A new perspective on quantum time correlation functions

Jianshu Cao and Gregory A. Voth
Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

(Received 20 August 1993; accepted 14 October 1993)

A theoretical analysis suggests that the path centroid variable in Feynman path integration occupies a central role in the behavior of the real time position autocorrelation function. Based on this analysis, an intriguing quasiclassical perspective on quantum correlation functions emerges.

One of the most challenging problems in condensed matter theory is the computation of quantum time correlation functions. The satisfactory solution of this problem will require a theoretical formalism which, to within an acceptable degree of accuracy, can be implemented efficiently on a computer for general many-body systems. The present Communication is devoted to one such formalism which is based on the properties of the path centroid variable in Feynman path integration[1] which is defined within the context of the imaginary time path integral as

$$\tilde{q}_0=\frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\tau\, q(\tau)\,. \tag{1}$$

In his derivation of an approximate quasiclassical expression for the partition function,[1] Feynman recognized that the path centroid was a particularly useful classical-like variable about which to define a quantum density, often called the "centroid density," defined as

$$\rho_c(q_c)=\int\cdots\int \mathscr{D}q(\tau)\delta(q_c-\tilde{q}_0)\exp\{-S[q(\tau)]/\hbar\}\,, \tag{2}$$

where $S[q(\tau)]$ is the imaginary time action functional. [The quantum partition function can be obtained from Eq. (2) by integration over the position of the centroid, q_c.] Feynman determined a variational effective potential for the centroid variable using the approximation of free particle motion to describe the action for the imaginary time path fluctuations about the centroid. Since Feynman's seminal work, several authors[2] have improved upon his theory by employing quadratic variational action functionals which more accurately approximate the exact action for the imaginary time path fluctuations about the centroid variable. The latter approach, therefore, improves the accuracy of the resulting variational partition function. More recently, the path integral centroid perspective has been extended to calculate equilibrium averages $\langle A\rangle$, the central result being that the quantum operator $\hat{A}$ is replaced by a Gaussian averaged effective classical function.[3] The centroid density has also become the centerpiece of a path integral formulation of quantum mechanical transition state theory.[4] To our knowledge, however, there has been little progress in the formulation of quantum *dynamics* from the path centroid perspective.

We have recently developed a theory[5] for quantum imaginary time correlation functions in terms of the centroid variable and its corresponding density function [Eqs. (1) and (2)]. Quite accurate analytic expressions are obtained through the use of general quadratic action functionals, a properly formulated diagrammatic perturbation theory, and suitable renormalization techniques. In principle, once a good approximation to the exact imaginary time correlation function is obtained, the real time correlation function can then be determined by the inverse Wick rotation $\tau\rightarrow it$ (i.e., by analytic continuation). In the course of this research, however, an even more promising perspective has begun to emerge on the role of the centroid variable in the theory of quantum time correlation functions. This perspective, which is the subject of the present Communication, offers a computationally powerful algorithm to calculate quantum time correlation functions in many-body systems.

To begin the analysis, it proves particularly useful to define the centroid-constrained imaginary time correlation function[5]

$$C_c(\tau,q_c)=\frac{\int\cdots\int \mathscr{D}q(\tau)\delta(q_c-\tilde{q}_0)(q(\tau)-\tilde{q}_0)(q(0)-\tilde{q}_0)\exp\{-S[q(\tau)/\hbar]\}}{\int\cdots\int \mathscr{D}q(\tau)\delta(q_c-\tilde{q}_0)\exp\{-S[q(\tau)]/\hbar\}}\,. \tag{3}$$

This correlation function, which describes the correlations of the imaginary time paths about the centroid variable, is related to the usual correlation function $C(\tau)\equiv\langle q(\tau)q(0)\rangle$ by the relationship

$$C(\tau)=\langle C_c(\tau,q_c)+q_c^2\rangle_{\rho_c}\,, \tag{4}$$

where the subscript "ρ_c" denotes averaging with the normalized centroid distribution $\rho_c(q_c)/\int dq_c\,\rho_c(q_c)$ [cf. Eq. (2)].

By definition, the centroid variable plays a central role in the behavior of the centroid-constrained correlation function in Eq. (3). A more subtle issue, however, is the role of the centroid variable in the *real time* quantum correlation function. In a formal sense, this information can be extracted from the exact centroid-constrained correlation function $C_c(\tau,q_c)$ through the analytic continuation $\tau \to it$. In a practical sense, however, such a procedure, whether analytic or numerical, is not tractable unless there is some prior simplification of the problem. Fortunately, such a simplification can be achieved through the variational determination of an effective quadratic action functional, given for a single degree-of-freedom by[2,5]

$$S_{\mathrm{eff}}[q(\tau)] = \int_0^{\hbar\beta} d\tau \left\{ \frac{m}{2} \dot{q}(\tau)^2 + V_{\mathrm{eff}}(q_c) + \frac{1}{2} m\bar{\omega}_c^2 [q(\tau) - q_c]^2 \right\}, \tag{5}$$

where $V_{\mathrm{eff}}(\tilde{q}_0)$ is the variational effective centroid potential and $\bar{\omega}_c$ is the variationally determined effective harmonic frequency, both quantities being evaluated at a given centroid position. As in other work, the latter parameter is determined with the help of the properly formulated[1,2] Gibbs–Bogoliubov–Feynman (GBF) variational principle[6] for the centroid density in Eq. (2). The optimized frequency is given by the solution of the transcendental equation

$$m\bar{\omega}_c^2 = \frac{1}{\sqrt{2\pi\bar{\alpha}_c}} \int dq\, V''(q_c+q) \exp(-q^2/2\bar{\alpha}_c), \tag{6a}$$

where the effective thermal width factor in the optimized reference system for a particular position of the path centroid is given by

$$\bar{\alpha}_c = \frac{1}{m\beta\bar{\omega}_c^2} \left[\frac{\hbar\beta\bar{\omega}_c/2}{\tanh(\hbar\beta\bar{\omega}_c/2)} - 1 \right]. \tag{6b}$$

With the above quadratic reference system in hand, the imaginary time correlation function in Eq. (4) can be determined analytically for the reference system, giving[5]

$$C(\tau) = \frac{1}{Z} \int dq_c\, \rho_c(q_c) \frac{\hbar}{2m\bar{\omega}_c} \frac{\cosh[\bar{\omega}_c(\tau - \hbar\beta/2)]}{\sinh(\hbar\beta\bar{\omega}_c/2)} - \langle (m\bar{\omega}_c^2\beta)^{-1} \rangle_{\rho_c} + \langle q_c^2 \rangle_{\rho_c}, \tag{7}$$

where $Z = \int \rho_c(q_c)\, dq_c$ is the partition function. The combined and second and third term in Eq. (7) can be shown[5] to be a representation in the effective quadratic reference system of the simple constant $\langle q \rangle^2$, where $\langle q \rangle$ is the thermal average of the variable q. From now on, those two terms will be replaced by $\langle q \rangle^2$.

Based on the expression in Eq. (7), it is now straightforward to analytically continue the above function to obtain the real time correlation function, the real part of which is given by

$$\bar{C}(t) = \frac{1}{Z} \int dq_c\, \rho_c(q_c) \frac{\hbar}{2m\bar{\omega}_c \tanh(\hbar\beta\bar{\omega}_c/2)} \times \cos(\bar{\omega}_c t) + \langle q \rangle^2. \tag{8}$$

At this level of the theory, the real time correlation function is seen to be the superposition of centroid correlation functions for effective harmonic oscillators defined at different centroid positions q_c. In turn, each centroid correlation function is weighted by the centroid density for that value of q_c. The above expression for the correlation function is therefore a quantum mechanical generalization of the classical "instantaneous normal mode" perspective for condensed matter systems.[7]

Up to this point, the arguments have remained within the limits of rigorous mathematical analysis. On the other hand, if the bounds of rigor are "loosened" a bit, one can arrive at an even more compelling result. In order to proceed in such a fashion, it proves beneficial to first introduce another real time centroid correlation function, given by

$$C^*(t) = \frac{1}{Z} \int dq_c\, \rho_c(q_c) \frac{1}{m\bar{\omega}_c^2\beta} \cos(\bar{\omega}_c t) + \langle q \rangle^2, \tag{9}$$

which is the exact analog of the classical correlation function for an effective harmonic oscillator with the centroid "frequency" $\bar{\omega}_c$. Due to the properties of the Dirac delta function, the above correlation function is related[5] to the one in Eq. (8) through their Fourier transforms, i.e.,

$$\tilde{C}^*(\omega) = \frac{\tanh(\hbar\beta\omega/2)}{(\hbar\beta\omega/2)} \tilde{\bar{C}}(\omega). \tag{10}$$

By noting that the first term on the right-hand side of Eq. (9) describes the correlation of fluctuations about the mean value $\langle q_c \rangle_{\rho_c} = \langle q \rangle$, Eq. (9) can then be rewritten as

$$C^*(t) = \frac{1}{Z} \int dq_c\, \rho_c(q_c) \langle q_c(t) q_c(0) \rangle_{\bar{\omega}_c}, \tag{11}$$

where $\langle q_c(t) q_c(0) \rangle_{\bar{\omega}_c}$ is a *quasiclassical* position correlation function calculated for dynamics on the locally quadratic potential energy surface defined for each initial centroid coordinate through the GBF variational procedure. The symbol $\langle \cdots \rangle_{\bar{\omega}_c}$ denotes initial condition averaging using the quadratic approximation to the centroid density.

At this point, however, one might ask whether Eq. (11) is, in fact, an approximation to some more accurate expression. Some insight into the answer is provided by an examination of the limiting behavior of Eq. (11) for (a) globally harmonic potentials and (b) exact classical dynamics. In the case of a global harmonic potential, the correlation function $\langle q_c(t) q_c(0) \rangle_{\bar{\omega}_c}$ in Eq. (11) is the same everywhere [i.e., independent of the q_c in Eq. (11)]. Since $Z^{-1} \int dq_c\, \rho_c(q_c)$ equals unity, Eq. (11) then reduces to the correlation function $\langle q_c(t) q_c(0) \rangle_{\rho_c}$. In the global harmonic limit, therefore, one can simply propagate the centroid variable *classically* using forces derived from the effective centroid potential, average the initial conditions using the centroid density, and calculate the classical-like centroid correlation function

$$C_c^*(t) = \langle q_c(t) q_c(0) \rangle_{\rho_c}. \tag{12}$$

The exact quantum harmonic correlation function is then determined from this centroid correlation function via Eq. (10). It should be noted that for general nonlinear potentials the analytically continued effective quadratic result in Eq. (9), which should be understood as a relatively short time approximation to the exact correlation function, further supports the notion of a quasiclassical time propagation of the centroid.

The second limiting behavior to consider is the case of exact classical dynamics. The approximate correlation function in Eq. (9) is given classically by

$$C^*_{\mathrm{cl}}(t)=\frac{1}{Z_{\mathrm{cl}}}\int dq_{\mathrm{cl}}\,\rho_{\mathrm{cl}}(q_{\mathrm{cl}})\langle q_{\mathrm{cl}}(t)q_{\mathrm{cl}}(0)\rangle_{\bar{\omega}_{\mathrm{cl}}}, \tag{13}$$

where the trajectories $q_{\mathrm{cl}}(t)$ are generated by an effective quadratic classical potential with frequency $\bar{\omega}_{\mathrm{cl}}$. The distribution based on this potential is used to average the initial conditions in the correlation function, while the second level of averaging is performed with the exact classical density $\rho_{\mathrm{cl}}(q_{\mathrm{cl}})$. The *exact* classical correlation function can be related to Eq. (13) by some mental mathematics. In particular, if the potential which generates the dynamics and averaging in the correlation function $\langle q_{\mathrm{cl}}(t)q_{\mathrm{cl}}(0)\rangle_{\bar{\omega}_{\mathrm{cl}}}$ is transformed into the *exact* potential, that correlation function becomes the exact classical correlation function. The "exterior" integration over classical distribution $\rho_{\mathrm{cl}}(q_{\mathrm{cl}})$ then becomes inconsequential and can be removed. The important point here is that the forces which generate the classical trajectories in $\langle q_{\mathrm{cl}}(t)q_{\mathrm{cl}}(0)\rangle$ are no longer the approximate linear ones as in Eq. (13), but are instead derived from the same nonlinear potential *which generates the exact equilibrium distribution*. The latter distribution is, of course, the classical limit of the centroid density. One might then argue that an analogous quantum mechanical limit of Eq. (11) is one in which the forces which generate the centroid trajectories in $q_c(t)$ are derived from the same effective potential which gives the *exact* centroid distribution. This notion is, of course, rigorously correct in the globally harmonic limit. It also seems logical that the forces which generate the centroid trajectory at some later time and position in space should be no different from the forces experienced by a centroid trajectory which is *initiated* at that same point in space.

Based on the above arguments and Eqs. (9)–(12), the following picture emerges for a centroid density-based calculation of the position time correlation function in quantum mechanics: The correlation function $C^*_c(t)$ in Eq. (12) should, in fact, be a centroid correlation function which is calculated using the exact centroid density to average the initial conditions. The centroid trajectories are to be calculated from effective classical equations of motion, given by

$$m\ddot{q}_c(t)=-\frac{dV_c(q_c)}{dq_c}, \tag{14}$$

where the effective centroid potential is given by

$$V_c(q_c)=-k_BT\ln[\rho_c(q_c)]\,. \tag{15}$$

The centroid force $F_c(q_c)$ defined in the right-hand side of Eq. (14) is a kind of quantum mechanical potential of mean force, given explicitly by

$$F_c(q_c)=-\frac{\int\cdots\int\mathscr{D}q(\tau)\delta(q_c-\tilde{q}_0)V'[q(0)]\exp\{-S[q(\tau)/\hbar]\}}{\int\cdots\int\mathscr{D}q(\tau)\delta(q_c-\tilde{q}_0)\exp\{-S[q(\tau)]/\hbar\}}\,. \tag{16}$$

To determine the functional form of the centroid momentum distribution used to average the centroid trajectory initial momenta, one needs only to examine the action functional for the imaginary time phase-space path integral,[8] given by

$$S_E[p(\tau),q(\tau)]/\hbar=\frac{1}{\hbar}\int_0^{\hbar\beta}d\tau\left\{\frac{p(\tau)^2}{2m}+V[q(\tau)]-ip(\tau)\dot{q}(\tau)\right\}=\beta\frac{\tilde{p}_0^2}{2m}+\beta\sum_{n\neq0}\left[\frac{\tilde{p}_n^2}{2m}+\frac{2\pi n}{\hbar\beta}\tilde{p}_n\tilde{q}_{-n}\right]+\frac{1}{\hbar}\int_0^{\hbar\beta}d\tau\,V[q(\tau)]\,, \tag{17}$$

where $\{\tilde{p}_n,\tilde{q}_n\}$ are the Fourier modes of the momentum and position paths, respectively. Remarkably, the momentum centroid $\tilde{p}_0$ is decoupled from position coordinates and generates precisely the classical momentum distribution. As the final step after the centroid correlation function $C^*_c(t)$ in Eq. (12) is calculated, the real part of the quantum position correlation function $\bar{C}(t)$ can be determined through the Fourier transform relationship in Eq. (10).

The above "centroid molecular dynamics" prescription for calculating the quantum position correlation function has both rigorous and *ad hoc* elements to it, though it is exact for globally harmonic systems and clearly has the correct classical limit. In order to subject centroid molecular dynamics (MD) to a numerical test, the above algorithm was applied to a quartic oscillator potential given by

$$V(q)=\tfrac{1}{2}q^2+g\tfrac{1}{24}q^4\,, \tag{18}$$

with the parameters $g=2.4$, $m=1.0$, $\hbar=1.0$, and $\beta=5.0$. The exact results were obtained by finding the eigenvalues and eigenvectors of the quartic Hamiltonian in a harmonic oscillator basis set. One hundred eigenstates were employed to yield the spectrum and time correlation function. The ground state energy was found to increase by 12% due to the quartic perturbation which is equivalent to a large anharmonic shift of a molecular vibrational spectrum. The centroid MD results were computed using the centroid forces from the variationally optimized quadratic reference system in Eq. (5). This reference system is extremely accurate for the potential in Eq. (18) and easy to implement numerically.

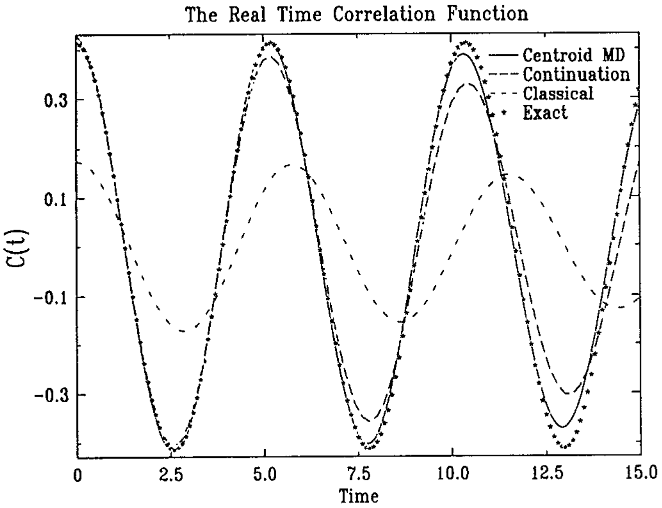

FIG. 1. A plot of the real time position autocorrelation function for the quartic oscillator described in Eq. (18). The stars show the numerically exact results, the solid line is for the centroid molecular dynamics method [Eqs. (12), (14)–(17)], the dashed line is for the analytically continued effective quadratic theory [Eq. (8)], and the dot–dashed line is for classical molecular dynamics.

In Fig. 1, the real part of the time correlation function is shown for the exact dynamics (stars), the centroid MD result (solid line), the analytically continued effective harmonic result in Eq. (8) (dashed line), and the classical limit (dot–dashed line). The centroid MD is clearly the superior result, capturing the shift of the quantum coherence and the (smaller) dephasing relative to the classical limit. The results shown in Fig. 1 are for a very low temperature system, the dynamics of which are dominated by only the ground and first excited vibrational states. The agreement between the centroid MD and the exact results will become even better at higher temperatures.

The present Communication has contained only a preliminary description of the centroid molecular dynamics method, the emphasis being on the position time correlation function. Future research will focus on an extension of the method to calculate more general correlation functions,[5,9] a more rigorous mathematical justification of the theory,[5] the development of practical algorithms for computing centroid dynamics, and applications of centroid MD to study the vibrational, activated, and diffusive dynamics of quantum particles in condensed phase systems.

This research was supported by the National Science Foundation and the Office of Naval Research. G.A.V. is a recipient of a National Science Foundation Presidential Young Investigator Award, a David and Lucile Packard Fellowship in Science and Engineering, an Alfred P. Sloan Foundation Research Fellowship, and a Dreyfus Foundation New Faculty Award.

[1] (a)R. P. Feynman, *Statistical Mechanics* (Addison-Wesley, Reading, MA, 1972), Chap. 3; (b) R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965), Chap. 10.

[2] R. P. Feynman and H. Kleinert, Phys. Rev. A **34**, 5080 (1986); R. Giachetti and V. Tognetti, Phys. Rev. Lett. **55**, 912 (1985); Phys. Rev. B **33**, 7647 (1986); W. Janke and H. Kleinert, Chem. Phys. Lett. **137**, 162 (1987); J. Cao and B. J. Berne, J. Chem. Phys. **92**, 162 (1987). See also Ref. 4.

[3] G. A. Voth, Phys. Rev. A **44**, 5302 (1991).

[4] G. A. Voth, D. Chandler, and W. H. Miller, J. Chem. Phys. **91**, 7749 (1989); G. A. Voth, Chem. Phys. Lett. **170**, 289 (1990); For a review of path integral quantum transition state theory, see G. A. Voth, J. Phys. Chem. **97**, 8365 (1993). See also the related work of M. J. Gillan, J. Phys. C **20**, 3621 (1987).

[5] J. Cao and G. A. Voth, J. Chem. Phys. (submitted).

[6] See, e.g., Ref. 1(a), Sec. 3.5.

[7] See, e.g., G. Seeley and T. Keyes, J. Chem. Phys. **91**, 5581 (1989); B.-C. Xu and R. M. Stratt, *ibid.* **92**, 1923 (1990), and references cited therein. Of particular relevance is the instantaneous normal mode perspective for classical correlation functions found in M. Buchner, B. M. Ladanyi, and R. M. Stratt, J. Chem. Phys. **97**, 8522 (1992).

[8] See, e.g., M. S. Swanson, *Path Integrals and Quantum Processes* (Academic, San Diego, 1992), Sec. 4.2.

[9] An *ad hoc* reactive flux procedure which is based on quasiclassical trajectories for the centroid variable has been proposed in G. K. Schenter, M. Messina, and B. C. Garrett, J. Chem. Phys. **99**, 1674 (1993). This method can be used to estimate dynamical corrections to the path integral quantum transition state theory rate constant (Ref. 4). While a derivation of this procedure from first principles does not yet exist, it is clearly in the same spirit as the present work.