Generalized Liouville time-dependent perturbation theory

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A generalized time-dependent perturbation theory is derived for superoperators. Instead of using the "standard" breakup of the Hamiltonian into a known zeroth order term and a correction, we use the approximate superpropagator to define the correction superoperator which is then used to obtain a series representation of the exact Liouville operator. The theory reduces to known limits and may be used for a perturbation expansion of classical Wigner and Husimi dynamics as well as for recent phase-space-based semiclassical approximations. The theory is demonstrated for a model quartic potential.

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Perturbation methods are a cornerstone in applied mathematics [1,2] and are indispensable tools in physics. The popular WKB method [2] might be viewed as a victory of perturbation treatment in stationary quantum mechanics whereas KAM theory [3] is a major trophy in revealing the stability of classical dynamics for nonintegrable systems. Perturbation theory is ubiquitous in the methodological development of all natural sciences. For example, spectroscopy, which is arguably the most convenient experimental technique for elucidating the underlying microscopic structure and dynamics of physical systems, relies especially on time-dependent perturbation theory [4]. Fermi's golden rule is a direct consequence of perturbation theory [5].

In quantum mechanics perturbation techniques are typically applied by assuming that the Hamiltonian describing the system may be divided into a zeroth order part $\hat{H}_0$ and a perturbation $\hat{H}_1$. The propagator of the zeroth order part is assumed to be known. One then expands the Schrödinger equation in a power series in the perturbation $\hat{H}_1$ to obtain the well known interaction picture of quantum mechanics [5].

This strategy may be insufficient. An important example is the widely used semiclassical initial value representation (SCIVR) approximation to the quantum propagator [6]. This class of approximations is nonperturbative as it includes all orders of $\hbar$. The SCIVR propagator is, however, not necessarily unitary so that the standard breakup of the Hamiltonian into two parts is not applicable. Instead, we have shown in recent years that one may use the SCIVR propagator to define a "correction operator" as the difference between the SCIVR dynamics and the exact dynamics [7]. Then one may expand the exact propagator in terms of a power series in the correction operator [8]. This time-dependent perturbation theory is a generalization of the "standard method" since it may be applied even when the underlying zeroth order Hamiltonian is not known explicitly. It is also useful in practice as numerical studies have shown that in many cases, the series generated in this manner converges rapidly [8].

In this paper we extend this perturbation theory to Liouville dynamics which deals directly with the evolution of physically measurable quantities and may have a correspondence to the classical counterpart [4,9–11]. In principle, any series expansion of the quantum propagator gives a series expansion for the time evolution under the superpropagator. However, not every approximate superpropagator is directly derived from underlying approximate propagators. An important example is the replacement of quantum Liouville dynamics with classical dynamics. There is no classical approximation of the propagator $\hat{K}(t)$. It is thus of interest to devise a perturbation theory directly within the Liouville superoperator formalism. The quasiclassical treatment of the superpropagator or more precisely its specific representation in phase space has been explored for several decades [9,11]. Since Liouvillian quantum dynamics involves two evolutions in reverse time direction which typically interfere, the classical limit may be subtle. Heller was among the first to point out this issue by noticing "the danger of the cross terms" [12]. Efforts to go beyond the zeroth order quasiclassical approximation abound [13], but they were not very successful. Recent studies have focused on the geometrical interpretation of the $\hbar$ asymptotics as obtained via semiclassical approximations [14].

A second class of examples for which the perturbation expansion of the Liouville operator is unknown is the forward-backward (FB) SCIVR propagation methodology [15,16]. The FBSCIVR is readily applied to systems with many degrees of freedom without losing important phase information [15,16] and at the same time is easier to compute than using separate SCIVR propagators for the forward and backward in time propagators. However, the methodology is *ad hoc*—the error involved is unknown.

A third class is based on Filinov filtering [17]. One way of overcoming the highly oscillatory integrand involved in the forward and backward time evolution is by applying the Filinov filtering technique which creates a smoother integrand [16]. Since the method mixes the forward and backward propagations it cannot be used in the context of generalized time-dependent perturbation theory for the separate propaga-

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tors. At the same time, Filinov filtering is problematic as one may be filtering out the signal with the noise [18]. A generalized Liouville time-dependent perturbation theory could put the Filinov filtering technique for correlation functions on a firmer basis.

We first review briefly the generalized perturbation theory for the quantum propagator. We assume the existence of a zeroth order approximate propagator $\hat{K}_0(t)$ which is exact at the initial time $t=0$ $[\hat{K}_0(0)=\hat{I}]$ whose time evolution equation is known. A correction operator which is assumed to be small in some sense is then defined as $\hat{C}(t)=(i\hbar\frac{\partial}{\partial t}-\hat{H})\hat{K}_0(t)$. Since the homogeneous part of this equation is the Schrödinger equation, one readily finds that the approximate propagator may be expressed in terms of the exact propagator through the integral equation:

$$\hat{K}_0(t)=\hat{K}(t)-\frac{i}{\hbar}\int_0^t dt_1\hat{K}(t-t_1)\hat{C}(t_1). \tag{1}$$

One then expands the exact propagator in a power series in the correction operator such that $\hat{K}(t)=\Sigma_{j=0}^{\infty}\hat{K}_j(t)$ and the zeroth order term is the known approximate propagator. The jth term is then obtained via the recursion relation

$$\hat{K}_{j+1}(t)=\frac{i}{\hbar}\int_0^t dt_1\hat{K}_j(t-t_1)\hat{C}(t_1). \tag{2}$$

This generalized perturbation theory has been used successfully in the context of SCIVR propagators [8,19], where the time dependence is generated from the classical equations of motion and the correction operator is not just a formal construct but is known.

The Liouville superoperator is defined by the relation

$$Ł\hat{O}=\frac{1}{\hbar}[\hat{O},\hat{H}] \tag{3}$$

where $\hat{O}$ is an arbitrary Hermitian operator in the Hilbert space. The superpropagator associated with the Liouville superoperator is

$$\hat{U}(t)=\exp(-iŁt) \tag{4}$$

so that $i\frac{\partial\hat{U}(t)}{\partial t}=Ł\hat{U}(t)$. The time evolution of any operator is then obtained as

$$\exp(-iŁt)\hat{O}=\hat{K}^{\dagger}(t)\hat{O}\hat{K}(t)=\hat{O}(t), \tag{5}$$

where $\hat{K}(t)=\exp(-i\hat{H}t/\hbar)$ is the quantum propagator.

We assume that there exists a known time-dependent approximate Liouville superoperator $Ł_0$ and its associated evolution superoperator $\hat{U}_0(t)$ such that

$$i\frac{\partial\hat{U}_0(t)}{\partial t}=Ł_0(t)\hat{U}_0(t) \tag{6}$$

and $\hat{U}_0(0)=\hat{I}$. The exact Liouville dynamics has already been defined by Eq. (4). We may then formally construct the "correction superoperator" $\hat{\Upsilon}(t)$ as

$$\hat{\Upsilon}(t)=i\frac{\partial\hat{U}_0(t)}{\partial t}-Ł\hat{U}_0(t)=[Ł_0(t)-Ł]\hat{U}_0(t). \tag{7}$$

As for the propagator, we can write down the formal solution of Eq. (7) as

$$\hat{U}_0(t)=\hat{U}(t)-i\int_0^t dt_1\hat{U}(t-t_1)\hat{\Upsilon}(t_1). \tag{8}$$

One then expands the exact superpropagator in a series in which the jth term is of the order $\hat{\Upsilon}^j$ to obtain the recursion relation

$$\hat{U}_{j+1}(t)=i\int_0^t dt_1\hat{U}_j(t-t_1)\hat{\Upsilon}(t_1). \tag{9}$$

This is the central formal result of this paper. We have derived a perturbation series solution for the exact superpropagator in terms of the known approximate one and its associated correction superoperator.

It is instructive to show that this generalized result reduces to the more "standard" perturbation theory when one divides the Hamiltonian into two parts $\hat{H}=\hat{H}_0+\hat{H}_1$. The zeroth order propagator is taken to be $\hat{K}_0(t)=\exp(-i\hat{H}_0t/\hbar)$ so that the zeroth order evolution superoperator is defined by $\hat{U}_0(t)\hat{O}=\hat{K}_0^{\dagger}(t)\hat{O}\hat{K}_0(t)$. The correction superoperator is then $\hat{\Upsilon}(t)\hat{O}=-\frac{1}{\hbar}[\hat{O}_0(t),\hat{H}_1]$ and with some straightforward algebra one finds that the generalized perturbation theory is identical to the standard time-dependent perturbation theory.

As another example for application of the methodology, we consider approximate evolution in a one-dimensional phase space (q,p) (generalization to N degrees of freedom is straightforward). The Wigner phase-space representation of an operator is well known to be $O_W(p,q;0)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}d\xi e^{ip\xi/\hbar}\langle q-\frac{\xi}{2}|\hat{O}|q+\frac{\xi}{2}\rangle$. Classical Wigner dynamics is defined such that the time evolved operator $O_W(p,q;t)$ is obtained by evolving q and p to time t using classical mechanics and the Wigner representation of the Hamiltonian. The classical Liouville operator $\mathcal{L}_{cl}^W$ is defined as $\mathcal{L}_{cl}^W F(q,p)=F(q,p)\Lambda H_W(q,p)\equiv\{F(q,p),H_W(q,p)\}$, and the Poisson-bracket operator

$$\Lambda=\frac{\overleftarrow{\partial}}{\partial q}\frac{\overrightarrow{\partial}}{\partial p}-\frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial q} \tag{10}$$

operates on both sides according to the direction of the arrows. The Wigner phase-space representation of the (exact) Liouville operator $\mathcal{L}_W$ is [9,11]

$$\mathcal{L}_W=H_W(q,p)\left[\frac{2}{\hbar}i\sin\left(\frac{\hbar}{2}\Lambda\right)\right]. \tag{11}$$

The classical Wigner approximation corresponds to choosing in $\mathcal{L}_W$ the zeroth order contribution with respect to $\hbar$ yielding $\hat{U}_{0,W}(t)=\exp[H_W(q,p)\Lambda t]$. The quantum correction operator is thus

$$\hat{\Upsilon}_W(t) = H_W(q,p) i\left[\Lambda - \frac{2}{\hbar}\sin\left(\frac{\hbar}{2}\Lambda\right)\right]\exp[H_W(q,p)\Lambda t]. \tag{12}$$

For classical Wigner dynamics, the generalized perturbation theory reduces to the time-dependent perturbation theory developed by Filinov *et al.* [20].

To gain further insight, we assume without loss of generality that $H_W(q,p)=p^2/(2m)+c_1q+c_2q^2+V_1(q)$ and this defines the nonlinear term $V_1(q)$. It is then a matter of some tedious algebraic manipulation to show that the explicit expression for the correction superoperator is

$$\hat{\Upsilon}_W(t) = -\frac{1}{\hbar}\left[V_1(\vec{z}) - V_1(\vec{z}^*) - i\hbar V_1'(q)\frac{\vec{\partial}}{\partial p}\right]U_{0,W}(t), \tag{13}$$

where we used the notation $\vec{z}=q+i\frac{\hbar}{2}\frac{\vec{\partial}}{\partial p}$, the star denotes complex conjugation, and the prime denotes the derivative with respect to the argument. Equivalently, one can show that $\hat{\Upsilon}_W(t)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}d\omega\tilde{V}_1(\omega)e^{iq\omega}[2\sinh(-\frac{\hbar\omega}{2}\frac{\vec{\partial}}{\partial p})+\hbar\omega\frac{\vec{\partial}}{\partial p}]U_{0,W}(t)$, where $\tilde{V}_1(\omega)$ is the Fourier transform of $V_1(q)$. For an initial condition $O_W(q,p)$ we have $U_{0,W}(t)O_W(q,p)=O_W(q_t,p_t)$ and

$$\hat{\Upsilon}_W(t)O_W(q,p) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}d\omega\tilde{V}_1(\omega)e^{iq\omega}\left[\Delta O_W(t) + \hbar\omega\frac{\vec{\partial}}{\partial p}O_W(q_t,p_t)\right], \tag{14}$$

where $\Delta O_W(t)=O_W(q_t,p_t^-)-O_W(q_t,p_t^+)$ with $(q_t,p_t^\pm)$ being the classical trajectory starting from $(q,p\pm\hbar\omega/2)$.

Consider other representations in phase space, say, $O_S(q,p)$ which is related to $O_W(q,p)$ through a transformation $\mathcal{T}$, i.e., $O_S(q,p)=\mathcal{T}O_W(q,p)$. One then obtains the exact Liouville operator as the result of the similarity transformation defined by $\mathcal{T}$, namely, $\mathcal{L}_S=\mathcal{T}\mathcal{L}_W\mathcal{T}^{-1}$. Let us take the Husimi representation associated with the coherent state $|g(q,p)\rangle$ as an example where $\langle x|g(q,p)\rangle=(\frac{\Gamma}{\pi})^{1/4}e^{-\Gamma/2(x-q)^2+(i/\hbar)p(x-q)}$. In this case one has $\mathcal{T}=e^{1/(4\Gamma)(\partial^2/\partial q^2)+\hbar^2\Gamma/4(\partial^2/\partial p^2)}$, where the derivatives without direction denote the operation on the right side. To make the Husimi quasiclassical dynamics exact for linear systems (using the same notation for the generic Hamiltonian as in the Wigner dynamics), one must choose the width of the wave packet to be set to $\Gamma=\sqrt{2mc_2}/\hbar$. Then, the exact Liouville operator is

$$i\mathcal{L}_H = \frac{p}{m}\frac{\partial}{\partial q} - (c_1+2c_2q)\frac{\partial}{\partial p} + \frac{i}{\hbar}[V_{1H}(\hat{y}) - V_{1H}(\hat{y}^*)] \tag{15}$$

with $\hat{y}=q+\frac{1}{2\Gamma}\frac{\partial}{\partial q}+i\frac{\hbar}{2}\frac{\partial}{\partial p}$. The quasiclassical Liouville operator ($\hbar\to0$ limit) is readily seen to be

$$i\mathcal{L}_{0,H} = \frac{p}{m}\frac{\partial}{\partial q} - (c_1+2c_2q)\frac{\partial}{\partial p} - V_{1H}'(q)\frac{\partial}{\partial p}. \tag{16}$$

The correction superoperator is then

$$\hat{\Upsilon}_H(t) = -\frac{1}{\hbar}\left[V_{1H}(\hat{y}) - V_{1H}(\hat{y}^*) - i\hbar V_{1H}'(q)\frac{\partial}{\partial p}\right]U_{0,H}(t) \tag{17}$$

or using Fourier transforms one finds that $\hat{\Upsilon}_H(t)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}d\omega e^{iq\omega}[2\tilde{V}_1(\omega)\exp(\frac{i\omega}{2\Gamma}\frac{\partial}{\partial q})\sinh(-\frac{\hbar\omega}{2}\frac{\partial}{\partial p})+\hbar\omega\tilde{V}_{1H}(\omega)\frac{\partial}{\partial p}]U_{0,H}(t)$.

Finally, we consider a numerical example, namely, dynamics in a quartic symmetric double well potential $V(q)=-(m\omega^2/2)q^2(1-q^2/(2q_a^2))$. This model was also used in Ref. [8] (a) to test the operator form of the generalized time-dependent perturbation theory. The correction operator is then $\hat{\Upsilon}_W(t)=(i/2)\hbar^2(m\omega^2/2)(q/q_a^2)(\vec{\partial}^3/\partial p^3)U_{0,W}(t)$. In this special case, the correction superoperator has only one term of order $\hbar^2$ so that the generalized perturbation theory reduces to the perturbation series obtained through the traditional $\hbar^2$ expansion [14] (b). We compute the time evolution of the autocorrelation of the projection operator $\hat{P}\equiv|\Psi\rangle\langle\Psi|$ for a Gaussian wave function $\langle q|\Psi\rangle=(\frac{\gamma}{\pi})^{1/4}\exp[-\frac{\gamma}{2}(q-q_0)^2]$. The parameters are chosen as in

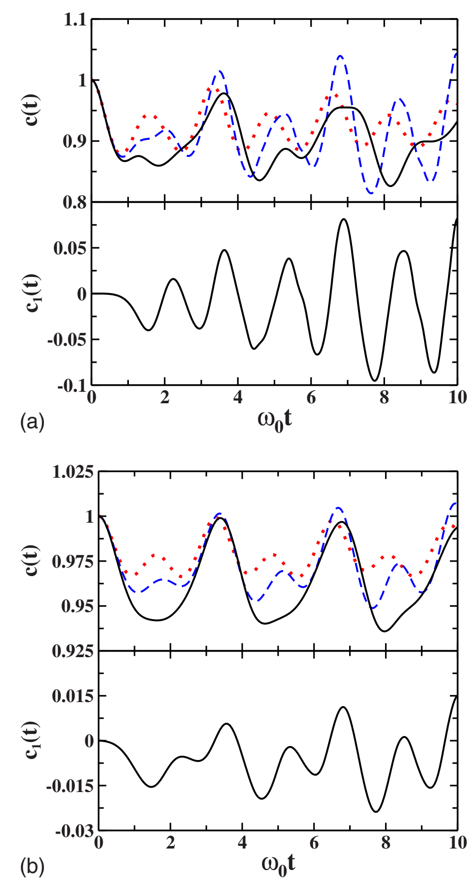

FIG. 1. (Color online) Autocorrelation function for a quartic double well potential. All quantities are plotted in dimensionless units. The top and bottom panels are for the respective masses 9 and 16. The dotted, dashed, and solid lines are the zeroth order classical, first-order corrected classical, and numerically exact quantum results, respectively. The bottom of each panel shows the first-order correction term.

Ref. [8]. (a): $\gamma=10$, $q_0=q_a=2$, and $\omega=\sqrt{2/m}$. The Wigner representation $P_W(q,p)$ of the operator $\hat{P}$ is $P_W(q,p) =(1/\pi\hbar)\exp[-\gamma(q-q_0)^2-(p^2/(\gamma\hbar^2))]$ and the autocorrelation function is $c(t)=2\pi\hbar\int dq dp P_W(q,p,0)P_W(q,p,t)$, where $P_W(q,p,t)$ is the Wigner representation of the (Heisenberg) projection operator at time t.

The results are shown in Fig. 1 for the masses $m=9$ and 16 in the top and bottom panels, respectively. The autocorrelation function $|c(t)|^2$ is plotted as a function of the reduced time $\omega_0 t$ where ω_0 is the frequency at the minima of the double well potential. The dotted lines are the classical result, the dashed lines are the first-order corrected classical Wigner results, and the solid line is the exact quantum result (obtained via numerical propagation using the split operator technique). The bottom of each panel shows the first-order correction term. These results are quite instructive. One notes that for early times the correction is small and it grows with time. As might be expected, the correction is smaller as the mass increases. Finally, in contrast to the operator perturbation theory as applied to this model, here the first-order correction provides a significant improvement only at rather short times. We have tried to extend these results to lower masses, however, the perturbation becomes very large very quickly (within 3 reduced time units for $m=1$) due to the large magnitude which develops for the third derivative. Thus, these results imply that classical Wigner dynamics should not be considered as a reliable approximation for highly quantum systems. From the point of view of the generalized perturbation theory these results demonstrate the viability of the formalism. When a system is classical-like, the computation of the first-order term leads to a small correction and thus provides an objective assessment of the validity of the classical Wigner dynamics.

In summary, we have derived a generalized time-dependent perturbation theory for the time evolution of operators. The theory reduces to known previous results based either on the interaction picture or on $\hbar$ expansions about the classical dynamics evolution. It enables one to construct a general class of zeroth order Liouville propagators, which are not necessarily derived from an underlying zeroth order Hamiltonian but through the perturbation expansion may still lead to the exact quantum time-dependent behavior. The present formulation turns the *ad hoc* forward-backward semiclassical approximation into a well defined zeroth order term in a perturbation series. It also provides a way of improving upon the classical dynamics approximation.

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