Evaluation of Nonlinear Quantum Time Correlation Functions within the Centroid Dynamics Formulation[†]

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A method to evaluate nonlinear centroid correlation functions is presented that is amenable to simple numerical computation. It can be implemented with the centroid molecular dynamics method for approximate quantum dynamics with no additional assumptions. Two nonlinear correlation functions are evaluated for a model potential using this scheme and compared with results from exact quantum calculations.

I. Introduction

Nonlinear quantum time correlation functions often play an important role in the measurement and description of quantum systems. Examples include the correlation functions that are found in theories describing quantum reaction rates[1] and in the analysis of neutron scattering experiments. However, the computation of such functions are usually difficult to perform. This is because a calculation of quantum time correlation functions involves the simulation of the time-dependent dynamics of the quantum system. Also, since such correlation functions are in general nonlinear in both the momentum and position operator, ensemble averaging to obtain the correlations becomes nontrivial due to the presence of off-diagonal matrix elements of nonlinear operators.

The centroid approach to approximate quantum dynamics[2−6] has proven to be a useful approximation in the evaluation of the time-dependent dynamics of quantum systems. This method also allows for the computation of approximate time correlation functions. It has been shown previously[6] that the correlation functions generated using the centroid molecular dynamics (CMD) approximation are related to the Kubo transformed quantum time correlation functions, if one of the operators is a linear combination of the momentum and position operators. However, the general form of this relation for both operators being nonlinear in position and momentum is rather complicated.[9] In ref 9, some examples of general nonlinear correlation functions were computed using these relations. However, such calculations tend to be expensive and complex. Consequently, there is still a need for a reasonably simple and computationally inexpensive method to calculate nonlinear correlation functions within the centroid formulation.

Feynman, in his work on path integrals and quantum field theory,[10] introduced the method of generating functionals to evaluate expectation values and perturbation expansions in quantum field theory. In this work, the quantity whose expectation value is to be evaluated is introduced as a small perturbation into the action functional. When the path integral is differentiated with respect to the strength of the perturbation, and the derivative evaluated for zero perturbation strength, the desired expectation value of the operator is obtained. This method is quite general

and can be used to treat nonlinear operator correlations. The present work proposes a similar approach to the calculation of general nonlinear correlation functions within the CMD formulation such that general correlations which depend only on the position operator are written in terms of derivatives of the centroid momentum variable. These derivatives are evaluated by means of finite difference approximations obtained by running separate centroid trajectories corresponding to appropriate perturbed potentials. This procedure allows for the calculation of very general types of correlation functions dependent on the position operator. Furthermore, it provides possible avenues for improved approximation schemes which go beyond the traditional CMD approximation to quantum time evolution.

This paper is organized as follows: In section II, the theoretical formulation of the method is presented, along with a brief description of the centroid approach to quantum dynamics. The implementation of the method in the context of the CMD approximation is then discussed. In section III, the implementation of the method for a model anharmonic potential is discussed, and results for two nonlinear correlation functions are presented and compared to exact calculations. The Concluding Remarks section includes a discussion of the advantages and drawbacks of the method, as well as possible applications to future work.

II. Theory

The formulation of the method for a general quantum system is first discussed. A brief introduction to the centroid approach is presented, and the implementation of the method in this framework is described.

Consider a correlation function of the form

$$C_{AB}^K(t) = \langle A^K(0)B(t) \rangle \tag{1}$$

Here, both A and B are assumed to be operators which are nonlinear in the position variables, i.e., they both satisfy $A = A(x)$ and $B = B(x)$. A^K is the Kubo transform

$$A^K(0) = \frac{1}{\beta}\int_0^\beta d\xi \exp[-(\beta - \xi)H]A(0)\exp(-\xi H) \tag{2}$$

The correlation function can thus be written as

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$$C_{AB}^{K}(t) = \frac{1}{Z} \text{Tr}\left\{ \int_0^\beta d\xi \exp[-(\beta - \xi)H]A(0) \exp(-\xi H) \right.$$
$$\left. \exp\left(\frac{iHt}{\hbar}\right)B(0) \exp\left(-\frac{iHt}{\hbar}\right)\right\} \quad (3)$$

If a perturbed Hamiltonian is defined by

$$H_\mu = H + \mu A \quad (4)$$

then, the Boltzmann operator for H_μ can be expanded in a Kubo perturbation expansion as

$$e^{-\beta H_\mu} = e^{-\beta H} - \mu \int_0^\beta d\lambda\, e^{-(\beta - \lambda)H} A\, e^{-\lambda H} +$$
$$\mu^2 \int_0^\beta d\lambda \int_0^\lambda e^{-(\beta - \lambda)H} A\, e^{-(\lambda - \xi)H} A\, e^{-\xi H} \quad (5)$$

As $\mu \to 0$, only the first term of the perturbation expansion remains nonzero, and if the thermal operator is differentiated with respect to μ, the coefficient of μ is obtained. This can be used to write the first part of the correlation function A^K as

$$\int_0^\beta d\lambda \exp[-(\beta - \lambda)H]A \exp(-\lambda H) = -\frac{\partial}{\partial \mu}\exp(-\beta H_\mu) \quad (6)$$

The derivative on the right-hand side of eq 6 is to be evaluated at a value $\mu = 0$. Equation 5 can also be used to derive another useful identity in the limit $\mu \to 0$

$$\text{Tr}[\exp(-\beta H_\mu)] =$$
$$\text{Tr}[\exp(-\beta H)] - \mu\beta\, \text{Tr}[\exp(-\beta H)A] + \dots \quad (7)$$

This leads to a connection between the derivative of the partition function for H_μ with the thermal average of A in the limit $\mu \to 0$, which can be written as

$$\frac{\partial}{\partial \mu} \text{Tr}[\exp(-\beta H_\mu)] = -\beta\langle A\rangle \,\text{Tr}[\exp(-\beta H)] \quad (8)$$

Correspondingly, if the integral, $F(x)$, of the operator $B(x)$ is defined by

$$B(x) = \frac{d}{dx} F(x) \quad (9)$$

and a Hamiltonian H_ν is defined by

$$H_\nu = H + \nu F(x) \quad (10)$$

the second part of the correlation function (eq 1) $B(t)$ can also be rewritten. The time-dependent momentum corresponding to these Hamiltonians is

$$p_{\mu\nu}(t) = \text{Tr}\left[\rho_\mu \exp\left(\frac{iH_\nu t}{\hbar}\right)p \exp\left(-\frac{iH_\nu t}{\hbar}\right)\right] \quad (11)$$

where the equilibrium density operator corresponding to the perturbation μA is

$$\rho_\mu = \frac{\exp(-\beta H_\mu)}{\text{Tr}[\exp(-\beta H_\mu)]} \quad (12)$$

Also, the following identity can be used:

$$\frac{i}{\hbar}[p, F(x)] = \frac{\partial F}{\partial x} \quad (13)$$

With this identity, the following relation can be obtained:

$$\frac{\partial^2}{\partial \nu \partial t} \exp\left(\frac{iH_\nu t}{\hbar}\right)p \exp\left(-\frac{iH_\nu t}{\hbar}\right) = -\frac{\partial F}{\partial x}(t) \quad (14)$$

Thus, if $F(x)$ is chosen to be the integral of the operator $B(t)$, the derivatives can be evaluated at $\nu = 0$ to obtain

$$-\frac{\partial}{\partial \nu}\dot{p}_\nu(t) = B(x, t) \quad (15)$$

or

$$B(x, t) = -\frac{\partial^2}{\partial \nu \partial t}\exp\left(\frac{iH_\nu t}{\hbar}\right)p \exp\left(-\frac{iH_\nu t}{\hbar}\right) \quad (16)$$

where the operator $p_\nu(t)$ in eq 15 is a Heisenberg momentum operator corresponding to the Hamiltonian H_ν. As before, the derivative on the right-hand side is to be evaluated at $\nu = 0$. Finally, eq 5 can be used to derive

$$\frac{\partial \rho_\mu}{\partial \mu} = -\frac{1}{Z_\mu} \int_0^\beta d\lambda \exp[-(\beta - \lambda)H]A \exp(-\beta H) +$$
$$\beta\langle A(0)\rangle \rho_\mu \quad (17)$$

The derivative of the momentum $p_{\mu\nu}(t)$ as $\mu, \nu \to 0$ can then be written using eqs 12 and 15 as

$$\frac{\partial^2}{\partial \mu \partial \nu}\dot{p}_{\mu\nu}(t) = -\text{Tr}\left[\frac{\partial \rho_\mu}{\partial \mu} B(t)\right] \quad (18)$$

Equations 6, 8, and 16−18 can be combined to obtain

$$C_{AB}^{K}(t) = \langle A(0)\rangle\langle B(0)\rangle + \frac{1}{\beta}\frac{\partial^2}{\partial \mu \partial \nu}3p_{\mu\nu}(t) \quad (19)$$

This equation is valid when $\mu = \nu = 0$. The identity $\langle B(t)\rangle = \langle B(0)\rangle$ has been used to derive eq 19. The first term on the right-hand side of eq 17 gives the Kubo transformed correlation function $C_{AB}^{K}(t)$ on multiplication with the operator $B(t)$ and performing the trace operation. The regular quantum time correlation can be recovered from the Kubo transformed correlation function using the well-known relation between their Fourier transforms

$$C_{AB}(\omega) = \frac{\hbar\beta\omega}{2}\left[1 + \coth\left(\frac{\hbar\beta\omega}{2}\right)\right]C_{AB}^{K}(\omega) \quad (20)$$

The average, $p_{\mu\nu}(t)$ (eq 12), is a nonequilibrium expectation value of the time-developed momentum operator evaluated for an initial Hamiltonian H_μ and a time development with a Hamiltonian H_ν. The derivatives with respect to μ and ν are evaluated at $\mu = 0$ and $\nu = 0$.

The equations derived above can be adapted to the computation of nonlinear quantum time correlation functions which depend on the momentum operator alone. This is because the momentum and position operators are dual to each other. More explicitly, the position operator acts as a derivative on a function of momentum, when its commutator with the function is evaluated, i.e.

$$[\hat{x}, G(\hat{p})] = i\hbar\frac{\partial G}{\partial p} \quad (21)$$

Thus, if the expectation value $x_{\mu\nu}(t)$ is defined in analogy to eq 12 and the Hamiltonian is perturbed by a momentum-dependent function $G(p)$, equations for quantum nonlinear time correlation functions which are functions of momentum can be derived.

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However, if the perturbation is of greater than quadratic order in the momentum, complications arise in the definition of the Feynman path integral. This method is of limited applicability in calculating quantum nonlinear momentum time correlation functions.

Equation 19 is the central result of this work. It is to be solved numerically to obtain quantum time correlation functions. The solution involves numerical evaluation of derivatives of the momentum expectation value in eq 19. The time-dependent momentum expectation can be well-approximated by the CMD approach to quantum dynamics.[2-6] This approach approximates the time evolution of the momentum operator through a classical molecular dynamics propagation of corresponding centroid momentum variables. A brief description is given below.

The CMD formulation of quantum dynamics[5,6] is a simple and powerful scheme to estimate quantum dynamical properties. In this scheme, the quantum density operator is rewritten using

$$\exp(-\beta H) = \int dx_c\, dp_c \int d\eta\, d\xi \, \exp[i\eta(x - x_c) + $$
$$i\xi(p - p_c) - \beta H] \quad (22)$$

The quantities x_c and p_c are centroid variables. This form can be used to rewrite the density operator as

$$\hat{\rho} = \int \frac{\delta_c(x_c, p_c)}{Z} \rho_c(x_c, p_c)\, dx_c\, dp_c \quad (23)$$

where Z is the partition function, δ_c is the centroid quasidensity operator,[5] and ρ_c is the quasiclassical centroid distribution function. In this formulation, quantum time propagation corresponds to a time propagation of the quasi density operator. Thus, quantum Kubo correlation functions are rewritten as

$$C_{AB}^K(t) = \int dx_c\, dp_c \rho_c(x_c, p_c)\, \mathrm{Tr}[\delta_c(x_c, p_c; t)A(-t)B(0)] \quad (24)$$

The CMD approximation consists of the following:

$$\delta_c(x_c, p_c; t) \approx \delta_c[x_c(t), p_c(t)] \quad (25)$$

The centroid position and momenta are propagated using Newton's laws with an effective centroid potential given by

$$\frac{dp_c}{dt} = -k_B T \frac{\partial}{\partial x_c}[-\ln \rho_c(x_c)] \quad (26)$$

where $\rho_c(x_c)$ is the position-dependent part of the centroid phase space distribution function, $\rho_c(x_c, p_c) = e^{-\beta p_c^2/2m} \rho_c(x_c)$.

The centroid approach is implemented for our problem using the equations described above. The expectation value of the momentum is evaluated by making the centroid transformation and the consequent approximation. The initial centroid force and distribution is generated using the adiabatic CMD (ACMD) scheme.[4,7,8] In this scheme, the zeroth-order normal mode is the centroid position variable, and thus, the CMD propagation is easily performed. Trajectory calculations for positive and negative values of perturbation strengths, μ and ν, are performed and the expectation value of the centroid momentum evaluated. Finally, this is used to calculate the correlation function from eq 19. To do this, finite difference approximations are used to calculate derivatives as illustrated below, such that

$$\frac{\partial p_\nu}{\partial \nu} \approx \frac{p_\nu - p_{-\nu}}{2\nu} \quad (27)$$

Here, p_ν is the value evaluated at a finite value of ν.

The method to calculate correlation functions can be implemented within the centroid formulation as follows. The equilibrium centroid distribution is generated in separate calculations for the perturbed Hamiltonians H_μ and $H_{-\mu}$. The centroid momentum is then propagated as a function of time with the Hamiltonian H_ν and $H_{-\nu}$ for the initial distribution from each of these perturbed Hamiltonians, H_μ and $H_{-\mu}$. The derivatives of the momentum are then obtained by taking finite differences with the variables, μ and ν, as well as for successive time steps to obtain the required correlation function. This is the most direct implementation of the approach proposed here.

The time-dependent momentum is well-approximated within the centroid molecular dynamics approximation since it is a linear operator. For adiabatic time propagation of the momentum operator, this approximation is a very good one. However, in eq 12, the expectation value of the momentum is due to a nonequilibrium time evolution. The centroid approximation is less accurate for such an evolution; hence, the momentum expectation value at each value of μ, ν is approximated by performing an equilibrium centroid time evolution with the two perturbing potentials summed together. Mathematically, this is equivalent to

$$p_{\mu\nu}(t) \approx \mathrm{Tr}\{\delta_{\mu\nu}^c[x_c(t), p_c(t)]\hat{p}\} \quad (28)$$

The approximate quasidensity operator is a CMD quasidensity operator derived from the Hamiltonian

$$H_{\mu\nu} = H + \mu A + \nu F \quad (29)$$

To evaluate the derivatives for each value of μ, the centroid momenta for corresponding positive and negative values of ν are subtracted and a finite difference obtained. This finite difference for successive time steps is also further subtracted to give the time derivative. Following this, the final finite difference between positive and negative ν is obtained. Thus, for calculation of a nonlinear time correlation function using the present approach, four separate centroid calculations are necessary.

Finally, the data obtained to evaluate the quantum Kubo transformed correlation function was Fourier transformed and multiplied by the prefactor in eq 20 to obtain the Fourier transformed quantum time correlation function. This Fourier transformed function was then inverted to obtain the actual quantum time correlation function. The Fourier transformations and convolutions were implemented within MATLAB.

III. Results and Discussion

To test the present method, two nonlinear correlation functions were calculated for the one-dimensional anharmonic model potential given by

$$V(x) = 0.5x^2 + 0.1x^3 + 0.01x^4 \quad (30)$$

The calculations performed utilize reduced units of $\hbar = 1$ and $m = 1$. The correlation functions calculated were the square correlation $\langle x^2(0)x^2(t)\rangle$ and the cubic correlation $\langle x^3(0)x^3(t)\rangle$, respectively. They were evaluated at a temperature given by $\beta = 10$ in reduced units. To evaluate the centroid dynamics, the ACMD technique was employed, with $P = 48$ beads chosen, for a simulation of 80 quasiparticles in a box of size 80 units. The ACMD propagation was performed by sampling the noncentroid normal modes using the VV-1 Nose−Hoover thermostat proposed by Jang and Voth.[11] To ensure equilibration, a Nose−Hoover chain of length 8 was used for the calculation
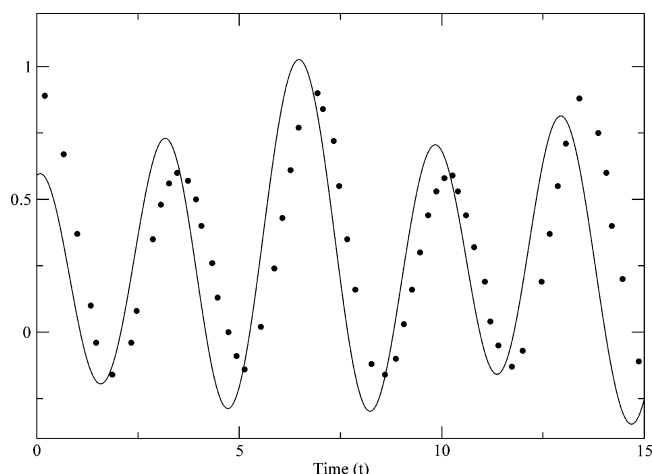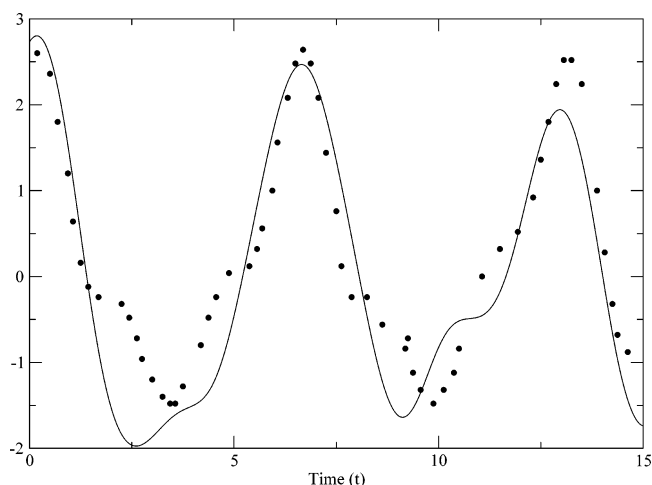
Figure 1. The square correlation function $\langle x^2(0)x^2(t)\rangle$ evaluated at $\beta = 10$ for the potential given by eq 30. The solid line is from the method described here, while the points are exact results.[3]

Figure 2. The cubic correlation function $\langle x^3(0)x^3(t)\rangle$ evaluated at $\beta = 10$ for the potential given by eq 30. The solid line is from the method described here, while the points are exact results.[3]

of the initial conditions for the correlation functions. The equilibration was performed for about 200 000 time steps in intervals of δt equal to 0.01 units for each of the separate trajectories.

For the square correlation, the choice of the perturbation is given by $\hat{A} = x^2$ and $\hat{F} = x^3$. Similarly, the cubic correlation function corresponds to $\hat{A} = x^3$ and $\hat{F} = x^4$. Perturbation strengths of $(|\mu|, |\nu|) = (0.02, 0.04)$ and $(|\mu|, |\nu|) = (0.04, 0.002)$ were used for the square correlation functions and the cubic correlation functions, respectively. The calculations were performed by taking the finite difference derivative of the momentum with respect to the perturbation corresponding to ν for each of the two values of μ. The finite differences so obtained for successive time steps were further subtracted to obtain the time derivative. Finally, the derivative with respect to μ was obtained by performing a finite difference of the result for the two values of μ from each other. The constant term in eq 19 was separately evaluated and added to the result to obtain the required correlation function. For the square correlation, the constant term was obtained from the squared value of the position correlation $\langle x(0)x(t)\rangle$ at $t = 0$. The corresponding term for the cubic correlation is small and was approximated by using the centroid position at $t = 0$. The results are plotted in Figures 1 and 2.

In Figure 1, the correlation function $\langle x^2(0)x^2(t)\rangle$ is plotted and compared with results obtained from an exact quantum time evolution.[3] The result obtained from this method also agrees reasonably well with the corresponding results obtained through a cumulant technique.[3] It shows good agreement with the exact quantum correlation function, except that the short-time behavior is underestimated by the method. Since quantum nonequilibrium evolution of the correlation is approximated by equilibrium CMD trajectories, transient effects at short times are not completely taken into account. This leads to underestimation of the short-time behavior. Thus, the present CMD method appears to approximate the quantum correlation reasonably well.

In Figure 2, the corresponding $\langle x^3(0)x^3(t)\rangle$ correlation function is plotted. It is clear from the results that it largely agrees well with the exact results.[3] However, the CMD calculated function is somewhat smoother than the quantum correlation function, which is most likely a consequence of the CMD approximation itself. These results demonstrate that the method proposed in this work is a viable alternative technique for the calculation of nonlinear correlation functions, at least when they are nonlinear functions of position only.

IV. Concluding Remarks

The method described in the present paper provides approximate CMD nonlinear correlation functions which show reasonably good agreement with the exact quantum results. This method is quite general and, in principle, does not rely on any further approximations beyond the CMD approximation. It is also easily parallelizable, and therefore, its numerical implementation is expected to be inexpensive. Furthermore, while the method has been implemented in the context of centroid dynamics, due to its simplicity it can be modified and applied within the framework of other approximate quantum dynamical methods to calculate correlation functions.[12] One such likely application is in the context of semiclassical initial value representations[13] to study quantum dynamics. The addition of perturbations is equivalent to "biasing" the system and observing its behavior as it returns to equilibrium after this biasing. Ideas similar to that described here have been used to calculate electron-transfer rates[14] by perturbing the ground state of donor acceptor systems. It is possible that the method described above can also be fruitfully modified to study such problems.

While the present method is attractive due to its simplicity and ease of implementation, it has certain drawbacks. The first one is in the context of its application within the centroid framework. The CMD approach to quantum dynamics may be a less accurate representation of the exact quantum dynamics for a nonequilibrium system. As a result, further modifications are necessary to get around this problem. In this work, this has been done by approximating the dynamics through equilibrium CMD trajectories, which closely approximate the nonequilibrium time evolution. A more serious and potential drawback of this technique is its numerical stability with respect to errors. As described before, this technique relies on finite difference calculations of the results of separately calculated trajectories. Furthermore, quantities corresponding to each trajectory are expected to have values which are roughly of the same order of magnitude. As a result, finite difference approximations between such quantities can be expected to have an increased sensitivity to fluctuations and statistical error in the values for individual trajectories. This can therefore be a source of inaccuracies and error in the final correlation function, so improvements in the accuracy of the method might be obtained through the use of improved nonequilibrium centroid propagation schemes.[15] This is an area for future research.

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