (21), can be integrated implicitly. For a detailed explanation of how to integrate equations of motion in an efficient way see the appendix.

G. Matrix Elements Of The Correction Operator

Matrix elements of the correction operator are given by [21, 28]

\[
\langle x|\hat{C}(\tau)|q(\tau)\rangle = -\langle V_{\text{anh}}(x, q, \tau) \rangle \langle x|K_0(\tau)|q(\tau)\rangle, \tag{25}
\]

where \( \langle V_{\text{anh}}(x, q, \tau) \rangle \) is the anharmonic remainder of the potential when it is expanded around \( q(\tau) \). If Gaussian averaging is used, expansion of the potential surface is given by [28]

\[
V(x) \equiv \langle V(q(\tau)) \rangle + \frac{1}{2}(\langle \nabla^T V(q(\tau)) \rangle (x - q(\tau))
\[\left. + \frac{1}{2}(x - q(\tau))^T \langle \nabla V(q(\tau)) \rangle (x - q(\tau)) \right. \]
\[\left. + \frac{1}{2}(x - q(\tau))^T \langle \nabla \nabla^T V(q(\tau)) \rangle (x - q(\tau)) \right. \]
\[\left. - \frac{1}{4}[\langle \nabla \nabla^T V(q(\tau)) \rangle G(\tau)] \right) + \langle V_{\text{anh}}(x, q, \tau) \rangle. \tag{26}
\]
If the bare potential is used in the calculations; then, the expansion of the potential surface is given by

\[ V(x) \equiv V(q(\tau)) + \frac{1}{2} (\nabla^T V(q(\tau))(x - q(\tau)) \\
+ (x - q(\tau))^T \nabla V(q(\tau))) \\
+ \frac{1}{2} (x - q(\tau))^T \nabla \nabla^T V(q(\tau))(x - q(\tau)) \\
+ V_{\text{anh}}(x, q, \tau). \]  

(27)

In this case, matrix elements of the correction operator are given by

\[ \langle x|\hat{C}(\tau)|q(\tau)\rangle = -V_{\text{anh}}(x, q, \tau) \langle x|K_0(\tau)|q(\tau)\rangle. \]  

(28)

H. Quantum Mechanical Calculations

In order to make a comparison of TEGA and PSTEGA calculations with a direct quantum mechanical calculation, quantum mechanical calculations are also performed. In order to calculate the density matrix elements, first the Hamiltonian matrix is diagonalized; then, the thermal propagator is expanded in the basis of the eigenstates of the Hamiltonian. If \( \phi_n(x) \) are the eigenstates of the Hamiltonian which are obtained as a result of diagonalization calculation; then, the matrix elements of the thermal propagator can be evaluated as follows:

\[ \langle x'|\exp(-\beta \hat{H})|x\rangle = \sum_n \langle x'|\exp(-\beta \hat{H})|\phi_n\rangle \langle \phi_n|x\rangle \\
= \sum_n \phi_n(x') \exp(-\beta E_n) \phi_n^*(x). \]  

(29)

This calculation, in the case of Eckart Barrier, duplicates the calculations of Miller et. al. [30].

III. CALCULATIONS AND RESULTS

The calculations are done for two different potential surfaces. One of them is an Eckart Barrier and the other one is a double well potential surface. The details of calculations and their results are given in the following subsections.
A. Eckart Barrier

The configuration matrix elements of the Eckart potential were previously studied by Miller et. al. [30]. The asymmetric Eckart barrier potential has the form

\[ V(x) = \frac{V_0(1 - \alpha)}{1 + \exp(-2ax)} + \frac{V_0(1 + \sqrt{\alpha})^2}{4 \cosh^2(ax)} \]  

where \( \alpha \) is the asymmetry parameter. The potential surface is symmetric when \( \alpha = 1 \). In the present study, the same parameters that were used by Miller et. al. [30], that is \( V_0 = 0.016 \)a.u., \( a = 1.3624 \)a.u. and \( \sqrt{m} = 1061 \)a.u. are used. Some computations for an asymmetric barrier with \( \alpha = 1.25 \) are also performed.

Since this is a one dimensional system, it is convenient to work with matrices of the zeroth order Boltzmann operator, equation (11), and the correction operator, equation (25), in the configuration space. Then, the final results are obtained by matrix multiplications and time integrations. The latter were all performed using the third order Simpson integrator [31]. An evenly spaced grid is taken for the coordinate \( y \) in a finite symmetric range, and a Gaussian form is defined around each grid point that satisfies the initial conditions given in equation (12). For the calculations presented in this paper 200 evenly spaced grid points in the range \((-8, 8)\) is sufficient for converging the configuration space matrix elements of the Boltzmann operator in the range \((-6, 6)\). For calculating time dependent averages as in equation (10), Gauss-Hermite quadrature is used.

To obtain the configuration matrix elements of the Boltzmann operator \( \exp(-\beta \hat{H}) \), the equations of motion, equations (13)-(15), were integrated up to the half time \( \hbar \beta / 2 \) using the adaptive step size Cash-Karp Runge-Kutta method [31]. The matrices of the TEGA propagator and the correction operator are calculated and stored at every time step. Then, the higher order terms in the series corresponding to half time are calculated recursively by using equation (19). Finally, by using the symmetric formula, equation (16), the matrix elements of the higher order terms in the series expansion of the Boltzmann operator are calculated to find the matrix elements corresponding to the full time.

The calculations are done at three different temperatures. Their results are given below.
FIG. 1: 3-D plots and contour plots of the first two terms in the series expansion of the thermal propagator at temperature $T = 2000^{\circ}$K for the symmetric Eckart barrier potential.

1. Symmetric Potential, $T = 2000^{\circ}$K

In the high temperature limit, the Boltzmann operator is well approximated in terms of classical mechanics. Since the TEGA reduces to the classical mechanical Boltzmann distribution, one expects it to be accurate in this limit. Figure 1 shows surface and contour plots of the matrix elements of the terms $\hat{K}^{(0)}(\beta)$ and $\hat{K}^{(1)}(\beta)$ at the temperature $T = 2000^{\circ}$K. In reduced variables, $\hbar\beta\omega^\dagger = 1.20$ which is small when compared to the reduced
crossover temperature of $2\pi$ between thermal activation and tunneling ($\omega^\dagger$ is the harmonic barrier frequency of the Eckart barrier). From the figure one notes that the first order term in the series expansion is indeed very small as compared to the zeroth order term.

2. Symmetric Potential, $T = 200^\circ\text{K}$

Figure 3 shows contour plots of the matrix elements of the imaginary time propagator $\sum_{j=0}^{N=3} \hat{K}^{(j)}(\beta)$, for $N = 0, 1, 2, 3$, respectively at the temperature $T = 200^\circ\text{K}$ (or $\hbar\beta\omega^\dagger = 12$), which is below the (reduced) crossover temperature of $2\pi$. At this temperature, tunneling becomes important so that the zero-th order contribution in the series representation is no longer sufficient. The contour plot of the matrix elements of the TEGA (zero-th order) propagator as shown in panel (a) of the Figure has a single saddle point structure as predicted by Liu and Miller [32]. As shown in panel (b) of figure 3, adding the first order term changes the structure of the contour plot completely such that there are two saddle points in the
FIG. 3: Contour plots of the matrix elements of the thermal propagator in the TEGA series expansion. Panels (a), (b), (c) and (d) correspond to the truncated series expansion of the order $N = 0, 1, 2, 3$ respectively at temperature $T = 200^\circ K$ for the symmetric Eckart barrier potential. In panel (a), the contour values are $10^{-n}$ with $n = 1, \ldots, 7$. The highest contour ($n = 1$) is the solid black line, and the lowest contour ($n = 7$) is the dark blue line. In panel (b) the contour values are $10^{-1}$ (dashed light blue line), $10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}$ (solid yellow line), $7.0 \times 10^{-6}, 6.0 \times 10^{-6}$ (solid red line), $4.0 \times 10^{-6}$ (solid light blue line), $6.0 \times 10^{-6}, 10^{-7}$ (solid dark blue line). The contour values for panels (c) and (d) are $10^{-1}$ (dashed red line), $10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, 6.0 \times 10^{-6}$ (solid yellow line), $5.0 \times 10^{-6}, 4.0 \times 10^{-6}$ (solid red line), $2.5 \times 10^{-6}$ (solid light blue line), $10^{-6}, 10^{-7}$ (solid dark blue line).
FIG. 4: One dimensional cuts along the anti-diagonal of the matrix elements of the thermal propagator are shown for the truncated series up to order 3 at temperature $T = 200^\circ K$ for the symmetric Eckart barrier potential.

3. Symmetric Potential, $T = 40^\circ K$

The reduced temperature when $T = 40^\circ K$ is $\hbar \beta \omega^\dagger = 60$, which is much larger than $2\pi$, so that this temperature corresponds to “deep” tunneling regime. As expected, when the temperature is lowered, the calculations become more demanding. The converged results are obtained only after including the fifth order term in the series expansion of the imaginary time propagator. The convergence can be followed from figure 6 where one dimensional cuts along the antisymmetric line for the different terms in the series are plotted. Contour plots are given in figure 5.

Interestingly, the structure becomes even more complicated. Along the antisymmetric line, there are three maxima. The saddle point reappears at the origin and there are four additional saddle points which are off of the antisymmetry line. This has implications for
FIG. 5: Contour plots of the matrix elements of the zeroth and fifth order truncated series representation of the thermal propagator at the temperature $T = 40^\circ$K for the symmetric Eckart barrier potential. In panel (a), the contour values are $10^{-n}$ with $n = 1, \ldots, 7$. The highest contour ($n=1$) is the black dashed line, and the lowest contour ($n=7$) is the dark blue line. In panel (b), the contour values are $10^{-1}$ (dashed red line), $10^{-2}$, $10^{-3}$, $10^{-4}$, $10^{-5}$, $10^{-6}$ (solid yellow line), $3.0 \times 10^{-7}$, $10^{-7}$, $10^{-8}$, $-10^{-8}$ (solid green line), $-5.0 \times 10^{-8}$ (solid dark blue line).

The quantum instanton method [30], where the two dividing surfaces are taken along the two saddle points, as found at the higher temperature. Presumably, one could still take the two dividing surfaces to be at the point on the antisymmetric line obtained from the intersection of the antisymmetric line and the line that connects each pair of saddle points. However, this needs to be studied in more detail.

4. **Asymmetric Potential, $T = 200^\circ$K**

The results of the TEGA calculation for the asymmetric potential are shown in figure\footnote{7}. Here too, it was necessary to include all terms up to fifth order for convergence. Due to the asymmetry of the barrier, a plot of the matrix elements $\langle -x | \hat{K}^{(N)}(\beta) | x \rangle$ do not show any structure. Besides, it is not helpful for following the convergence of the results, either. For
FIG. 6: One dimensional cuts along the anti-diagonal of the matrix elements of the thermal propagator at temperature $T = 40^\circ$K for the symmetric Eckart barrier potential.

these reasons, they are not plotted. In this case, the reduced temperature $\hbar \beta \omega^\dagger = 12.5$ is below the crossover temperature, however not very much lower so that again one has only
FIG. 7: Contour plots of the matrix elements of the zeroth and fifth order truncated series representation of the thermal propagator at temperature $T = 200^\circ K$ for the asymmetric Eckart barrier potential. In panel (a), the contour values are $10^{-n}$ with $n = 0, \ldots, 6$. The highest contour ($n = 0$) appears only on the upper right corner of the graph, and the lowest contour ($n = 6$) is the green line. In panel (b), the contour values are $1, 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 3.0 \times 10^{-5}, 2.5 \times 10^{-5}$ (yellow line), $2.3 \times 10^{-5}$ (solid light blue line), $2.1 \times 10^{-5}, 10^{-5}$ (solid dark blue line), $10^{-6}$.

two saddle points. Contour plots of matrix elements for the zeroth order approximation and the converged results are given in figure [7]

5. A Comparison Of The Results With The Results Of Miller et. al.

The matrix elements of the Boltzmann operator for the symmetric and asymmetric Eckart barrier had been calculated previously by Miller et. al. However, in that paper, authors did not provided contour values in the plots. For this reason, their calculations are duplicated. First, the Hamiltonian matrix is diagonalized in a sinc DVR basis [33]. Then, the configuration matrix elements of the Boltzmann operator are calculated by using equation [29] In the diagonalization calculation, grid spacing is taken to be 0.05a.u. where the grid ranges from $-20$ a.u. to 20 a.u.
FIG. 8: A comparison of the results of quantum mechanical and the converged TEGA calculations of the matrix elements $\langle -x|\hat{K}(\beta)|x \rangle$ for the symmetric Eckart barrier potential at temperature $T = 2000^\circ K$.

For the results of the calculations at temperatures $T = 2000^\circ K$ and $T = 200^\circ K$, when the contour plots of the results of the quantum mechanical calculations were prepared (with the same contour values that are used in the contour plots of TEGA calculations), there was no visual difference between them and the contour plots of the TEGA calculations so that they are not given. The results of the quantum mechanical and the TEGA calculations of the matrix elements $\langle -x|\hat{K}(\beta)|x \rangle$ are compared in figures 8 and 9 for the temperatures $T = 2000^\circ K$ and $T = 200^\circ K$, respectively. From figure 8, it can be seen that the agreement between the quantum mechanical results and the TEGA results is perfect at temperature $T = 2000^\circ K$. At temperature $T = 200^\circ K$, agreement is still quite good, but the results differ a little bit in the tunneling region.

On the other hand, when the results of two different calculations are compared for $T = 40^\circ K$, they differ both quantitively and qualitatively. The contour plot of the results of quantum mechanical calculation is given in figure 10. In the contour plot, there are still two saddle points as in the $T = 200^\circ K$ case. However, the TEGA calculation predict more than two saddle points at that temperature. The difference of the results can also be seen
FIG. 9: A comparison of the results of quantum mechanical and the converged TEGA calculations of the matrix elements $\langle -x|\hat{K}(\beta)|x \rangle$ for the symmetric Eckart barrier potential at temperature $T = 200^\circ$K.

From figure 11 where the results of the two calculations are given for the matrix elements $\langle -x|\hat{K}(\beta)|x \rangle$. The difference in the results can be attributed to the fact that the way that the quantum mechanical calculation is performed is not a proper way of calculating the matrix elements of the imaginary time propagator especially at such low temperatures. Because, in this calculations one is imposing artificial infinite potential walls at the boundaries which does not make sense if the potential surface of the system does not support bound states. Since the Eckart potential has a continuous spectrum and do not have any bound states, introduction of these artificial infinite walls is a source of error, because it discretizes a continuous system. The errors might be expected to be small at high temperatures, which can also be seen from the comparisons of the results at temperatures $T = 2000^\circ$K and $T = 200^\circ$K. However, the errors can be significant at low temperatures. Miller et. al. did not make these calculations at $T = 40^\circ$K anyway. Furthermore, as will be seen in section III B increasing number of saddle points is again observed in double well calculations both with proper quantum mechanical calculations and also with TEGA and PSTEGA calculations.
FIG. 10: Contour plot of the results of the quantum mechanical calculation of the matrix elements $\langle x_2 | \exp(-\beta \hat{H}) | x_1 \rangle$ for the symmetric Eckart barrier potential at temperature $T = 40^\circ$K. In the figure, contour values are $10^{-2}$ (dashed red line), $10^{-3}$, $10^{-4}$, $10^{-5}$, $10^{-6}$, $3 \times 10^{-7}$ (solid light blue line), $2 \times 10^{-7}$, $10^{-7}$, $5 \times 10^{-8}$ (solid green line).

Finally, a quantum mechanical calculation of the matrix elements of the Boltzmann operator for the asymmetric Eckart barrier potential at temperature $T = 200^\circ$K results in very good agreement with the TEGA calculations. The contour plot of the results of quantum mechanical calculation is given in figure 12.

B. Double Well Potential

Calculations are done with a one dimensional double well potential surface which has the form

$$V(x) = V_0(ax^4 + bx^2 + c),$$

where $V_0 = 0.004$ a.u., $a = 1.0$ (a.u.)$^{-4}$, $b = -4.0$ (a.u.)$^{-2}$, $c = 4.0$. The mass of the particle is taken to be $m = 1061.0$ a.u. The calculations are done by using both the bare potential and
FIG. 11: A comparison of the results of quantum mechanical and the converged TEGA calculations of the matrix elements $\langle -x | \hat{K}(\beta) | x \rangle$ for the symmetric Eckart barrier potential at temperature $T = 40^\circ K$.

also the Gaussian averaging. Three different temperatures are used in the calculations which are: $T = 2000^\circ K$, $T = 400^\circ K$, and $T = 100^\circ K$. In order to calculate the matrix elements of the density matrix, the same numerical procedure that was used in the Eckart Barrier calculations is followed. Firstly, an equally spaced grid of 300 points in the range [-3:3] is taken. Then, the Coherent States, that are formed around these grid points are propagated up to half time using the adaptive step size Cash-Karp Runge-Kutta method [31]. The matrices of the zeroth order approximations to the propagator and the correction operator are stored in every time step. Then, the matrices of the higher order terms in the series expansion of the propagator is obtained by using the recursion formula (equation 6). Time integrations are performed with third order Simpson’s integration. Finally, by using the symmetric formula, equation (9), matrix elements corresponding to full time is calculated. Please note that, Gaussian averages of the potential and its derivatives can be calculated analytically for the potential surface studied here. Quantum mechanical calculations are done with the same parameters given in section IIIA 5 for the Eckart barrier calculations. The results that are obtained with the TEGA and the PSTEGA methods will be presented
FIG. 12: Contour plot of the results of quantum mechanical calculation of the matrix elements $\langle x_2 | \exp(-\beta \hat{H}) | x_1 \rangle$ for the asymmetric Eckart barrier potential at temperature $T = 200^\circ K$. The contour values are the same with the ones that are used in figure 7 in the following subsections. Before that, it should be noted that all of the results in this section are scaled with the partition function which is $Z = \text{Tr}[\exp(-\beta \hat{H})]$.

1. $T = 2000^\circ K$

In figure 13 a contour plot of the matrix elements of the Boltzmann operator at temperature $T = 2000^\circ K$ is shown. That figure is prepared by using the results of the zeroth order TEGA calculation with the averaged potential. The results of the other calculations, including the quantum mechanical calculation, give almost the identical results so that it was not necessary to prepare different graphs for different calculations. This can be realized easily from figure 14 in which the matrix elements $\langle -x | \exp(-\beta \hat{H}) | x \rangle$ are plotted for all of the five different calculations. As it can be seen from the figure, there is no way to differentiate between different graphs. Therefore, at high temperatures use of the bare potential in
FIG. 13: A contour plot of the matrix elements of the Boltzmann operator at temperature $T = 2000^\circ$K. All of the different calculations gives almost identical results so that the same graph is obtained from all of them. The contour values are: $5 \times 10^{-1}, 10^{-1}, 5 \times 10^{-2}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}$, and $10^{-6}$.

Propagation does not lead to a worse zeroth order approximation than the use of the Gaussian averaged potential. This can be attributed to the fact that such high temperatures involve very short time propagation so that the Gaussians which are very narrow initially do not get much broadened. Therefore, use of such narrow Gaussians for averaging is like using delta functions, which is the same thing with using bare potentials. Consequently, use of the bare potential for such short propagation times does not lead to a significant error in the zeroth order approximations.

2. $T = 400^\circ$K

At temperature $T = 400^\circ$K, tunneling becomes important so that the zeroth order approximations to the thermal propagator does not lead to accurate results. In fact, as it is
FIG. 14: One dimensional cuts along the anti-diagonal of the matrix elements of the Boltzmann operator is shown at temperature $T = 2000^\circ$K. In the figure there exists five different plots (results of both TEGA and PSTEGA calculations calculated with both the Gaussian averaged potential and the bare potential, and also the results of quantum mechanical calculation). However, there is no way to differentiate between them.

They do not even give the correct qualitative picture since they always lead to a single saddle point at (0,0). Nevertheless, use of the series representation of the propagator converges to the right answers. In order to make a comparison of the TEGA and the PSTEGA calculations, the results of the quantum mechanical calculation is shown in figure 15. Converged results of the TEGA and PSTEGA calculations are shown in figure 16. For the Gaussian averaged potential calculations, it was necessary to include terms up to third order. Convergence of the Gaussian averaged potential calculations are shown for the matrix elements $\langle -x|K^{(i)}(\beta)|x \rangle$ in figure 17. It can be seen from the figure that the zeroth order approximation leads to quite bad results both qualitatively and quantitatively. Inclusion of the first order correction gives accurate results in some parts of the configuration space, but not in the tunneling region. In order to get accurate results also in the tunneling region, it is necessary to include even the third order correction terms.

For the bare potential calculations, it was necessary to include even the forth order correction terms in order to converge the results. Besides, it was necessary to use smaller
FIG. 15: A contour plot of the matrix elements of the thermal propagator obtained with a quantum mechanical calculation at temperature $T = 400\,^\circ\text{K}$. The contour values are the same with the ones that are used in figure 16.

time steps in time integrations. Contour plots of the converged results of the TEGA and PSTEGA calculations are shown in figure 16. In figure 18 convergence of the results is shown for the matrix elements $\langle -x|K^{(i)}(\beta)|x \rangle$ for $i = 0, \ldots, 3$. Comparing the results in this figure with the results obtained with Gaussian averaged potential calculations, shown in figure 17, it can be seen that the use of the bare potential leads to much lower accuracy in the zeroth order approximations. Nevertheless, the calculations converge to quite accurate results. Besides, despite the fact that fluctuations in the results for the bare potential calculations are much bigger than the fluctuations in the results for the Gaussian averaged calculations, it can be said that the series representations show similar convergence properties for both of the calculations since one of them converges at the third order and the other at the fourth order.
$T = 400^\circ K$

FIG. 16: Contour plots of the matrix elements of the thermal propagator at temperature $T = 400^\circ K$ is shown in panels (a), (b), (c) and (d) for TEGA calculation with the Gaussian averaged potential, PSTEGA calculation with the Gaussian averaged potential, TEGA calculation with the bare potential and PSTEGA calculation with the bare potential, respectively. The results of the Gaussian averaged calculations refer to truncated series of order 3 while the results of the bare potential calculations refer to truncated series of order 4. Time step that is used in bare potential calculations was half of the time step that is used in Gaussian averaged calculations. The contour values are: $5 \times 10^{-1}$ (dashed green line), $10^{-1}$, $10^{-2}$, $10^{-3}$, $4 \times 10^{-4}$, $3.2 \times 10^{-4}$ (solid yellow line), $2.7 \times 10^{-4}$ (solid light blue line), $10^{-4}$, $10^{-5}$ and $10^{-6}$ (solid green line).
\[ T = 400^\circ \text{K} \]

**FIG. 17:** One dimensional cuts along the anti-diagonal of the matrix elements of the thermal propagator is shown at temperature \( T = 400^\circ \text{K} \) for TEGA and PSTEGA calculations with the Gaussian averaged potential. In the figure, panels (a), (b), (c) and (d) refer to the results of the truncated series of order \( N = 0, 1, 2 \) and 3, respectively. Results of quantum mechanical calculations are also shown in each panel.

3. \( T = 100^\circ \text{K} \)

At temperature \( T = 100^\circ \text{K} \), tunneling becomes even more important. Besides, the calculations get more demanding because of the increasing propagation time.
$T = 400^\circ$K

![Graphs showing results of TEGA and PSTEGA calculations at different orders N = 0, 1, 2, 3, and 4.](image)

**FIG. 18:** One dimensional cuts along the anti-diagonal of the matrix elements of the thermal propagator at temperature $T = 400^\circ$K. The results of TEGA and PSTEGA calculations are obtained by using the bare potential. The panels (a), (b), (c) and (d) refer to the results of the truncated series of order $N = 0, 1, 2,$ and 3, respectively. The results of quantum mechanical calculations are also shown in each panel.

A contour plot of the results of quantum mechanical calculation is shown in panel (a) of figure 19. Contour plots of the results of TEGA and PSTEGA calculations with the Gaussian averaged potentials is shown in panels (b) and (c) of the same figure. At this temperature,
FIG. 19: Contour plots of the matrix elements of the Boltzmann operator at temperature $T = 100^\circ$K. The results of quantum mechanical calculation, TEGA calculation with the Gaussian averaged potential, PSTEGA calculation with the Gaussian averaged potential, and TEGA calculation with the bare potential are shown in panels (a), (b), (c) and (d), respectively. Results of the Gaussian averaged calculations refer to truncated series of order 3 while the result of the bare potential calculation refers to truncated series of order 4. The contour values are: $5 \times 10^{-1}$ (dashed red line), $10^{-1}, 10^{-2}, 10^{-3}, 5 \times 10^{-4}$ (solid yellow line), $2 \times 10^{-4}$ (solid light blue line), $10^{-4}, 10^{-5}$ and $10^{-6}$.
FIG. 20: One dimensional cuts along the anti-diagonal of the matrix elements of the thermal propagator at temperature $T = 100^\circ K$. The panels (a), (b), (c) and (d) refer to truncated series of order $N = 1, 2, 3$ and 4, respectively. Results of quantum mechanical calculations are also shown in each panel.

The series for the PSTEGA calculation with the bare potential surface does not converge. On the other hand, the series for the TEGA calculation with the bare potential surface still converges. A contour plot of the results of the TEGA calculation with the bare potential is shown in panel (d) of figure 19. All of the graphs looks very similar. In order to converge the
series, it was necessary to include terms up to order 3 for the Gaussian averaged potential surface calculations and terms up to order 4 for the bare potential calculations.

Convergence of the results can again be followed from the antisymmetric line. In figure one dimensional cuts along the anti-diagonal of the matrix elements of the thermal propagator is shown for the truncated series of order \( N = 1, 2, 3, 4 \) in panels \((a), (b), (c)\) and \((d)\) respectively. The results of quantum mechanical calculation is also shown in each panel.

Another thing which needs to be noted about the contour plots is the presence of more than two saddle points. As in the Eckart Barrier calculations, it is again observed that the saddle points move away from the antisymmetric line. From figure it can be seen that there exists four saddle points.

4. A Discussion Of The Results

In Eckart Barrier calculations, it was observed that the results of the quantum mechanical calculations do not agree with the results of TEGA calculations at low temperatures. It was argued that the discrepancy between the TEGA and the quantum mechanical results should be related with the artificial discretization of a continuous system by imposition of wrong boundary conditions to quantum mechanical calculations. On the other hand, double well potential surface has a discrete spectrum and do not support any scattering states. Therefore, the bound state calculation is a proper way of performing a quantum mechanical calculation for calculating the matrix elements of the equilibrium density matrix. The agreement of the results of quantum mechanical calculation with the results of the TEGA and PSTEGA calculations are very good in this case at all temperatures. This also supports that the reason of the discrepancy in the Eckart barrier calculations is related with the imposition of wrong boundary conditions to quantum mechanical calculations.

Considering the zeroth order TEGA and PSTEGA approximations, their accuracy depends on the temperature. At high temperatures, where the system is almost classical, zeroth order approximations lead to accurate results. As the temperature is lowered, accuracy of the zeroth order approximations gets worse as expected since the quantum effects becomes important at low temperatures. As shown by Liu and Miller [32], TEGA always leads to a single saddle point at \((0,0)\). A similar analysis can also be made for PSTEGA and it can be shown that it is also the case for PSTEGA. Therefore, both TEGA and PSTEGA
do not even lead to correct structure at low temperatures where the tunneling effects are important. Nevertheless, if the series expansion converges, both of them converge to the correct answers even at low temperatures.

Use of the bare potential results in lower accuracy in the zeroth order approximation compare to use of the Gaussian averaged potential. Higher accuracy of the results of Gaussian averaged calculations can be attributed to the fact that Gaussian averaging of the potential surface results from variational principles. Nevertheless, use of the bare potential leads to faster integration of equations of motion. However, it also leads to slower convergence of the series expansion. Besides, the results fluctuate more during convergence if the bare potential is used. In this study, it was not possible to converge the results at 100 °K with the PSTEGA method if the calculations are done with the bare potential. On the other hand, if Gaussian averaged potential is used, the series expansion for the PSTEGA method still converges, and it gives accurate results at that temperature.

One thing needs to be noted about PSTEGA calculations. While integrating the equations of motion initial width of the Gaussian wave packet is arbitrary. However, this does not mean that one can take any value for the initial width and converge the calculations to the correct results. While doing PSTEGA computations, it was necessary to figure out which initial width gives the best answers. This is done by comparing the results of PSTEGA calculations with the results of TEGA calculations. It was seen that if the initial width of the Gaussian is taken to be \( \approx 1 \) (in mass weighted coordinates), then the results of TEGA and the PSTEGA methods are almost identical for the Gaussian averaged calculations. This is true for both the zeroth order approximations and also for the truncated series of any order. In other words, \( n^{\text{th}} \) order PSTEGA expansion and \( n^{\text{th}} \) order TEGA expansion gives identical results within numerical accuracy if the initial arbitrary width of the Gaussians in PSTEGA calculations is chosen good.

IV. DISCUSSIONS AND CONCLUSIONS

The TEGA and the PSTEGA series representations of the thermal propagator were tested for two different potential surfaces. The results show that the number of terms needed in the series increases as the temperature is lowered. However, even for a reduced temperature as low as \( \hbar \beta \omega^\dagger = 60 \) the expansion converges by the time one reaches the fifth order in the series.
In real time, this would make the computation prohibitive, since it would be impossible to converge such high order terms using Monte Carlo methods for a multidimensional system. In imaginary time, the integrand is much less oscillatory and so there is hope that even when dealing with many degrees of freedom, one could converge the higher order terms.

Even if it turns out that it is not practical to converge the higher order terms of the series when the system is “complex”, there is value in the present computation. It does show that the series converges rather rapidly and that the series at least in principle does lead to the correct result.

In this paper, numerical convergence properties of the TEGA and the PSTEGA series representations of the imaginary time propagator are compared. It is shown that if the initial arbitrary width of the Gaussians are chosen good; then, TEGA and PSTEGA methods gives identical results within numerical accuracy. Although, the PSTEGA method involves a phase space integration, it is shown in the appendix that the momentum coordinates can be integrated implicitly, so that the PSTEGA method can also be implemented in configuration space. Thus, in both the TEGA and the PSTEGA methods, number of equations of motion scales linearly with the dimension of the problem.

It is seen that the Gaussian averaging is important especially at low temperatures. The use of the bare potential leads to very low accuracy for the zeroth order term of the series representation such that it causes the series representation not to converge at low temperatures.

Another important thing which puts a challenge to semiclassical analysis is that it is observed that the number of the saddle points of the matrix elements \( \langle x' | \hat{K}(\beta) | x \rangle \) increases as the temperature is lowered. Semiclassically, it is obvious why one should expect two saddle points. As analyzed by Miller et. al. \cite{30}, the two saddle points correspond semiclassically to the two turning points of the classical periodic orbit on the upside down potential energy surface whose half period is \( \hbar \beta \). However, it is found that as the temperature is lowered, additional saddle points show up. These point out the need for perhaps a deeper semiclassical analysis at low temperature. They also create a challenge to the quantum instanton method which used the two saddle points to identify the relevant dividing surfaces for thermal rate computations. At the low temperatures, at which one finds more than two saddle points, it is not clear which saddle points should be used within the quantum instanton method context. This question may become even more acute when dealing with asymmetric systems.
An Efficient Way of Integrating Equations of Motion for PSTEGA Calculations

Equation (21) can be integrated implicitly to give

\[ p(\tau) = c(\tau)p(0), \]  

(32)

where \( c(\tau) \) is given by

\[ c(q, \tau) = \exp \left( - \int_0^\tau d\tau' \hbar^2 G(\tau')^{-1} \right), \]

(33)

with the initial condition \( c(q, 0) = I \), which can be integrated with the equation of motion

\[ \frac{\partial c(q, \tau)}{\partial \tau} = -\hbar^2 G(\tau)^{-1} c(q, \tau). \]

(34)

It is useful to define some auxiliary equations of motion that helps to integrate Gaussian integrals of \( p(\tau) \). With the following definitions:

\[ k(q, \tau) = \int_0^\tau d\tau' c(q, \tau')^T c(q, \tau') \]

(35)

\[ w(q, \tau) = \exp \left( - \int_0^\tau d\tau' \langle V(q(\tau')) \rangle + \frac{\hbar^2}{4} \text{Tr}[G(\tau')^{-1}] \right), \]

(36)

\[ s(q, \tau) = \frac{1}{\hbar} \int_0^\tau d\tau' c(q, \tau') G(\tau') \langle \nabla V(q(\tau')) \rangle \]

(37)

and integrating the following equations of motion,

\[ \frac{\partial k(q, \tau)}{\partial \tau} = c(q, \tau)^T c(q, \tau), \quad k(q_0, 0) = 0, \]

(38)

\[ \frac{\partial w(q, \tau)}{\partial \tau} = -w(q, \tau) \left( \langle V(q(\tau)) \rangle + \frac{\hbar^2}{4} \text{Tr}[G(\tau)^{-1}] \right), \quad w(q_0, 0) = I, \]

(39)

\[ \frac{\partial s(q, \tau)}{\partial \tau} = c(q, \tau)^T G(\tau) \langle \nabla V(q(\tau)) \rangle, \quad s(q_0, 0) = 0, \]

(40)

matrix elements of the zeroth order approximation to the propagator can be obtained as

\[ \langle x|\hat{K}_0(\tau)|x' \rangle = \int \frac{dp dq}{2\pi} \langle x|\hat{K}_0(\tau)|g(p, q, 0) \rangle \langle g(p, q, 0)|x' \rangle \]

(41)

\[ = \int \frac{dq}{2\pi} \frac{(2\pi)^{N/2}}{\sqrt{\det(k(q, \tau))}} w(q, \tau) \left( \frac{1}{\det(G(\tau)G(0))} \right)^{1/4} l(q, x, x', \tau), \]

(42)

where

\[ l(q, x, x', \tau) = \exp \left( -\frac{1}{2}(t(q, \tau)^T k(q, \tau)^{-1} t(q, \tau) + (x - q(\tau))^T G(\tau)^{-1} (x - q(\tau)) \right) \]

\[ + (x' - q_0) G(0)^{-1} (x' - q_0)), \]

(43)
where
\[ t(q, \tau) = \frac{1}{\hbar}s(q, \tau) + \frac{1}{\hbar}c(q, \tau)(x - q(\tau)) - \frac{1}{\hbar}(x' - q_0). \] (44)

If the calculations are done with the bare potential, the following term should be added to
the expression in parenthesis in equations (36) and (39),
\[ \frac{1}{4}\text{Tr}[\nabla\nabla^T V(q(\tau))G(\tau)]; \] (45)

and also the Gaussian averagings of the potential and its derivatives are not performed.

Although, the integration scheme described above increases the number of equations
of motion per particle. It reduces the phase space integration to a configuration space
integration so that the total number of equations of motion is greatly reduced.
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