Boltzmann-conserving classical dynamics in quantum time-correlation functions: 'Matsubara dynamics'

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Quantum Time-Correlation Functions

These describe a whole host of dynamical properties, including

- Chemical reaction rates (flux-side correlation functions)
- Dipole absorption spectra (dipole moment autocorrelation functions)
- Diffusion constants (velocity autocorrelation functions).

The quantum time-correlation function for the operators $\hat{A}$ and $\hat{B}$ is

$$C_{AB}(t) = \mathrm{Tr}\left[e^{-\beta\hat{H}}\hat{A}e^{+i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}\right]$$

and combines quantum Boltzmann statistics and quantum dynamics.

- Most single-surface chemistry can likely be understood with a combination of quantum Boltzmann statistics and classical dynamics.
- For example, an accurate description of liquid water involves lots of quantum statistics with very little quantum phase effects.
- Classical dynamics is much easier to compute than quantum dynamics.

Linearised Semiclassical Initial Value Representation (LSC-IVR)

Linearised Semiclassical Initial Value Representation (LSC-IVR) is the existing theory for combining quantum statistics and classical dynamics for quantum real-time correlation functions.

- Truncation of the quantum Liouvillian to zeroth order in powers of $\hbar^2$ gives the classical dynamics.
- The quantum Boltzmann distribution is not conserved.
- Detailed balance is not satisfied.
- These shortcomings render LSC-IVR inadequate for a correct description of quantum statistics and classical dynamics.

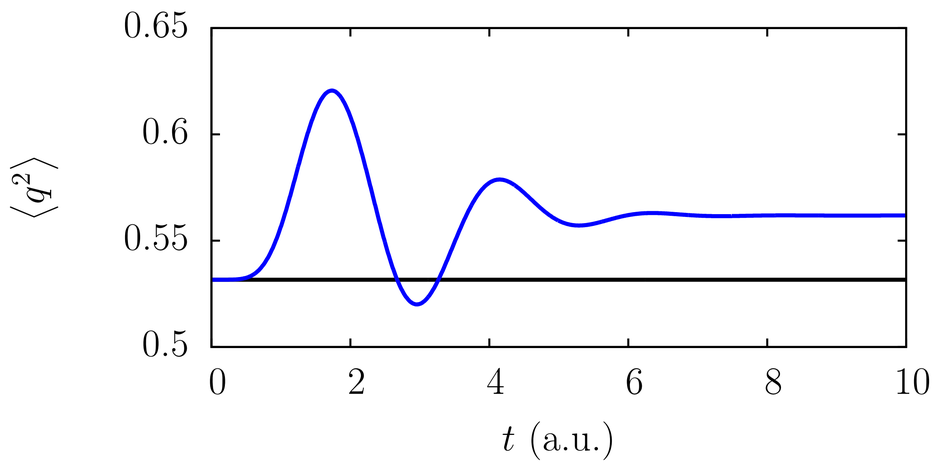

Figure 1 : Time-dependence of thermal expectation values in LSC-IVR. Exact quantum (black) and LSC-IVR (blue).

Matsubara Dynamics

We have discovered another theory which successfully combines quantum statistics and classical dynamics: Matsubara dynamics.[1]

- Truncation of the quantum Liouvillian in normal mode derivatives, to the lowest Matsubara frequencies, gives the Matsubara Liouvillian, $\mathcal{L}_{\mathcal{M}}$, (classical dynamics).
- The quantum Boltzmann distribution is conserved.
- Detailed balance is satisfied.

The corresponding correlation function is

$$C_{AB}^{[M]}(t) \propto \int d\widetilde{\mathbf{P}} \int d\widetilde{\mathbf{Q}}\; A(\widetilde{\mathbf{Q}}) e^{-\beta[H_M(\widetilde{\mathbf{P}},\widetilde{\mathbf{Q}})+i\theta_M(\widetilde{\mathbf{P}},\widetilde{\mathbf{Q}})]} e^{\mathcal{L}_M t} B(\widetilde{\mathbf{Q}})$$

where the Matsubara Hamiltonian is given by

$$H_M(\widetilde{\mathbf{P}},\widetilde{\mathbf{Q}}) = \frac{\widetilde{\mathbf{P}}^2}{2m} + \widetilde{U}_M(\widetilde{\mathbf{Q}})$$

and the potential, $\widetilde{U}_M(\widetilde{\mathbf{Q}})$, is dependent upon M Matsubara modes only.

Comparison of LSC-IVR and Matsubara Dynamics

The distribution function in Matsubara dynamics contains a complex exponential of a phase

$$\theta_M(\widetilde{\mathbf{P}},\widetilde{\mathbf{Q}}) = \sum_{n=-(M-1)/2}^{(M-1)/2} \widetilde{P}_n \widetilde{\omega}_n \widetilde{Q}_{-n}$$

where $\widetilde{\omega}_n = 2\pi n/\beta\hbar$ is the n^{th} Matsubara frequency and the summation is taken over all M of the normal modes which remain after truncation of the quantum Liouvillian. The classical Matsubara dynamics conserves this phase by virtue of maintaining smooth particle distributions in imaginary time.

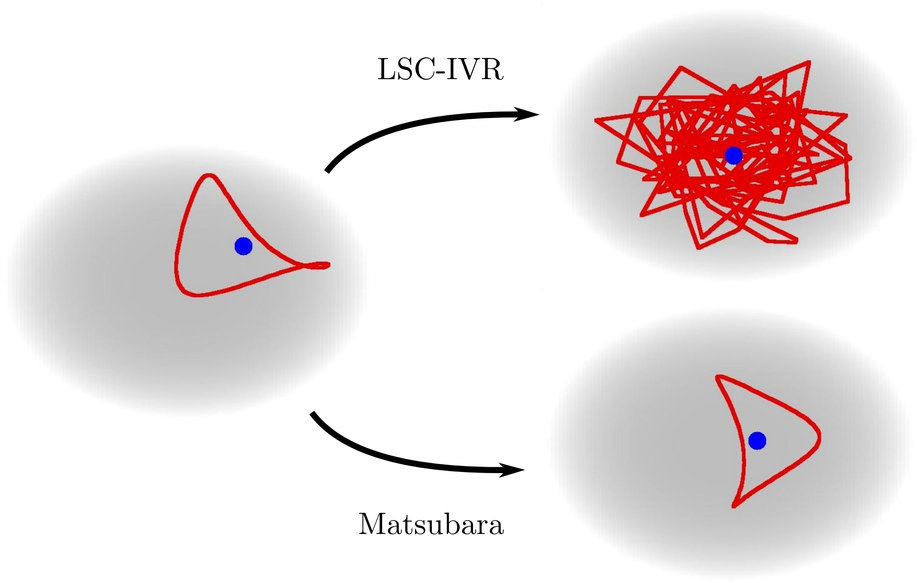

Figure 2 : Comparison of LSC-IVR evolution and Matsubara evolution for a two-dimensional quartic potential.

LSC-IVR evolution leads to jagged imaginary time particle distributions which prevent conservation of the phase and the quantum Boltzmann distribution as a result. This often leads to poor agreement with quantum time-correlation functions.

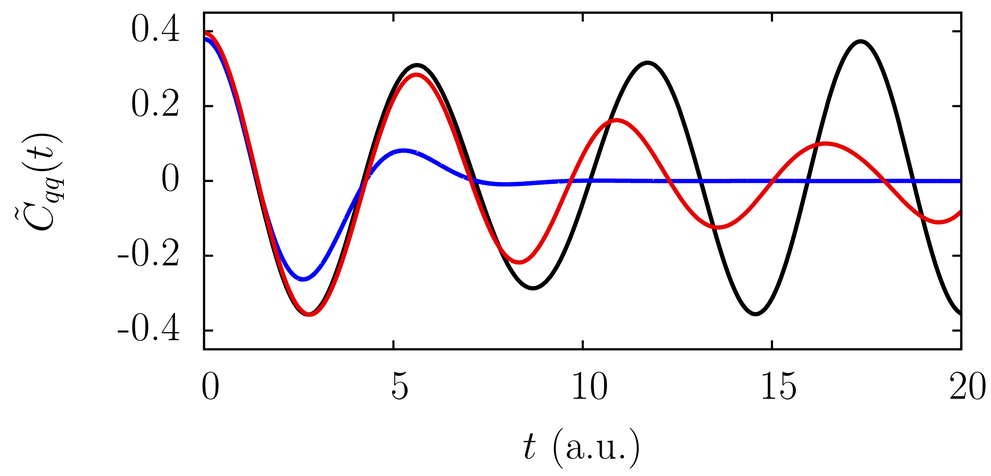

Figure 3 : Comparison of LSC-IVR and Matsubara dynamics for a one-dimensional quartic potential. Exact quantum (black), LSC-IVR (blue) and Matsubara dynamics (red).

Significance

- The Matsubara dynamics time-correlation function is the starting point for any approximate method of treating quantum statistics and classical dynamics.
- Existing approximate methods - LSC-IVR, Centroid Molecular Dynamics (CMD) and Ring Polymer Molecular Dynamics (RPMD) - can all be explained by Matsubara dynamics.
- Matsubara dynamics may lead to other computationally tractable approximate methods.
- Matsubara dynamics explains how quantum statistics and classical dynamics should be combined in quantum time-correlation functions.

References

[1] T. J. H. Hele, M. J. Willatt, A. Muolo and S. C. Althorpe, *J. Chem. Phys.* **142**, 134103 (2015).