A semiclassical hybrid approach to linear response functions for infrared spectroscopy

Frank Grossmann

Institute for Theoretical Physics, Technische Universität Dresden, D-01062 Dresden, Germany

E-mail: frank@physik.tu-dresden.de

Received 30 November 2015, revised 28 January 2016
Accepted for publication 25 February 2016
Published 22 March 2016

Abstract
Based on the integral representation of the semiclassical propagator of Herman and Kluk (HK), and in the limit of high temperatures, we formulate a hybrid expression for the correlation function of infrared spectroscopy. This is achieved by performing a partial linearization inside the integral over the difference of phase space variables that occurs after a twofold application of the HK propagator. A numerical case study for a coupled anharmonic oscillator shows that already for a total number of only two degrees of freedom, one of which is treated in the simplified manner, a substantial reduction of the numerical effort is achieved.

Keywords: linear response, infrared spectroscopy, semiclassical initial value representation, semiclassical hybrid dynamics, anharmonic oscillator

1. Introduction
The calculation of quantum mechanical correlation functions plays a central role in the theoretical understanding of the interaction between matter and radiation or particles [1]. In the case of infrared (IR) spectroscopy the relevant linear response correlation function is given by (see e.g., (5.18c) in [2])

\[ R^{(1)}(t) = \frac{i}{\hbar} \text{Tr} \{ \hat{q}^T(t) [\hat{q}, \hat{\rho}] \}, \]  

(1)

where \( \hat{q} \) is denoting the (column) vector of position space operators of the IR active degrees of freedom (DOF) (which may be a subset of the total number of DOFs) and the proportionality constant, relating position to the dipole operator is suppressed. \( \hat{\rho} \) is the equilibrium thermal density operator of the complete system. The calculation of the expression above, e.g., in position or energy basis becomes more and more evolved the higher the total number of DOF. Approximative ways to calculate the correlation function are therefore highly desirable.

One way to proceed is to approximate the density matrix by its high temperature limit and to approximate the two time-evolution operators appearing in the Heisenberg operator \( \hat{q}(t) \) by two semiclassical initial value representations (SC-IVR) [3] of Herman–Kluk (HK) type [4]. Numerically even this approximate approach is barely possible if the number of DOFs exceeds, say 3 or 4, because of the emergence of two SC propagators, for every time step, double phase space integrals have to be done, which, for 4 DOFs amounts already to a 16 fold integral to be calculated at each time step. A formidable reduction of the numerical effort can be achieved by using classical mechanics, e.g., in a classical Wigner or so-called linearized semiclassical (LSC) description. There the double phase space integral is reduced to a single phase space integral after performing the integral over the difference of phase space variables in a linearization approximation. Quantum effects, like beatings in the time-signal (revivals) due to the decrease of the anharmonic oscillator’s level spacing thereby are lost, however [5, 6]. This shortcoming can be circumvented by refraining from the use of purely classical trajectories. In [7], four different ways of improving on the purely classical approach but sticking to the single phase space integral are compared. Alternatively, the mean trajectory approach of Loring and collaborators is still using classical trajectories but incorporates an additional quantization condition of an action into the LSC-IVR expression [5, 8].

Here we want to follow a different approach that is close in spirit to the SC hydrid approach to many particle quantum dynamics put forth previously [9]. We keep the full complexity of the double phase space integral in the DOF that is IR active and perform a linearization leading to an LSC-IVR type...
expression in the remaining DOF. This way, we gain a result whose complexity is dramatically reduced if the number of inactive DOF is large. Retaining the full (SC) complexity for the IR active degree of freedom will allow, however, to still describe some relevant quantum features in the dynamics.

The paper is organized as follows: in section 2 the full HK approach to the linear response function is briefly reviewed. Then the hybrid approach to that quantity is introduced, which is based on a partial linearization of the full SC expression. Numerical results at different levels of approximation are then shown in section 3 for a Morse oscillator coupled a harmonic bath degree of freedom. Finally, some conclusions and an outlook are given. In the appendix a redetermination of the fully linearized version of the SC theory is given.

2. SC hybrid expression for IR spectroscopy

As shown in [3, 5] the SC linear response (or correlation) function for IR spectroscopy for a system of \(N\) DOF, in the case of high temperature \(T\), is given by

\[
R_{\text{hk}}^{(1)}(t) = \frac{\beta}{mQ(2\pi\hbar)^{2N}} \int d^{2N}z_1 \int d^{2N}z_2 \exp \{-\beta H(z)\}
\]

\[
\times \hat{\rho}(q_1 + \frac{i}{2\hbar}\gamma^{-1}p) \times C(z_1, t) C^*(z_2, t) \langle z_1 | z_2 \rangle \times \exp \left\{ -\frac{i}{\hbar} \left[ S(z_1, t) - S(z_2, t) \right] \right\},
\]

where the (row) vectors \(z_i^T = (p_i^T, q_i^T)\), with \(i = 1, 2\), consist of momenta and position vectors and

\[
z = \frac{z_1 + z_2}{2},
\]

\[
\Delta z = z_1 - z_2
\]
denote the average and difference vectors, respectively, and the \(\langle z_1 | z_2 \rangle\) indicate ket vectors that, in position representation, are normalized Gaussians

\[
\langle x | z \rangle = \left( \frac{\det \gamma}{\pi^N} \right)^{1/4} \exp \left\{ -\frac{1}{2} (x - q_i)^T \gamma (x - q_i) \right\}
\]

\[
+ \frac{i}{\hbar} p_i^T (x - q_i)
\]

with a positive definite, real valued and diagonal width parameter matrix \(\gamma \) for a wide range of whose entries all the numerical results are independent of their value, although in molecular systems there is an ‘optimal’ choice (in the sense of ease of convergence) of the entries, determined by the frequency of the oscillations around the minimum of the harmonic approximation of the respective part of the potential.

Furthermore \(\beta = 1/kT\) with Boltzmann constant \(k\), and use has been made of the helpful identities [3]

\[
\langle z_1 | q, \hat{A} | z_2 \rangle = i\hbar \langle z_1 | z_2 \rangle \frac{\partial}{\partial p} \langle z_1 | \hat{A} | z_2 \rangle,
\]

the second of which being valid in the high temperature limit for the canonical density operator \(\hat{\rho} \sim \exp \{-\beta H\}\), with \(H(z)\) the classical Hamiltonian (taken at the average variables), and

\[
Q = \frac{1}{(2\pi\hbar)^N} \int d^{2N}z \exp \{-\beta H(z)\},
\]

the classical partition function. Equation (7) therefore is the purely classical canonical density, see also [10]. The high-temperature limit has been seen to yield surprisingly good results, also for intermediate temperatures, see e.g. [3, 6]. In passing we note that the full integral expression in (2) is real (as it has to be by comparison to (1)), as can be seen by the structure of the integrand.

The dynamical part of the approximate response function has been gained by the use of the SC HK [4] time-evolution operator

\[
\exp \{-i\hat{H}/\hbar\} \approx \int d^{2N}z \exp \left\{ \frac{i}{\hbar} \int C(z, t) |z\rangle \langle z| \right\}
\]

\[
= \int d^{2N}z \exp \left\{ \frac{i}{\hbar} S(z, t) \right\} |z\rangle
\]

with the HK prefactor

\[
S(z, t) = \sqrt{\det \mathbf{H}},
\]

where

\[
h = \frac{1}{2} \left( \mathbf{m}_{11} + \gamma \mathbf{m}_{22} \gamma^{-1} - i/\gamma \mathbf{m}_{21} - \frac{1}{i\hbar} \mathbf{m}_{12} \gamma^{-1} \right).
\]

The \(\mathbf{m}_{ij}\) are sub-blocks of the monodromy matrix

\[
\mathbf{M} = \begin{pmatrix} \mathbf{m}_{11} & \mathbf{m}_{12} \\ \mathbf{m}_{21} & \mathbf{m}_{22} \end{pmatrix} \equiv \begin{pmatrix} \frac{\partial p_i}{\partial q_j} & \frac{\partial p_i}{\partial q_j} \\ \frac{\partial q_i}{\partial q_j} & \frac{\partial q_i}{\partial q_j} \end{pmatrix}.
\]

Furthermore, \(S(z, t) = \int_0^t dt' L\) is the classical action functional with the Lagrangian \(L = T - V\). Frequently, the HK propagator is referred to as a SC-IVR of the propagator, because the only dynamical quantities that enter the final expression are solutions of classical initial value problems. Its historical precursor is the frozen Gaussian wavepacket dynamics of Heller [11].

Another prominent IVR, but this time of the wavefunction, is the thawed Gaussian wavepacket dynamics (TGWD) of Heller [12], which is based on a single classical trajectory (the center trajectory of the Gaussian wavepacket). There is a close connection between the HK propagator applied to a Gaussian wavepacket and TGWD. By doing an expansion of the exponent in the HK expression up to second order around the wavepacket center (also referred to as ‘linearization’, because the positions and momenta are expanded up to first order) and performing the resulting Gaussian integral, TGWD follows from the HK-propagator applied to a Gaussian wavepacket [9, 13, 14]. We stress...
that this procedure is inferior to a stationary phase approximation; the TGWD therefore is not a strict SC theory. The question, however, is if something similar can be done for the correlation function of IR spectroscopy. As noted previously [3] and as shown in the appendix, using calculus analogous to the one used in [9], this is indeed the case. There exists, however, no wavepacket center in the SC correlation function for IR spectroscopy to expand around, but one expands around the center variable and the linearization is performed in the difference variables after a transformation to mean and difference variables for the double phase space integral in (2). The final result (A24) is referred to as the LSC-IVR for IR spectroscopy [3, 7, 15].

This connection between the full HK and the linearized expression now serves as the starting point to the hybrid approach to IR spectroscopy. First we rewrite equation (2) in a form appropriate for numerical calculations [3]

\[
\begin{align*}
R^{(1)}_{\text{HK}}(t) &= \frac{\beta}{mQ(2\pi\hbar)^{N+1}} \int d^{2N}x \exp \{-\beta H(z)\} \mathbf{p}_S^T \\
&\times \int d^{2N}\Delta z \left\{ \mathbf{q}_i + \frac{i}{2\hbar} \gamma^{-1} \Delta \mathbf{p}_i \right\} \\
&\times C(\mathbf{z} + \Delta \mathbf{z}/2, t) C(\mathbf{z} - \Delta \mathbf{z}/2, t) \\
&\times \exp \left\{ \frac{1}{\hbar} \left[ S(\mathbf{z} + \Delta \mathbf{z}/2, t) - S(\mathbf{z} - \Delta \mathbf{z}/2, t) \right] \right\} \\
&\times \exp \left\{ -\frac{1}{4}(\Delta \mathbf{q}_i^T \gamma^{-1} \Delta \mathbf{q}_i + \Delta \mathbf{q}_i^T \gamma \Delta \mathbf{q}_i) \\
&- \frac{i}{\hbar} \mathbf{p}_i^T \Delta \mathbf{q}_i + \frac{1}{\hbar} \mathbf{p}_i \Delta \mathbf{q}_i \\
&- \frac{1}{4\hbar^2}(\Delta \mathbf{p}_i^T \gamma^{-1} \Delta \mathbf{p}_i + \Delta \mathbf{p}_i^T \gamma^{-1} \Delta \mathbf{p}_i) \right\},
\end{align*}
\]

(13)

For the remaining ‘bath’ DOF we use the phase space variables \( \mathbf{p}_B \) and \( \mathbf{q}_B \) of ‘dimension’ \( n \). The double phase space integration over the harmonic modes shall now be treated in a linearized fashion as indicated in the appendix. In this way that sub phase-space double-integral condenses into a single phase-space integral and a hybrid expression of the form

\[
\begin{align*}
\hat{R}^{(1)}_{\text{hy}}(t) &= \frac{\beta}{mQ(2\pi\hbar)^{N+n}} \int d^{2N}x \exp \{-\beta H(z)\} \mathbf{p}_S^T \\
&\times \int d^{2n}\Delta \mathbf{z} \left\{ \mathbf{q}_{S,i} + \frac{i}{2\hbar} \gamma^{-1} \Delta \mathbf{p}_{S,i} \right\} \\
&\times \left[ \mathbf{h}(\mathbf{z} + \Delta \mathbf{z}/2, t) \mathbf{h}^*(\mathbf{z} - \Delta \mathbf{z}/2, t) \right] \\
&\times \exp \left\{ -\frac{i}{4}(\Delta \mathbf{q}_{S,i}^T \gamma^{-1} \Delta \mathbf{q}_{S,i} + \Delta \mathbf{q}_{S,i}^T \gamma \Delta \mathbf{q}_{S,i}) \\
&- \frac{i}{\hbar} \mathbf{p}_{S,i}^T \Delta \mathbf{q}_{S,i} + \frac{1}{\hbar} \mathbf{p}_{S,i} \Delta \mathbf{q}_{S,i} \\
&- \frac{1}{4\hbar^2}(\Delta \mathbf{p}_{S,i}^T \gamma^{-1} \Delta \mathbf{p}_{S,i} + \Delta \mathbf{p}_{S,i}^T \gamma^{-1} \Delta \mathbf{p}_{S,i}) \right\}
\end{align*}
\]

(14)

emerges where \( \Delta \mathbf{z} \) denotes difference variables which are zero in the harmonic DOFs, \( \gamma_B \) is the sub-block of the width parameter matrix corresponding to the system DOFs (the width parameter matrix contains no coupling between its sub-blocks), and the vertical bars under the square root denote taking the determinant.

Furthermore, we used the \( 2n \times 2n \) matrix

\[
\mathbf{A}_B = \frac{1}{4\hbar^2} \begin{pmatrix}
\begin{array}{cccc}
\gamma^{-1} & \mathbf{m}_{B1}^T \gamma^{-1} \mathbf{m}_{B1} & \mathbf{m}_{B2}^T \gamma^{-1} \mathbf{m}_{B2} & \mathbf{m}_{B3}^T \gamma^{-1} \mathbf{m}_{B3} \\
\mathbf{m}_{B1} \mathbf{m}_{B1}^T \gamma^{-1} & \mathbf{m}_{B2} \mathbf{m}_{B2}^T \gamma^{-1} & \mathbf{m}_{B3} \mathbf{m}_{B3}^T \gamma^{-1} \\
\mathbf{m}_{B2} \mathbf{m}_{B2}^T \gamma & \mathbf{m}_{B3} \mathbf{m}_{B3}^T \gamma & \mathbf{m}_{B4} \mathbf{m}_{B4}^T \\
\mathbf{m}_{B3} \mathbf{m}_{B3}^T \gamma^{-1} & \mathbf{m}_{B4} \mathbf{m}_{B4}^T \gamma^{-1} & \mathbf{m}_{B1} \mathbf{m}_{B1}^T \gamma^{-1} & \mathbf{m}_{B2} \mathbf{m}_{B2}^T \gamma^{-1} & \mathbf{m}_{B3} \mathbf{m}_{B3}^T \gamma^{-1} & \mathbf{m}_{B4} \mathbf{m}_{B4}^T \\
\mathbf{m}_{B2} \mathbf{m}_{B2}^T \gamma & \mathbf{m}_{B3} \mathbf{m}_{B3}^T \gamma & \mathbf{m}_{B4} \mathbf{m}_{B4}^T & \mathbf{m}_{B1} \mathbf{m}_{B1}^T \gamma^{-1} & \mathbf{m}_{B2} \mathbf{m}_{B2}^T \gamma^{-1} & \mathbf{m}_{B3} \mathbf{m}_{B3}^T \gamma^{-1} & \mathbf{m}_{B4} \mathbf{m}_{B4}^T \\
\end{array}
\end{pmatrix}
\]

(15)

by integrating over mean and difference variables, defined in equations (3), (4). Now we assume that there are \( m \) (anharmonic) IR active modes of a molecule coupled to a number \( n \) of, e.g., harmonic modes, that could either be modes of the same molecule or could be modes of a solvent environment. Then we will keep the full HK expression for the anharmonic modes (our ‘system of interest’) and will perform a transition to the classical (linearized) form of the expression for the remaining DOF in a similar spirit as it was done for the wavefunction in [9].

To proceed, we denote the momenta and coordinates of the portion of the total number of DOF, which we want to treat with the full HK approach, i.e., the IR active DOF, by the ‘system’ vectors \( \mathbf{p}_S \) and \( \mathbf{q}_S \) with \( m = N - n \) entries, with \( \gamma_B \) denoting the bath sub-block of the width parameter matrix. The \( \mathbf{m}_B \) matrices are rectangular \( N \times n \) sub-blocks of the stability matrix, see also [9].

Formally, the expression in equation (14) does not look as compact as the starting expression (2) but for applications it has the decisive advantage to be a much less high-dimensional integral (the second phase space integral is only \( 2m \) dimensional), in complexity somewhere in between the full double phase space integral expression and the linearized, single phase space integral (A24) of the appendix. We stress that the bath DOF are not traced out as in reduced expressions in the spirit of Feynman and Vernon [16]. They are explicitly taken into account dynamically, comprising their coupling to the system dynamics, see also [9]. In addition
there is no restriction with respect to the form of the coupling between system and bath, although below we will specify this to be bilinear.

Similar ideas have appeared in the literature before. For related semiclassically spirited work, see [17–19]. Analogous simplifications of the double phase space integral may occur in the large body of work that is based on the forward–backward idea of the Makri and Miller groups with or without using a Filinov transformation [20–24]. It has been stressed, however, that for dipole–dipole correlation functions, the standard forward–backward methods do not go beyond the level of LSC-IVR [23]. A recent review of analogous quantum classical hybrid approaches is given in [25].

3. Numerical results

The model system of interest that we study in the following is a 1D Morse oscillator with unit mass and the potential

$$V_M(x) = D[1 - \exp(-\alpha x)]^2.$$  \hspace{1cm} (16)

The dimensionless potential parameters $D = 100$ and $\alpha = 0.2 \sqrt{2}$ are the same that have been used in a dissipative case study based on hierarchical equations of motion [6]. The eigenenergies (setting also $\hbar$ equal to unity)

$$E_n = \omega_e (n + 1/2) - x_e \omega_e(n + 1/2)^2, \quad n = 0, 1, ....$$  \hspace{1cm} (17)

Of the Morse potential [26] contain the two parameters $\omega_e = \alpha \sqrt{2D}$ and $x_e = \omega_e/(4D)$, corresponding to the frequency of harmonic oscillations around the potential minimum and the anharmonicity constant.

For this initial study of the method, and to be able to compare to exact quantum results, the number of bath DOF of unit mass shall also be restricted to one, and the coupling between system and bath is taken bilinear such that the full Hamiltonian of the 2 DOF problem is given by

$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{SB}$$

$$= \frac{\hat{p}_S^2}{2} + V_M(x_S) + \left(\frac{\hat{p}_B^2}{2} + D(\chi x_B)^2 - \eta x_S x_B \right),$$  \hspace{1cm} (18)

where $\chi$ can be used to tune the harmonic mode in or out of ‘resonance’ with the Morse oscillator and $\eta$ denotes the coupling strength.

In the following, we will show comparisons of full quantum (for a description of the numerical method used, please see [6]), full HK, full LSC-IVR and hybrid results for the linear response function. As has been highlighted in figure 1(a) of [5] as well as in [6] (see also figure 1(a) below), in the case of just one single anharmonic degree of freedom without coupling to a bath mode, the full quantum response function shows a beating pattern with fast oscillations corresponding to roughly the harmonic frequency around the minimum of the potential curve and recurrence periods proportional to $1/(\omega_e x_e)$ [5]. The full HK result shows almost complete agreement with the full quantum result [5] (see also figure 3(a) below).

Figure 1. The fully quantum linear response correlation function of an infrared active 1D Morse oscillator for dimensionless temperature $T = 7$: (a) without coupling ($\eta = 0$) (b) with coupling ($\eta = 0.1$) to a harmonic oscillator with $\chi = 0.9$.

Figure 2. The LSC-IVR linear response correlation function of an infrared active 1D Morse oscillator for dimensionless temperature $T = 7$: (a) without coupling ($\eta = 0$) (b) with coupling ($\eta = 0.1$) to a harmonic oscillator with $\chi = 0.9$. 

4
For the potential parameters considered herein, we show a comparison between the uncoupled and the coupled correlation function in the fully quantum case in figure 1. There it can be seen that the coupling introduces additional complexity into the beating signal without coupling, displayed in panel (a). So in panel (b) after a dimensionless time around $t = 40$, the signal deviates from the one in panel (a) and also the maximum amplitude of the signal at around $t = 80$ is reduced although a remnant of the recurrence time scale is still clearly observed. For larger values of the coupling the deviations from the result without coupling set in earlier in time and are more severe at later times (not shown).

Furthermore, for reasons of completeness, we also show the corresponding results in the LSC-IVR case of the appendix in figure 2. Firstly, there is no recurrence in the signal without coupling to be observed. As has been noticed in [5] this recurrence is a quantum effect and the corresponding time scale goes to infinity in the classical limit. The coupling induces additional complexity into the signal but its overall height after around $t = 30$ is still marginal.

In figure 3 the same comparison is now made between the corresponding full HK signals (both DOF are sampled in the mean as well as in the difference phase space variables) and very similar (although not identical) results as in the quantum case of figure 1 can be observed.

In figure 4 the central result of the present study is displayed. This is an implementation of the correlation function of (14) in the hybrid case. It can be seen that, although the difference variables of the harmonic DOF is unsampled (i.e. it is described on the linearized level of the appendix), the sampling of the difference variables of the anharmonic degree DOF is enough to reproduce the recurrence in the time series to a surprisingly high degree. Similar to the full quantum and the HK case, the amplitude of the revival is diminished compared to the uncoupled case, which is a first sign of a quantum-classical transition.

The computational strategy to tackle the phase space integrals for the classical trajectory based methods was to use Monte Carlo integration with importance sampling [27] for both, the integral over the mean as well as the one over the difference variables. For the difference variable integration, the weight function is given by the Gaussian exponential terms in equation (13) and Box–Muller sampling was used [28]. The two entries of the $\gamma$ matrix in the 2d case were chosen as $\gamma_{\alpha} = \sqrt{2D_{\alpha}}$, respectively $\gamma_{\beta} = \chi\sqrt{2D_{\alpha}}$. For the mean variables we again employ a Gaussian weight function with temperature-dependent width factors which for the system degree of freedom is determined by the harmonic approximation to the Morse potential (the kinetic energy is already a quadratic form). The classical trajectories (i.e. the solution of Hamilton’s equations) were propagated together with the classical action and the stability information using a symplectic integration scheme (position Verlet) [29] with a time step of $\Delta t = 0.04$. More information on the numerical procedure can be found in section 2.3.4 of [30].

With the importance sampling procedure described above, in the case of a single degree of freedom and for LSC-IVR around $10^6$ trajectories are enough for converged results to within line thickness as long as the correlation function has not decayed to too small values and $10^7$ trajectories are enough in the HK case, that is plagued by the sign problem [24], for a single DOF. The HK calculations require the determination of the stability information and the evaluation of exponentials and also of square roots of complex numbers, however, and therefore are much more time consuming (by more than just an order of magnitude) than the LSC-IVR ones.

The higher the dimensionality of the integral, the better the Monte Carlo method is suited. Therefore we do not need a...
lot more trajectories to get converged results in the 2 DOF case for the LSC-IVR as well as for the HK calculations. In the 2d HK case $4 \times 10^3$ trajectories are needed to converge the results also for later times. This high number can be reduced by more than an order of magnitude, if the hybrid idea put forth herein is used. In the hybrid case, whose results are displayed in figure 4, only $10^5$ trajectories were necessary for convergence in the 2 DOF case. At short times (during the initial decay of the correlation) less trajectories will generally be needed and a thorough convergence check at any given instance of time (which is prohibitive) would uncover a different number of trajectories depending on the time considered. The trajectory numbers given here are always for the later times and because we have to propagate all those trajectories anyways to the very end (because they will eventually all be needed), they are conveniently used for the calculations at any instance of time.

Alternative integration strategies can be envisaged (e.g. applying a Metropolis algorithm for the mean variable integral [3]). Most recent success in improving the convergence of SC calculations has been reported in a study that employs a sampling along the fastest growing manifold of a defining trajectory [31]. For the first account of the new methodology presented here we have not tried to optimize the numerical details, however.

4. Conclusions and outlook

We have formulated a SC hybrid approach to linear IR spectroscopy which is based on the same idea as the SC hybrid dynamics put forth previously for wavefunctions [9] as well as for density matrices [32] and, after a Fourier transform, has also been combined with time-averaging for the calculation of power spectra [33]. A partial linearization in the difference variables of the full double HK expression for the correlation function leads to a working formula with a reduced dimensionality of the remaining integral to be performed numerically. Already in the case of a single DOF treated in the simplified manner, a substantial reduction of the numerical effort has been achieved, as demonstrated for an anharmonic oscillator bilinearly coupled to a harmonic one. We do observe a reduction of the amplitude of the recurrence of the correlation function in the full quantum as well as in the SC results due to the coupling of the harmonic mode, which is a first indication of a quantum-classical transition. If more harmonic oscillators will be coupled to the system of interest and are treated by the proposed methodology, we expect to observe a complete quantum-classical transition, i.e., a decaying correlation without any revivals. In addition, it would also be interesting to investigate the effects of coupling that is not bilinear in the system and bath coordinates. The presented methodology is capable of handling this case as well.

The work herein is based on a double HK expression, that involves a double phase space integration if no further approximations are made. There exist alternative phase space approaches based on SC approximations in a Wigner–Weyl representation of quantum mechanics [34–36]. It will be very worthwhile to examine the connections between the HK and the Wigner–Weyl approach in the present context [37]. Furthermore, in future work, we want to extend the idea presented here to arbitrary temperatures as well as to the calculation of higher order correlation functions needed for nonlinear spectroscopic techniques.

Acknowledgments

The author would like to thank Jiri Vanicek and Alfredo M Ozorio de Almeida for valuable discussions and the Max-Planck-Institute for the Physics of Complex Systems for the opportunity to take part in the meetings of the Advanced Study group on ‘Semiclassical Methods: Insight and Practice in ‘Many’ Dimensions’ led by Eric J Heller and Steven Tomsovic. Financial support by the Deutsche Forschungsgemeinschaft under GR 1210/4-2 is gratefully acknowledged.

Appendix. LSC-IVR for $R^{(1)}(t)$ in the case of $N$ DOF

In this appendix we recall the derivation of the LSC-IVR approximation for linear IR spectroscopy. A simplification of the full HK expression (2) can be achieved by expanding the classical actions in the exponent around the mean phase space point $\bar{z}$ up to second order, using

$$S(\mathbf{z}, t) \approx S(\bar{z}) + \frac{\partial S}{\partial \mathbf{z}}(\mathbf{z} - \bar{z}) + \frac{1}{2} \frac{\partial^2 S}{\partial \mathbf{z}^2}(\mathbf{z} - \bar{z})^2,$$  \hspace{1cm} (A1)

$$S(\mathbf{z}, t) \approx S(\bar{z}) + \frac{\partial S}{\partial \mathbf{z}}(\mathbf{z} - \bar{z}) + \frac{1}{2} \frac{\partial^2 S}{\partial \mathbf{z}^2}(\mathbf{z} - \bar{z})^2.$$  \hspace{1cm} (A2)

Taking the action difference, the second order term cancels and by using

$$\frac{\partial S}{\partial \mathbf{p}} = \mathbf{p},$$  \hspace{1cm} (A3)

$$\frac{\partial S}{\partial \mathbf{q}} = \mathbf{p},$$  \hspace{1cm} (A4)

we get

$$S(\mathbf{z}, t) - S(\mathbf{z}, t) \approx \mathbf{p} \cdot \Delta \mathbf{z} + (\mathbf{p}_2 - \mathbf{p}) \cdot \Delta \mathbf{q}. \hspace{1cm} (A5)$$

In the overlaps of the Gaussians appearing in the HK time-evolution operator

$$\left< \mathbf{z}_{2,t} | \mathbf{z}_{1,i} \right> = \exp \left\{ -\frac{1}{4} \Delta \mathbf{q}^T \Gamma \Delta \mathbf{q} - \frac{i}{\hbar} \mathbf{p}_1^T \Delta \mathbf{q}, \right. \hspace{1cm} (A6)

$$- \frac{1}{4\hbar^2} \Delta \mathbf{p}_1^T \Gamma^{-1} \Delta \mathbf{p}_1 \right\},$$

the linear expansions

$$\Delta \mathbf{p}_1 = \mathbf{m}_1 \Delta \mathbf{p} + \mathbf{m}_2 \Delta \mathbf{q}, \hspace{1cm} (A7)$$

$$\Delta \mathbf{q}_1 = \mathbf{m}_2 \Delta \mathbf{p} + \mathbf{m}_2 \Delta \mathbf{q} \hspace{1cm} (A8)$$

are made and the phase factors in (2) cancel out. Consistently, we take a zeroth order expansion of the preexponential factor (i.e., we set $\Delta \mathbf{z} = 0$ in the prefactor [3]) and change from the volume elements $d^{2N}z_1d^{2N}z_2$ to $d^{2N}z_1d^{2N}z_2$ (the absolute value
of the Jacobian is unity). Then, the intermediate result
\[ R^{(1)}_{\text{IR}}(t) = \frac{\beta}{m Q (2\pi\hbar)^N} \int d^N z \int d^N \Delta z \exp \{ -\beta H(z) \} \]
\[ \times \tilde{p}^\dagger \tilde{q}^\dagger |C(\tilde{z}, t)|^2 \]
\[ \times \exp \left\{ -\frac{1}{4\hbar^2} \Delta p^\dagger (\gamma^{-1} + \tilde{m}^\dagger_1 \gamma^{-1} \tilde{m}_{11} + \hbar^2 \tilde{m}^\dagger_2 \gamma^2 \tilde{m}_{21}) \Delta p \right\} \]
\[ - \frac{1}{4} \Delta q^\dagger \left[ \gamma + \tilde{m}^\dagger_1 \gamma \tilde{m}_{12} + \frac{1}{\hbar^2} \tilde{m}^\dagger_2 \gamma^{-1} \tilde{m}_{12} \right] \Delta q \]
\[ - \frac{1}{2} \Delta q^\dagger \left[ \tilde{m}^\dagger_2 \gamma \tilde{m}_{21} + \frac{1}{\hbar^2} \tilde{m}^\dagger_2 \gamma^{-1} \tilde{m}_{21} \right] \Delta p \} \]  
(A9)
for the LSC-IVR result emerges.

The expression in (A9), however, can be further simplified by noting that
\[ I = \int d^N \Delta z \left\{ \frac{|C(\tilde{z}, t)|^2}{(2\pi\hbar)^N} \left( \exp \{ -\Delta z^\dagger A \Delta z \} \right) \right\} \]
\[ = |C(\tilde{z}, t)|^2 \left( \frac{\pi^{2N}}{(2\pi\hbar)^N} \right)^{1/2} \]
holds for the integral over the difference coordinate, with
\[ |C(\tilde{z}, t)|^2 = \left( \det \left[ \frac{1}{2} [\tilde{m}_{11} + \gamma \tilde{m}_{22} \gamma^{-1} + i/\hbar \gamma \tilde{m}_{21} + \frac{1}{\hbar} \tilde{m}_{12} \gamma^{-1}] \right] \right)^{1/2} \]
\[ \times \left( \det \left[ \frac{1}{2} [\tilde{m}_{11} + \gamma \tilde{m}_{22} \gamma^{-1} - i/\hbar \gamma \tilde{m}_{21} - \frac{1}{\hbar} \tilde{m}_{12} \gamma^{-1}] \right] \right)^{1/2} \]
(A11)
and
\[ A = \frac{1}{4\hbar^2} \left( \gamma^{-1} + \frac{1}{\hbar} \tilde{m}^\dagger_1 \gamma^{-1} \tilde{m}_{11} + \frac{1}{\hbar^2} \tilde{m}^\dagger_2 \gamma^2 \tilde{m}_{21} + \frac{1}{\hbar^2} \tilde{m}^\dagger_2 \gamma^{-1} \tilde{m}_{21} \right) \]
where we have used the relations [9]
\[ \frac{m_{11}^T \tilde{m}_{11} - m_{21}^T \tilde{m}_{21}}{m_{12}^T \tilde{m}_{12} - m_{11}^T \tilde{m}_{11}} = 1, \]
\[ m_{11}^T \tilde{m}_{11} - m_{12}^T \tilde{m}_{12} = 0, \]
\[ m_{21}^T \tilde{m}_{21} - m_{11}^T \tilde{m}_{11} = 0, \]
valid for the sub matrices of the monodromy matrix and where the superscript \( \dagger \) indicates the (Hermitian) adjunct of the matrix.

The determinant of the block matrix is given by
\[ \det A = \det \left( \begin{array}{cc} a_{11} & a_{12} \\ a_{21} & a_{22} \end{array} \right) = \det(a_1 a_2 - a_1 a_2) \]
(A20)

After a bit of algebra we can manipulate the difference of block matrix products into the helpful intermediate form
\[ a_1 a_2 - a_1 a_2 = a_1 a_2 a_1 a_2 = \frac{1}{16} \left( r^\gamma - \frac{i}{\hbar} s^\gamma \right) \]
\[ \times \left( r^\gamma - \frac{i}{\hbar} s^\gamma \right) \]
(A21)

Now because of \( \det a = \det a^T \) this cancels the determinants from the preexponential factor as well as all constants and we
\[ A = \frac{1}{4\hbar^2} \left( \gamma^{-1} + \frac{1}{\hbar} \tilde{m}^\dagger_1 \gamma^{-1} \tilde{m}_{11} + \frac{1}{\hbar^2} \tilde{m}^\dagger_2 \gamma^2 \tilde{m}_{21} + \frac{1}{\hbar^2} \tilde{m}^\dagger_2 \gamma^{-1} \tilde{m}_{21} \right) \]
(A12)
get
\[ I = 1, \]
(A23)

a result that, albeit along different lines, has been proven before [3, 10].

The final result for the linear IR correlation function in the LSC approximation therefore is
\[ R^{(1)}_{\text{IR}}(t) = \frac{\beta}{m Q (2\pi\hbar)^N} \int d^N z \exp \{ -\beta H(z) \} \tilde{p}^\dagger \tilde{q}, \]
(A24)
with \( Q \) defined in equation (8). We stress that, firstly, the width parameter matrix \( \gamma \) does not appear in the final expression any more and secondly, the quantity \( \hbar \) only enters in the prefactor of the final expression in the same manner as in classical statistical mechanics and does not appear together with any dynamical quantities any more. In addition to the classical approximation to the thermal density operator of equation (7), now also the dynamical part of the correlation function is treated classically.

Phys. Scr. 91 (2016) 044004  F Grossmann
and therefore equation (A24) is a purely classical result, sometimes also called the classical Wigner result.

We note that this final result can also be proven along different lines. In [15], e.g., the derivation started directly from the path integral, without invoking an intermediate SC approximation. In [10], however, it was shown that this result can be gained by starting from a double phase space integral with HK propagators and, instead of the linearization recapitulated here, by doing a stationary phase integration in the difference variable in the high temperature limit (for low temperatures, the stationary phase condition $z_1 = z_2$ is only approximately fulfilled).

Furthermore, if the two time evolution operators in the original expression (2) are due to different Hamiltonians and both position operators are replaced by unit operators, then calculus analogous to the one reviewed here leads to the an expression still involving a phase factor, which is called dephasing representation of fidelity decay [38]. Finally, we note that the calculations performed in this appendix become trivial in the case of $N = 1$, i.e., for a single degree of freedom, because then the sub-block matrices in (A20) become numbers and do commute!

References

[1] Tanimura Y 2006 J. Phys. Soc. Japan 75 082001
[2] Mukamel S 1995 Principles of Nonlinear Optical Spectroscopy (New York: Oxford University Press)
[3] Noid W G, Ezra G S and Loring R F 2003 J. Chem. Phys. 119 1003
[4] Herman M F and Kluk E 1984 Chem. Phys. 91 27
[5] Gruenbaum S M and Loring R F 2008 J. Chem. Phys. 128 124106
[6] Grossmann F 2014 J. Chem. Phys. 141 144305
[7] Liu J and Miller W H 2007 J. Chem. Phys. 126 234110
[8] Moberg D R, Alemy M and Loring R F 2015 J. Chem. Phys. 143 084101
[9] Grossmann F 2006 J. Chem. Phys. 125 014111
[10] Herman M F and Coker D F 1999 J. Chem. Phys. 111 1801
[11] Heller E J 1981 J. Chem. Phys. 75 2923
[12] Heller E J 1975 J. Chem. Phys. 62 1544
[13] Grossmann F 1999 Commun. At. Mol. Phys. 34 141
[14] Deshpande S A and Ezra G S 2006 J. Phys. A: Math. Gen. 39 5067
[15] Shi Q and Geva E 2003 J. Chem. Phys. 118 8173
[16] Feynman R P and Vernon F L 1963 Ann. Phys. (N.Y.) 24 118
[17] Sun X and Miller W H 1997 J. Chem. Phys. 106 916
[18] Ovchinnikov M and Apkarian V A 1998 J. Chem. Phys. 108 2277
[19] Antipov S V, Ye Z and Ananth N 2015 J. Chem. Phys. 142 184102
[20] Thomoson K and Makri N 1999 J. Chem. Phys. 110 1343
[21] Sun X and Miller W H 1999 J. Chem. Phys. 110 6635
[22] Wang H, Thoss M and Miller W H 2000 J. Chem. Phys. 112 47
[23] Thoss M, Wang H and Miller W H 2001 J. Chem. Phys. 114 9220
[24] Zhao Y and Makri N 2002 Chem. Phys. 280 135
[25] Kapral R 2015 J. Phys.: Condens. Matter 27 073201
[26] Morse P M 1929 Phys. Rev. 34 57
[27] Press W H, Teukolsky S A, Vetterling W T and Flannery B P 1992 Numerical Recipes in Fortran 2nd edn (Cambridge: Cambridge University Press)
[28] Kluk E, Herman M F and Davis H L 1986 J. Chem. Phys. 84 326
[29] Gray S K, Noid D W and Sumpter B G 1994 J. Chem. Phys. 101 4062
[30] Grossmann F 2013 Theoretical Femtosecond Physics: Atoms and Molecules Strong Laser Fields 2nd edn (Berlin: Springer)
[31] Kocia L and Heller E J 2014 J. Chem. Phys. 141 181102
[32] Goletz C-M and Grossmann F 2009 J. Chem. Phys. 130 244107
[33] Buchholz M, Grossmann F and Ceotto M 2016 J. Chem. Phys. 144 094102
[34] Ovchinnikov M and Apkarian V A 1998 J. Chem. Phys. 118 8173
[35] Dittrich T, Viviescas C and Sandoval L 2006 Phys. Rev. Lett. 96 070403
[36] Dittrich T, Gomez E A and Pachon L A 2010 J. Chem. Phys. 132 214102
[37] Ovchinnikov M and Apkarian V A 1998 J. Chem. Phys. 118 8173
[38] Vanicek J 2006 Phys. Rev. E 73 046204