SC-IVR Code Package:
Theory and Reference Manual

Matthew S. Church
Ananth Group
Cornell University
msc336@cornell.edu
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This document serves as a reference manual for the SC-IVR code package provided on the Ananth Group website. The package contains a variety of methods that compute the real-time correlation function within the framework of the semiclassical initial value representation. This document provides some theoretical background and useful references; outlines the structure of the program; and describes how it may be used or altered.

Contents

1 Theoretical Overview

1.1 The Van Vleck-Gutzwiller Propagator

The semiclassical initial value representations (SC-IVR) can be rigorously derived from Feynman's real-time path integral in the limit that $\hbar$ tends to zero. One begins with Feynman's propagator,

$$\langle \mathbf{q}_t | e^{-\frac{i}{\hbar}\hat{H}t} | \mathbf{q}_0 \rangle \;=\; \int D[\mathbf{q}(t)]\; e^{\frac{i}{\hbar}S[\mathbf{q}(t)]} \tag{1}$$

where $S[\mathbf{q}(t)]$ is the classical action associated with path $\mathbf{q}(t)$, and $D[\mathbf{q}(t)]$ is the path differential, and applies the method of stationary phase to obtain an asymptotic approximation in the semiclassical limit ($\hbar \to 0$),

$$\langle \mathbf{q}_t | e^{-\frac{i}{\hbar}\hat{H}t} | \mathbf{q}_0 \rangle_{SC} \;=\; \sum_{\text{classical paths}} \sqrt{\frac{1}{(2\pi i\hbar)^N} \det\left|\frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0}\right|^{-1}}\; e^{\frac{i}{\hbar}S[\mathbf{q}(t)]}. \tag{2}$$

The approximation replaces the continuous sum over the phase of all paths connecting $\mathbf{q}_0$ and $\mathbf{q}_t$ in (1) by a discrete sum over the phase of all classical trajectories in (2). The prefactor of (2) captures quadratic fluctuations around the classical paths, and thus is a source of quantum information. Equation (2) is known as the Van Vleck-Gutzwiller propagator.

There are several practical challenges to consider when computing (2). First of all we are faced with a laborious root-search problem, meaning we need to find all trajectories that satisfy the double-ended boundary condition. Secondly there is the inverse of a determinant appearing in the prefactor, which can blow up to infinity if $\frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0}$ becomes a singular matrix.

1.2 Van Vleck SC-IVR

Some of the practical challenges of (2) can be removed by going into the initial value representation. First, use completeness to write down the time evolution operator as

$$e^{-\frac{i}{\hbar}\hat{H}t} \;=\; \int \mathrm{d}\mathbf{q}_t \int \mathrm{d}\mathbf{q}_0\, |\mathbf{q}_t\rangle\, \langle \mathbf{q}_t | e^{-\frac{i}{\hbar}\hat{H}t} | \mathbf{q}_0 \rangle\, \langle \mathbf{q}_0 |\,,$$

and then insert the Van Vleck-Gutzwiller propagator of (2),

$$e^{-\frac{i}{\hbar}\hat{H}t} \approx \frac{1}{(2\pi i\hbar)^{\frac{N}{2}}} \sum_{\text{classical paths}} \int \mathrm{d}\mathbf{q}_t \int \mathrm{d}\mathbf{q}_0\, \det\left|\frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0}\right|^{-\frac{1}{2}} e^{\frac{i}{\hbar}S_t(\mathbf{p}_0,\mathbf{q}_0)}\, |\mathbf{q}_t\rangle\, \langle \mathbf{q}_0|\,. \tag{3}$$

Now make a transformation to initial conditions,

$$\sum_{\text{classical paths}} \int \mathrm{d}\mathbf{q}_t \;=\; \int \mathrm{d}\mathbf{p}_0 \left|\frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0}\right|, \tag{4}$$

to yield the Van Vleck-IVR (VV-IVR),

$$e^{-\frac{i}{\hbar}\hat{H}t} \;\approx\; \frac{1}{(2\pi i\hbar)^{\frac{N}{2}}} \int \mathrm{d}\mathbf{p}_0 \int \mathrm{d}\mathbf{q}_0\, \det\left|\frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0}\right|^{\frac{1}{2}} e^{\frac{i}{\hbar}S_t(\mathbf{p}_0,\mathbf{q}_0)}\, |\mathbf{q}_t\rangle\, \langle \mathbf{q}_0|\,. \tag{5}$$

The conversion to initial conditions removes the double-ended boundary condition, and we also avoid the issue of dealing with a singular prefactor since the determinant now sits in the numerator. A momentum-based IVR is also possible,

$$e^{-\frac{i}{\hbar}\hat{H}t} \;\approx\; \frac{1}{(2\pi i\hbar)^{\frac{N}{2}}} \int \mathrm{d}\mathbf{p}_0 \int \mathrm{d}\mathbf{q}_0 \,\det\left|\frac{\partial \mathbf{p}_t}{\partial \mathbf{q}_0}\right|^{\frac{1}{2}} e^{\frac{i}{\hbar}S_t(\mathbf{p}_0,\mathbf{q}_0)} \left|\mathbf{p}_t\right\rangle \left\langle \mathbf{p}_0\right| . \qquad (6)$$

1.3 Herman-Kluk SC-IVR

An appealing alternative to (4) and (5) is the HK-IVR, which works in a basis of coherent states,

$$e^{-\frac{i}{\hbar}\hat{H}t} \;\approx\; \frac{1}{(2\pi\hbar)^{N}} \int \mathrm{d}\mathbf{p}_0 \int \mathrm{d}\mathbf{q}_0 \, C_t(\mathbf{p}_0,\mathbf{q}_0)\, e^{\frac{i}{\hbar}S_t(\mathbf{p}_0,\mathbf{q}_0)} \left|\mathbf{p}_t\mathbf{q}_t\right\rangle \left\langle \mathbf{p}_0\mathbf{q}_0\right| . \qquad (7)$$

The prefactor in this representation is given by

$$C_t(\mathbf{p}_0,\mathbf{q}_0) \;=\; \det\left|\gamma_t^{\frac{1}{2}}\mathbf{M}_{qq}\gamma_0^{-\frac{1}{2}} + \gamma_t^{-\frac{1}{2}}\mathbf{M}_{pp}\gamma_0^{\frac{1}{2}} - i\hbar\gamma_t^{\frac{1}{2}}\mathbf{M}_{qp}\gamma_0^{\frac{1}{2}} + \frac{i}{\hbar}\gamma_t^{-\frac{1}{2}}\mathbf{M}_{pq}\gamma_0^{-\frac{1}{2}}\right|^{\frac{1}{2}} \qquad (8)$$

($\mathbf{M}_{\alpha\beta} = \frac{\partial \alpha_t}{\partial \beta_0}$). The coherent states are minimum uncertainty Gaussian wavepackets,

$$\begin{aligned} \langle \bar{\mathbf{x}}|\mathbf{q}\,\mathbf{p}\rangle \;&=\; \left(\frac{\det|\gamma|}{\pi^N}\right)^{\frac{1}{4}} e^{-\frac{1}{2}(\bar{\mathbf{x}}-\mathbf{q})\cdot\gamma\cdot(\bar{\mathbf{x}}-\mathbf{q})+\frac{i}{\hbar}\mathbf{p}\cdot(\bar{\mathbf{x}}-\mathbf{q})} \\ \langle \bar{\mathbf{p}}|\mathbf{q}\,\mathbf{p}\rangle \;&=\; \left(\frac{1}{\det|\gamma|\pi^N}\right)^{\frac{1}{4}} e^{-\frac{1}{2}(\bar{\mathbf{p}}-\mathbf{p})\cdot\gamma^{-1}\cdot(\bar{\mathbf{p}}-\mathbf{p})-\frac{i}{\hbar}\bar{\mathbf{p}}\cdot\mathbf{q}}, \end{aligned} \qquad (9)$$

with the $N \times N$ diagonal matrix γ determining the spread of the wavepacket in $\mathbf{p}$ and $\mathbf{q}$. The HK-IVR is more well-behaved than (4) or (5) from a numerical standpoint, mainly because the Gaussian wavefunctions are easy to integrate, and because the coherent state overlaps provide a convenient choice for importance sampling $(\mathbf{p}_0, \mathbf{q}_0)$,

$$\langle \mathbf{p}_0^{'}\,\mathbf{q}_0^{'}|\mathbf{p}_0\,\mathbf{q}_0\rangle \;=\; e^{-\frac{1}{4}(\mathbf{q}_0^{'}-\mathbf{q}_0)\cdot\gamma\cdot(\mathbf{q}_0^{'}-\mathbf{q}_0)-\frac{1}{4}(\mathbf{p}_0^{'}-\mathbf{p}_0)\cdot\gamma^{-1}\cdot(\mathbf{p}_0^{'}-\mathbf{p}_0)+\frac{i}{2\hbar}(\mathbf{p}_0^{'}+\mathbf{p}_0)\cdot(\mathbf{q}_0^{'}-\mathbf{q}_0)}. \qquad (10)$$

The derivation of (6) is not as straightforward as its predecessors, but the references below provide plenty of detail.

1.4 SC-IVR Correlation Functions

We will be interested in computing real-time correlation functions of the form

$$C_{AB}(t) \;=\; \mathrm{Tr}\left[\hat{A}\,e^{\frac{i}{\hbar}\hat{H}t}\hat{B}\,e^{-\frac{i}{\hbar}\hat{H}t}\right], \qquad (11)$$

with operator $\hat{A}$ representing the initial state of the system, and operator $\hat{B}$ the observable of choice. A semiclassical approximation for (10) can be made by inserting any pair of SC-IVRs in place of the time-evolution operators. The Van Vleck representation (DVV-IVR) gives

$$\begin{aligned} C_{AB}(t) \;=\; \frac{1}{(2\pi\hbar)^N} \int \mathrm{d}\mathbf{p}_0 \int \mathrm{d}\mathbf{q}_0 \int \mathrm{d}\mathbf{p}_t^{'} \int \mathrm{d}\mathbf{q}_t^{'}\, e^{\frac{i}{\hbar}[S_t(\mathbf{p}_0,\mathbf{q}_0)+S_{-t}(\mathbf{p}_t,\mathbf{q}_t)]} \\ \times \det\left|\mathbf{M}_{qp}\,\mathbf{M}_{qp}^{'}\right|^{\frac{1}{2}} \langle \mathbf{q}_0|\hat{A}|\mathbf{q}_0^{'}\rangle\,\langle \mathbf{q}_t^{'}|\hat{B}|\mathbf{q}_t\rangle \end{aligned} \qquad (12)$$

with $(\mathbf{p}_0, \mathbf{q}_0)$ and $(\mathbf{p}_t^{'}, \mathbf{q}_t^{'})$ the initial conditions of a forward and backward trajectory, respectively. Similarly, the momentum representation is given by

$$\begin{aligned} C_{AB}(t) \;=\; & \frac{1}{(2\pi i\hbar)^N} \int \mathrm{d}\mathbf{p}_0 \int \mathrm{d}\mathbf{q}_0 \int \mathrm{d}\mathbf{p}_t^{'} \int \mathrm{d}\mathbf{q}_t^{'}\, e^{\frac{i}{\hbar}[S_t(\mathbf{p}_0,\mathbf{q}_0)+S_{-t}(\mathbf{p}_t,\mathbf{q}_t)]} \\ & \times \det\left|\mathbf{M}_{pq}\,\mathbf{M}_{pq}^{'}\right|^{\frac{1}{2}} \langle \mathbf{p}_0|\hat{A}|\mathbf{p}_0^{'}\rangle\, \langle \mathbf{p}_t^{'}|\hat{B}|\mathbf{p}_t\rangle\,. \end{aligned} \tag{13}$$

Finally, there is the Herman-Kluk correlation function (DHK-IVR),

$$\begin{aligned} C_{AB}(t) \;=\; & \frac{1}{(2\pi i\hbar)^{2N}} \int \mathrm{d}\mathbf{p}_0 \int \mathrm{d}\mathbf{q}_0 \int \mathrm{d}\mathbf{p}_t^{'} \int \mathrm{d}\mathbf{q}_t^{'}\, e^{\frac{i}{\hbar}[S_t(\mathbf{p}_0,\mathbf{q}_0)+S_{-t}(\mathbf{p}_t,\mathbf{q}_t)]} \\ & \times C_t(\mathbf{p}_0,\mathbf{q}_0) C_{-t}(\mathbf{p}_t^{'},\mathbf{q}_t^{'})\; \langle \mathbf{p}_0\mathbf{q}_0|\hat{A}|\mathbf{p}_0^{'}\mathbf{q}_0^{'}\rangle\, \langle \mathbf{p}_t^{'}\mathbf{q}_t^{'}|\hat{B}|\mathbf{p}_t\mathbf{q}_t\rangle\,. \end{aligned} \tag{14}$$

Approximations (11), (12), and (13) are fully capable of describing all quantum effects one may be interested in, however, the oscillatory nature of the phase makes convergence difficult to achieve in multidimensional systems.

1.5 Linearized SC-IVR

One approach to the sign problem of the previous section is to linearize the phase or, in other words, only assume contributions from trajectory pairs that are extremely close to one another. The method is derived by taking equation (11) and converting to mean and difference variables: $\Delta_\alpha = \alpha_t^{'} + \alpha_t$, $\bar{\alpha} = \frac{1}{2}(\alpha_t^{'} + \alpha_t)$, with $\alpha = \mathbf{p}, \mathbf{q}$. Then we expand all time-dependent quantities to first order in the difference variables, and end up with a single phase space average over the Wigner distributions of the two operators,

$$C_{AB}(t) \;=\; \frac{1}{(2\pi\hbar)^N} \int \mathrm{d}\mathbf{p}_0 \int \mathrm{d}\mathbf{q}_0\, A_w(\mathbf{p}_0,\mathbf{q}_0)\, B_w(\mathbf{p}_t,\mathbf{q}_t). \tag{15}$$

This is known as the LSC-IVR, and its Wigner distributions are given by

$$A_w(\mathbf{p},\mathbf{q}) \;=\; \int \mathrm{d}\bar{\mathbf{q}}\, e^{-\frac{i}{\hbar}\mathbf{p}\cdot\bar{\mathbf{q}}}\, \langle \mathbf{q} + \frac{1}{2}\bar{\mathbf{q}}|\hat{A}|\mathbf{q} - \frac{1}{2}\bar{\mathbf{q}}\rangle\,. \tag{16}$$

While it is a very popular and useful result, the LSC-IVR generally fails at describing long-time coherence effects because of the imposed phase cancellation. In this way, the LSC-IVR is virtually a classical result.

1.6 Mixed Quantum-Classical IVR

Though the DHK-IVR of (14) is the most appealing approach to incorporate quantum effects in MD simulations, convergence is often too difficult to achieve. The interference between forward-backward trajectory pairs gives rise to a formidable sign program. So the approach from here is to assume that many of the contributions from forward-backward pairs will average to zero, namely those that diverge over time. We make this assumption in the form of a modified Filinov transformation, which serves to pre-average many of the oscillatory contributions to zero, and accelerate the calculation. The derivation involves performing a modified Filinov transformation to (14), which amounts to multiplying the integrand of (14) by a damping factor,

$$F(\mathbf{z}\,;\mathbf{c}) \;=\; \det\left|\mathbb{I} + i\mathbf{c}\frac{\partial^2\phi}{\partial\mathbf{z}^2}\right|^{\frac{1}{2}} e^{-\frac{1}{2}\frac{\partial\phi}{\partial\mathbf{z}}^T\mathbf{c}\frac{\partial\phi}{\partial\mathbf{z}}}\,, \tag{17}$$

which down-weights the phase, $\phi(\mathbf{z})$, where it varies quickly. The diagonal matrix of tuning parameters, $\mathbf{c}$, determines the strength of the filtering, as we'll see. After selectively constructing (17), inserting it into (14), and making some simplifications, one arrives at the MQC-IVR:

$$\begin{aligned} C_{AB}(t) \;=\; & \frac{1}{(2\pi\hbar)^{2N}} \int \mathrm{d}\mathbf{p}_0 \int \mathrm{d}\mathbf{q}_0 \int \mathrm{d}\boldsymbol{\Delta}_p \int \mathrm{d}\boldsymbol{\Delta}_q \, e^{\frac{i}{\hbar}[S_t(\mathbf{p}_0,\mathbf{q}_0)+S_{-t}(\mathbf{p}_t,\mathbf{q}_t)]} \\ & \times D_t(\mathbf{p}_0,\mathbf{q}_0,\boldsymbol{\Delta}_p,\boldsymbol{\Delta}_q;\mathbf{c}_p,\mathbf{c}_q)\,\langle\mathbf{p}_0\mathbf{q}_0|\hat{A}|\mathbf{p}_0^{'}\mathbf{q}_0^{'}\rangle\,\langle\mathbf{p}_t^{'}\mathbf{q}_t^{'}|\hat{B}|\mathbf{p}_t\mathbf{q}_t\rangle \\ & \times e^{-\frac{1}{2}\boldsymbol{\Delta}_q^T\mathbf{c}_q\boldsymbol{\Delta}_q} e^{-\frac{1}{2}\boldsymbol{\Delta}_p^T\mathbf{c}_p\boldsymbol{\Delta}_p}, \end{aligned} \tag{18}$$

with $\boldsymbol{\Delta}_q = \mathbf{q}_t^{'} - \mathbf{q}_t$ and $\boldsymbol{\Delta}_p = \mathbf{p}_t^{'} - \mathbf{p}_t$. The prefactor, D_t, is given by

$$\begin{aligned} D_t \;=\; 2^{-\frac{N}{2}} \det(\gamma_0\mathbf{G})^{\frac{1}{2}} \det\Big| & \frac{1}{2}(\mathbf{M}^b_{pp} - i\gamma_0\mathbf{M}^b_{qp})(\mathbf{G}^{-1}+\mathbb{I})(\mathbf{M}^f_{pp}\gamma_0 + i\mathbf{M}^f_{pq}) \\ & + (\gamma_0\mathbf{M}^b_{qq} + i\mathbf{M}^b_{pq})(\frac{1}{2}\gamma_t + \mathbf{c}_p)\mathbf{G}^{-1}(\mathbf{M}^b_{pp}\gamma_0 + i\mathbf{M}^f_{pq}) \\ & + \frac{1}{2}(\mathbf{M}^b_{qq} + i\mathbf{M}^b_{pq})(\mathbf{G}^{-1}+\mathbb{I})(\mathbf{M}^f_{qq} - i\mathbf{M}^f_{qp}\gamma_0) \\ & + (\mathbf{M}^b_{pp} - i\gamma_0\mathbf{M}^b_{qp})(\frac{1}{2}\gamma_t + \mathbf{c}_q)\mathbf{G}^{-1}(\mathbf{M}^b_{qq} - i\mathbf{M}^f_{qp}\gamma_0)\Big|^{\frac{1}{2}} \end{aligned}$$

Note that as $(\mathbf{c}_p,\mathbf{c}_q) \to 0$ we recover the original DHK-IVR, and as $(\mathbf{c}_p,\mathbf{c}_q) \to \infty$ we effectively perform stationary phase approximation and obtain a result similar to the LSC-IVR,

$$C_{AB}(t) \;=\; \frac{1}{(2\pi\hbar)^N} \int \mathrm{d}\mathbf{p}_0 \int \mathrm{d}\mathbf{q}_0 \,\langle\mathbf{p}_0\mathbf{q}_0|\hat{A}|\mathbf{p}_0\mathbf{q}_0\rangle\,\langle\mathbf{p}_t\mathbf{q}_t|\hat{B}|\mathbf{p}_t\mathbf{q}_t\rangle\,, \tag{19}$$

which we will refer to as the Husimi-IVR. Choosing intermediate values of $\mathbf{c}_p$ and $\mathbf{c}_q$ for different degrees of freedom gives one the ability to control the extent to which those modes are treated in the classical or quantum limit of SC theory. Descriptions of the two implementations of this theory are given in the following sections.

1.6.1 Forward-Backward

The MQC-IVR was originally derived under the Forward-Backward implementation; the expression is given by (18). As a matter of implementation, we first sample a set of initial conditions for the forward trajectory, $(\mathbf{p}_0,\mathbf{q}_0)$, as well as a set of displacements at time t, $(\boldsymbol{\Delta}_p,\boldsymbol{\Delta}_q)$. For example, if operator $\hat{A}$ is the projection of an initial coherent state, $\hat{A} = |\mathbf{p}_i\mathbf{q}_i\rangle\langle\mathbf{p}_i\mathbf{q}_i|$, the sampling distribution will be of the following form,

$$\omega(\mathbf{p}_0,\mathbf{q}_0,\boldsymbol{\Delta}_p,\boldsymbol{\Delta}_q) \;=\; |\langle\mathbf{p}_0\mathbf{q}_0|\mathbf{p}_i\mathbf{q}_i\rangle|^2 e^{-\frac{1}{2}\boldsymbol{\Delta}_q^T\mathbf{c}_q\boldsymbol{\Delta}_q} e^{-\frac{1}{2}\boldsymbol{\Delta}_p^T\mathbf{c}_p\boldsymbol{\Delta}_p}. \tag{20}$$

We proceed by propagating the set of points, $(\mathbf{p}_0,\mathbf{q}_0)$, with the classical equations of motion up to time t, $(\mathbf{p}_t,\mathbf{q}_t)$, at which point operator $\hat{B}$ will act on the state of the system and induce a phase space jump,

$$\begin{aligned} \mathbf{p}_t \to \mathbf{p}_t + \boldsymbol{\Delta}_p = \mathbf{p}_t^{'} \\ \mathbf{q}_t \to \mathbf{q}_t + \boldsymbol{\Delta}_q = \mathbf{q}_t^{'}, \end{aligned} \tag{21}$$

we then propagate the new trajectory backwards to time $t = 0$ at point $(\mathbf{p}_0^{'}, \mathbf{q}_0^{'})$. The phase and prefactor are calculated along the two trajectories and the final result is obtained by averaging over the number of trajectories used.

The dimensionality of the integral (18) can be reduced if operator $\hat{B}$ is purely a function of the position or momentum operator, $\hat{B} = B(\hat{\mathbf{q}})$ or $\hat{B} = B(\hat{\mathbf{p}})$. For example, when $\hat{B} = B(\hat{\mathbf{q}})$ we can collapse the coherent states at time t to position states by evaluating the following limit,

$$\lim_{\gamma_t \to \infty} \det(\gamma_t)^{\frac{1}{2}} \langle \mathbf{p}_t^{'} \mathbf{q}_t^{'} | B(\hat{\mathbf{q}}) | \mathbf{p}_t \mathbf{q}_t \rangle \; = \; (4\pi)^{\frac{N}{2}} \delta(\mathbf{\Delta}_q) B\left(\frac{\mathbf{q}_t^{'} + \mathbf{q}_t}{2} \right). \tag{22}$$

After inserting (22) into (18) and evaluating the integral over $\mathbf{\Delta}_q$ we arrive at

$$\begin{aligned} C_{AB}(t) \; &= 2^{-2N} \pi^{-\frac{3N}{2}} \int \mathrm{d}\mathbf{p}_0 \int \mathrm{d}\mathbf{q}_0 \int \mathrm{d}\mathbf{\Delta}_p \, e^{\frac{i}{\hbar}[S_t(\mathbf{p}_0, \mathbf{q}_0) + S_{-t}(\mathbf{p}_t, \mathbf{q}_t)]} \\ &\quad \times D_q(\mathbf{p}_0, \mathbf{q}_0, \mathbf{\Delta}_p; \mathbf{c}_p) \, \langle \mathbf{p}_0 \mathbf{q}_0 | \hat{A} | \mathbf{p}_0^{'} \mathbf{q}_0^{'} \rangle \, B(\mathbf{q}_t) e^{-\frac{1}{2} \mathbf{\Delta}_p^T \mathbf{c}_p \mathbf{\Delta}_p}, \end{aligned} \tag{23}$$

with the simplified prefactor given by

$$\begin{aligned} D_q(\mathbf{p}_0, \mathbf{q}_0, \mathbf{\Delta}_p; \mathbf{c}_p) \; = \; \det \Big| \gamma_0^{-1} \mathbf{c}_p \Big[& (\mathbf{M}_{pp}^b - i\gamma_0 \mathbf{M}_{qp}^b)(\mathbf{M}_{pp}^f \gamma_0 + i\mathbf{M}_{pq}^f) \\ & + (\gamma_0 \mathbf{M}_{qq}^b + i\mathbf{M}_{pq}^b)(\mathbf{M}_{qq}^f - i\mathbf{M}_{qp}^f \gamma_0) \\ & + (\mathbf{M}_{pp}^b - i\gamma_0 \mathbf{M}_{qp}^b) \mathbf{c}_p^{-1} (\mathbf{M}_{qq}^f - i\mathbf{M}_{qp}^f \gamma_0) \Big] \Big|^{\frac{1}{2}}. \end{aligned} \tag{24}$$

Similarly, we can evaluate the limit that $\gamma_t \to 0$ to recover an expression when operator $\hat{B}$ is of the type $\hat{B} = B(\hat{\mathbf{p}})$,

$$\begin{aligned} C_{AB}(t) \; &= \frac{1}{(2\pi\hbar)^{2N}} \int \mathrm{d}\mathbf{p}_0 \int \mathrm{d}\mathbf{q}_0 \int \mathrm{d}\mathbf{\Delta}_q \, e^{\frac{i}{\hbar}[S_t(\mathbf{p}_0, \mathbf{q}_0) + S_{-t}(\mathbf{p}_t, \mathbf{q}_t)]} \\ &\quad \times D_p(\mathbf{p}_0, \mathbf{q}_0, \mathbf{\Delta}_q; \mathbf{c}_q) \, \langle \mathbf{p}_0 \mathbf{q}_0 | \hat{A} | \mathbf{p}_0^{'} \mathbf{q}_0^{'} \rangle \, B(\mathbf{p}_t) e^{-\frac{1}{2} \mathbf{\Delta}_q^T \mathbf{c}_p \mathbf{\Delta}_q}, \end{aligned} \tag{25}$$

with the prefactor

$$\begin{aligned} D_p(\mathbf{p}_0, \mathbf{q}_0, \mathbf{\Delta}_q; \mathbf{c}_q) \; = \; \det \Big| \gamma_0^{-1} \mathbf{c}_q \Big[& (\mathbf{M}_{pp}^b - i\gamma_0 \mathbf{M}_{qp}^b)(\mathbf{M}_{pp}^f \gamma_0 + i\mathbf{M}_{qp}^f) \\ & + (\gamma_0 \mathbf{M}_{qq}^b + i\mathbf{M}_{pq}^b)(\mathbf{M}_{qq}^f - i\mathbf{M}_{qp}^f \gamma_0) \\ & + (\gamma_0 \mathbf{M}_{qq}^b + i\mathbf{M}_{pq}^b) \mathbf{c}_q^{-1} (\mathbf{M}_{pp}^f \gamma_0 + i\mathbf{M}_{pq}^f) \Big] \Big|^{\frac{1}{2}}. \end{aligned} \tag{26}$$

1.6.2 Forward-Forward

From a numerical standpoint, the implementation of the Forward-Backward methods of the previous section are tedious; all phase space jumps must be explored at every time step. A much more efficient approach is the Forward-Forward implementation where both trajectories are propagated forward in time, and the contributions from large phase space displacements are regulated at time $t = 0$ rather than time t. The derivation is nearly identical to the previous one, though we begin by writing (14) with a change of variables,

$$\begin{aligned} C_{AB}(t) \; &= \frac{1}{(2\pi\hbar)^{2N}} \int \mathrm{d}\mathbf{p}_0 \int \mathrm{d}\mathbf{q}_0 \int \mathrm{d}\mathbf{p}_0^{'} \int \mathrm{d}\mathbf{q}_0^{'} \, e^{\frac{i}{\hbar}[S_t(\mathbf{p}_0,\mathbf{q}_0) - S_t(\mathbf{p}_0^{'},\mathbf{q}_0^{'})]} \\ &\times C_t(\mathbf{p}_0,\mathbf{q}_0)\, C_t(\mathbf{p}_0^{'},\mathbf{q}_0^{'}) \; \langle \mathbf{p}_0\mathbf{q}_0|\hat{A}|\mathbf{p}_0^{'}\mathbf{q}_0^{'}\rangle \; \langle \mathbf{p}_t^{'}\mathbf{q}_t^{'}|\hat{B}|\mathbf{p}_t\mathbf{q}_t\rangle \, , \end{aligned} \tag{27}$$

so that we are now integrating over the initial conditions of a pair trajectories, $(\mathbf{p}_0, \mathbf{q}_0)$ and $(\mathbf{p}_0^{'}, \mathbf{q}_0^{'})$, that are each propagated forward in time. We then introduce a damping factor, as before, and end up with the new implementation,

$$\begin{aligned} C_{AB}(t) \; &= \frac{1}{(2\pi\hbar)^{2N}} \int \mathrm{d}\mathbf{p}_0 \int \mathrm{d}\mathbf{q}_0 \int \mathrm{d}\mathbf{p}_0^{'} \int \mathrm{d}\mathbf{q}_0^{'} \, e^{\frac{i}{\hbar}[S_t(\mathbf{p}_0,\mathbf{q}_0) - S_t(\mathbf{p}_0^{'},\mathbf{q}_0^{'})]} \\ &\times D_t(\mathbf{p}_0,\mathbf{q}_0,\mathbf{p}_0^{'},\mathbf{q}_0^{'};\mathbf{c}_p,\mathbf{c}_q) \; \langle \mathbf{p}_0\mathbf{q}_0|\hat{A}|\mathbf{p}_0^{'}\mathbf{q}_0^{'}\rangle \; \langle \mathbf{p}_t^{'}\mathbf{q}_t^{'}|\hat{B}|\mathbf{p}_t\mathbf{q}_t\rangle \\ &\times e^{-\frac{1}{2}\boldsymbol{\Delta}_{q_0}^T \mathbf{c}_q \boldsymbol{\Delta}_{q_0}} e^{-\frac{1}{2}\boldsymbol{\Delta}_{p_0}^T \mathbf{c}_p \boldsymbol{\Delta}_{p_0}} , \end{aligned} \tag{28}$$

with $\boldsymbol{\Delta}_{p_0} = \mathbf{p}_0^{'} - \mathbf{p}_0$ and $\boldsymbol{\Delta}_{q_0} = \mathbf{q}_0^{'} - \mathbf{q}_0$, and the prefactor given by

$$\begin{aligned} D_t \; = \; \det(\frac{1}{2}\gamma_t^{-1}\mathbf{G})^{\frac{1}{2}} \det \Bigg| & \frac{1}{2}(\mathbf{M}_{pp}^f - i\gamma_t\mathbf{M}_{qp}^f)(\mathbf{G}^{-1} + \mathbb{I})(\mathbf{M}_{pp}^b\gamma_t + i\mathbf{M}_{pq}^b) \\ & + (\gamma_t\mathbf{M}_{qq}^f + i\mathbf{M}_{pq}^f)(\frac{1}{2}\gamma_0^{-1} + \mathbf{c}_p)\mathbf{G}^{-1}(\mathbf{M}_{pp}^b\gamma_t + i\mathbf{M}_{pq}^b) \\ & + \frac{1}{2}(\gamma_t\mathbf{M}_{qq}^f + i\mathbf{M}_{pq}^f)(\mathbf{G}^{-1} + \mathbb{I})(\mathbf{M}_{qq}^b - i\mathbf{M}_{qp}^b\gamma_t) \\ & + (\mathbf{M}_{pp}^f - i\gamma_t\mathbf{M}_{qp}^f)(\frac{1}{2}\gamma_0 + \mathbf{c}_q)\mathbf{G}^{-1}(\mathbf{M}_{qq}^b - i\mathbf{M}_{qp}^b\gamma_t)\Bigg]^{\frac{1}{2}} . \end{aligned}$$

To carry out the simulation, we generate a set of correlated trajectory pairs with the following sampling distribution,

$$\omega(\mathbf{p}_0,\mathbf{q}_0,\mathbf{p}_0^{'},\mathbf{q}_0^{'}) \; = \; |\, \langle \bar{\mathbf{p}}\, \bar{\mathbf{q}}|\mathbf{p}_i\mathbf{q}_i\rangle\, |^2 e^{-\frac{1}{2}\boldsymbol{\Delta}_{p_0}\mathbf{c}_p\boldsymbol{\Delta}_{p_0}} e^{-\frac{1}{2}\boldsymbol{\Delta}_{q_0}\mathbf{c}_q\boldsymbol{\Delta}_{q_0}} , \tag{29}$$

with $\bar{\mathbf{p}} = \frac{1}{2}(\mathbf{p}_t^{'} + \mathbf{p}_t)$ and $\bar{\mathbf{q}} = \frac{1}{2}(\mathbf{q}_t^{'} + \mathbf{q}_t)$. We then use the mean and difference variables to recover $(\mathbf{p}_0, \mathbf{q}_0)$ and $(\mathbf{p}_0^{'}, \mathbf{q}_0^{'})$, and propagate them forward in time. The phase and prefactor are then calculated along each trajectory.

1.7 Useful References

MQC-IVR	A.V. Antipov, Z. Ye and N. Ananth. *J. Chem. Phys.* **142**, 184102 (2015)
SC-IVRs	W.H. Miller, *J. Phys. Chem. A.* **105**, 2942 (2001)
SC-IVRs	M. Thoss and H. Wang. *Annu. Rev. Phys. Chem.* **55**, 299 (2004)
HK-IVR	K.G. Kay, *J. Chem. Phys.* **100**, 4377 (1994)
HK-IVR	E. Kluk, M. Herman, and H.L. Davis. *J. Chem. Phys.* **84**, 326 (1986)
	M.C. Gutzwiller. "Chaos in Classical and Quantum Mechanics" Springer-Verlag (1990)
	D. Tannor. "Introduction to Quantum Mechanics: A Time Dependent Perspective" University Science Books (2007)
	M.S. Child. "Semiclassical Mechanics with Molecular Applications" Oxford University Press 2^{nd} Ed.(2014)

2 SC-IVR Code Package

2.1 Overview

The package contains FORTRAN programs that compute the SC-IVR correlation functions of (14), (15), (18), (19), (23), (25) and (28) for 1D or multidimensional systems. The input file `theory.in` allows you to choose which SC-IVR to use, and defines all simulation parameters one would need. We provide three model systems that may serve as a template for other systems of your choosing; the harmonic oscillator,

$$V(x) \;=\; \frac{1}{2}m\omega^2 x^2, \tag{30}$$

an anharmonic oscillator

$$V(x) \;=\; \frac{1}{2}m\omega^2 x^2 - 0.1x^3 + 0.1x^4, \tag{31}$$

and a 2D system-bath model where (31) is coupled to a harmonic mode

$$V(x,y) \;=\; \frac{1}{2}m_x\omega_x^2 x^2 - 0.1x^3 + 0.1x^4 + \frac{1}{2}m_y\omega_y^2 y^2 + kxy; \tag{32}$$

In each case, the program computes a quantity of the form

$$\langle B\rangle_t \;=\; \langle \mathbf{p}_i\mathbf{q}_i| e^{\frac{i}{\hbar}\hat{H}t}\hat{B}e^{-\frac{i}{\hbar}\hat{H}t}|\mathbf{p}_i\mathbf{q}_i\rangle\,, \tag{33}$$

which is (11) with an initial coherent state projection for operator $\hat{A} = |\mathbf{p}_i\mathbf{q}_i\rangle\langle\mathbf{p}_i\mathbf{q}_i|$. The program is equipped to compute $\langle q\rangle_t$ or $\langle p\rangle_t$ for any of the provided models.
While sitting in the parent directory, specify the input parameters in the file `theory.in`, and then execute the bash script `execute.sh`. This will generate a directory called `EXPERIMENT` which contains the program you specified. Typing `make` while sitting in the `EXPERIMENT` directory will compile the program, and typing `./dyn.x` will start the simulation. If you intend to parallelize the calculation with MPI, then use `jobrun.sh` to submit the script (see below, this script will need to be edited according to your computational resources). Note that executing the bash script again will overwrite the existing `EXPERIMENT` directory, so it should be renamed to be safe. When the simulation is complete, a file named `TCF.out` will contain the real and imaginary parts of the correlation function as a function of time, and a file named `MC.configs` contains the initial phase space configurations of the classical trajectories.

2.2 The Makefile, External Libraries, and the MPI Submission Script

In the directory `makefiles` is a universal makefile. When the script `execute.sh` is run, the makefile is copied into the `EXPERIMENT` directory, and a simple search-and-replace routine tailors the makefile to your specifications. Depending on your operating system, the makefile may need to be edited. Note that we specify paths to the LAPACK and BLAS libraries, and mpif90 is used as well. Also note that we do NOT encourage you to edit the names of any FORTRAN files, modules or scripts that do not sit in the `EXPERIMENT` directory, as this may prevent the program from assembling the `EXPERIMENT` directory appropriately.

In the directory `Scripts` there is a submission script called `jobrun.sh`. This uses the Portable Batch System (PBS) scheduler, and will need to be edited if another scheduler is used.

2.3 Tutorial 1: 1D Anharmonic Oscillator

In the parent directory, set up the input file to compute the average position of the anharmonic oscillator with the Husimi-IVR,

```
Degrees of freedom
1
Level of theory ( ...
2
Implementation ( ...
1
Type of observable ...
1
Model Potentials ( ...
2
List the diagonal ...
1.0
List the coherent state and ...
1.0     0.0     1.414     1.414     10.0     10.0
Timestep, number of timesteps, ...
0.05     1600     1e-5
Number of trajectories
120000
List the frequencies ...
1.414
```

The bilinear coupling applies only to the 2D model, and will be neglected with 1D systems. Leave an arbitrary number for the tuning parameters if the MQC-IVR is not being used, in this case we use 10.0. Also, even though the `Implementation` line is irrelevant in this case, leave it as 1 for the Husimi and LSC-IVRs. Execute the bash script with `sh execute.sh`. This generates a directory called `EXPERIMENT` which contains the program specified by the input file. Rename the experiment directory and `cd` into it. There are several FORTRAN files in the experiment directory. The input file in this directory is called `input_1D`. The file `MonteCarlo_1D.f90` contains subroutines that generate initial configurations for each of the 1D implementations, `params_1D.f90` contains the global parameters and a subroutine that reads the input file, `traj_1D.f90` contains subroutines that propagate the classical trajectories (depending upon the type of SC-IVR), `potential_1D.f90` contains the model potentials, `jobrun.sh` is a submission script for jobs using MPI, and `supply_1D.f90` contains a symplectic integrator and various subroutines that compute matrix elements and prefactors. The file `HUS_timecorr_1D.f90` contains the program which computes the correlation function, drawing upon the subroutines that you originally specified in `theory.in`. Start the simulation with `./dyn.x` ($\sim$ 20sec) and plot the result contained in the file `TCF.out`.

Now go back to the parent directory and start a new experiment, identical to the previous one but with the Forward-Forward MQC-IVR and $c_p = c_q = 10$. The input file `theory.in` should read

```
Degrees of freedom
1
Level of theory ( ...
3
Implementation ( ...
1
Type of observable ...
1
Model Potentials ( ...
2
List the diagonal ...
1.0
List the coherent state and ...
1.0     0.0     1.414     1.414      10.0     10.0
Timestep, number of timesteps, ...
0.05    1600     1e-5
Number of trajectories
120000
List the frequencies ...
1.414
```

Compile and run the program as before (∼ 1min) and compare the two results. The large amplitudes at later times should be apparent in the MQC-IVR result.

2.4 Tutorial 2: 2D Anharmonic Oscillator

Now we will compute the average momentum of an anharmonic oscillator that is coupled to a heavy harmonic mode with the Husimi-IVR. The `theory.in` file should read

```
Degrees of freedom
2
Level of theory ( ...
2
Implementation ( ...
1
Type of observable ...
2
Model Potentials ( ...
2
List the diagonal ...
1.0     25.0
List the coherent state and ...
1.0     0.0     1.414     1.414      10.0     10.0
1.0     0.0     8.333     8.333      1e8    1e8
Timestep, number of timesteps, ...
0.05    1600     1e-5
Number of trajectories
36000
List the frequencies ...
1.414 0.333
```

```
Bilinear coupling ...
2.0
```

With this input file, generate an EXPERIMENT directory, compile, run the simulation (∼ 1min), and plot the result.
In order to observe the average momentum of the harmonic mode rather than the anharmonic mode, vi into the file HUS_timecorr_1D.f90 and change the doflabel in line 37 from 1 to 2. Compile and run the simulation.

2.5 Altering the Code

We do not advise that you alter any files, directories, or scripts unless they are sitting in an EXPERIMENT folder. In order to design your own experiment, it is suggested that you use theory.in to generate an EXPERIMENT directory with the SC-IVR of your choosing with an arbitrary model potential. Then while working in the EXPERIMENT directory you have the freedom to alter the potential and any subroutine you may wish to edit.

2.5.1 Tutorial 3: Creating a New Experiment I

Here is a brief example of how one can create their own SC-IVR experiment. We wish to calculate the average position of the anharmonic oscillator which is now coupled to two identical harmonic bath modes. We arbitrarily choose to use the Forward-Forward MQC-IVR and a large tuning parameter to set up theory.in as follows

```
Degrees of freedom
3
Level of theory ( ...
3
Implementation ( ...
1
Type of observable ...
1
Model Potentials ( ...
2
List the diagonal ...
1.0     25.0     25.0
List the coherent state and ...
1.0     0.0     1.414     1.414      1e8       1e8
1.0     0.0     8.333     8.333      1e8       1e8
1.0     0.0     8.333     8.333      1e8       1e8
Timestep, number of timesteps, ...
0.05    1600     1e-5
Number of trajectories
36000
```

Generate an EXPERIMENT directory with this input file and cd into it. The potential subroutine is defined in potential_mD.f90, vi into this file and edit the potential to include the second harmonic mode (with the same frequency as the other harmonic mode). Compile and run the program.

2.5.2 Prefactors and Coherent State Matrix Elements

In a given EXPERIMENT directory, there is a file called supply_1D.f90 or supply_mD.f90 which contains subroutines that compute matrix elements of operator $\hat{B}$, the coherent state overlap, and all the semiclassical prefactors. If your operator $\hat{B}$ is not the position or momentum operator then a new expression will need to be derived and implemented into the code. As a brief example, say we want to repeat the calculation in Tutorial 1 but with a different observable, say $\hat{B} = \hat{q}^2$ rather than $\hat{B} = \hat{q}$. Use the same theory.in file as in Tutorial 1 and generate an EXPERIMENT directory, and cd into that directory. In the file supply_1D.f90 go to the subroutine Hus_Bq at line 137. Using completeness and (9) we derive the new expression,

$$\begin{aligned} \langle p_t q_t|\hat{q}^2|p_t q_t\rangle &= \int \mathrm{d}\bar{q}\,\bar{q}^2\,\langle p_t q_t|\bar{q}\rangle\,\langle\bar{q}|p_t q_t\rangle \\ &= q_t^2 + \frac{1}{2\gamma_t} \end{aligned} \tag{34}$$

Now replace $Bq = q$ with $Bq = q^2 + InverseWidthT/2.d0$. Also, enter a line that says `use parameters, only :  InverseWidthT` above the `implicit none` statement. Compile the program and run the simulation.

2.5.3 Introducing Other Hamiltonians

Begin by arranging the input file theory.in to compute, say, the average position (or momentum) of either of the 1D oscillator systems with the IVR of your choice, and generate the EXPERIMENT directory. Open the file potential_1D.f90 and create a subroutine that computes the potential energy as well as its first and second derivatives (use the other two subroutines as a reference). If your potential is parametrized, you can hard code the values of those parameters directly into your new subroutine. A more convenient option would be to open the params_1D.f90 file and define your parameters in the global module, include a line for them in the input_1D file, and make sure the subroutine input in params_1D.f90 reads those parameters appropriately. The latter option allows you to redefine your potential parameters without having to recompile the program. The only remaining thing to do is replace the tag of the potential subroutine in the files traj_1D.f90 and supply_1D.f90. We provide a simple bash script for you to accomplish this easily. While sitting in your EXPERIMENT directory, copy the bash file with

```
cp ../Scripts/renamePot.sh .
```

Execute the interactive script with `sh renamePot.sh` , enter the dimensionality of the system, enter the tag of the potential subroutine you have created, and the script will search and replace the program accordingly.