Static and dynamic quantum effects in molecular liquids: A linearized path integral description of water

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Structure, transport properties, and IR spectra including quantum effects are calculated for a flexible simple point charge model of liquid water. A recently introduced combination of a variational local harmonic description of the liquid potential surface and the classical Wigner approximation for the dynamics is used. The potential energy and interatomic radial distribution functions are in good agreement with accurate results from the literature and are significantly closer to experiment than predictions found from classical theory. The oxygen and hydrogen velocity correlation functions are also calculated, and the corresponding molecular diffusion coefficient is in good accord with existing theoretical estimates including quantum effects. Of most interest, an ab initio quantum correction factor is obtained to correct the far IR spectrum of water. When corrected, a spectrum based on a classical simulation yields results that agree well with experiment. Combined with internal tests of consistency, these observations indicate that this quite flexible approach will be effective for a variety of molecular problems involving the dynamics of light nuclei.

Although the molecular-level description of the structure and dynamics of disordered condensed phases, such as liquids, glasses, and globular proteins, is normally, and generally successfully, described by using classical mechanics, the underlying accurate description is, of course, quantum mechanical. It is simply that the quantum effects can be sufficiently small as to be unimportant in many contexts. Nevertheless, for lower temperatures and lighter masses, quantum effects will become increasingly important. For low-temperature (~30 K or less) simple liquids, such as liquid helium and molecular hydrogen with low masses, quantum effects associated with positional uncertainty are expected to substantially broaden features in the liquid structure, and the diffusion of these effectively larger but “softer” objects is expected to be significantly altered from the classical description, even in the absence of coherent quantum dynamics (1, 2). For a molecular hydrogen-bonded liquid, such as water, the low mass of the hydrogen atom causes the intramolecular vibrations to behave quantum mechanically to quite high temperatures, and the intermolecular vibrational modes, including the relatively high-frequency librational motions (~250–900 cm⁻¹) resulting from the frustrated rotation of molecules, are significantly quantum mechanical at room temperature, where the available thermal energy, ~200 cm⁻¹, is considerably smaller than the librational quantum spacing (3).

In recent years, there has been a great deal of progress in our ability to accurately evaluate equilibrium, time-independent properties of liquids, and related materials with complete consideration of quantum mechanics. For the most part, these have been based on simulations implementing discretized path integral forms (3, 4). For dynamics, the problem is far more challenging. Approaches based on enumeration of available quantum states, which are familiar from small-molecule molecular dynamics and scattering, are completely infeasible for a many-body system at finite temperature. Direct attack via a path integral approach is also quite limited, because interference between alternative paths of particles must be considered, and the need to sum largely canceling terms to obtain the result is very poorly suited to numerical evaluation when the quantum effects are not dominant. In the case where only a few quantum states are involved, such as electronic systems, there is the opportunity to work directly in the space of the relevant eigenstates (5–7). But for most nuclear problems, including, for example, molecular or proton diffusion in room-temperature liquid water, one is in a regime where there are a myriad of relevant quantum states but significant quantum character remains. Few theoretically well founded approaches have been put forward that can address this regime in a theoretically and computationally feasible way.

Some alternative approaches, such as quantum mode coupling theory (8), can be developed for liquids composed of atomic materials, but the generalization to molecular materials is problematic. The primary approach that has seen considerable application is the so-called centroid molecular dynamics (CMD) approach (9, 10). In essence, the method involves the computation of the classical dynamical trajectories of particles on an effective potential surface that is obtained via a particular quantum average over the true potential surface. The correlation functions (CFs) obtained from these trajectories for linear operators of position and momentum can be related to the quantum CFs of these operators, assuming that the classical propagation of the classical-like centroid variables is a good approximation. For nonlinear operators, the same relation of CFs can be assumed to hold, but for highly nonlinear operators, the results obtained by this route deteriorate (11).

Many important material properties, such as diffusion constants, energy transfer and reaction rates, inelastic scattering intensities, and spectra can be expressed in terms of time CFs. Further, there can be substantial quantum effects in the results (12). Hence, theories, such as CMD, which focus on access to these CFs, rather than for the detailed atomistic trajectories, are quite valuable. Nevertheless, the practicality of such an approach derives from the fact that the results are evaluated as averages over trajectories that can be computed by using classical dynamics; however, the phase space weighting of the trajectories or the effective forces acting on particles need not be simply the same as in a fully classical description. In this article, we consider the ability of a recently introduced approach for the evaluation of CFs for quantum mechanical condensed-phase systems that

This paper was submitted directly (Track II) to the PNAS office. Abbreviations: CMD, centroid molecular dynamics; CF, correlation function; VCF, velocity correlation function; VCF, velocity correlation factor; CMD, centroid molecular dynamics; CF, correlation function; VCF, velocity correlation factor; LPI, linearized path integral; FK, Feynman and Kleinert; SPC, simple point charge; SPCf, SPC flexible; MC, Monte Carlo; RDF, radial distribution function; QCF, quantum correction factor.

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share these desirable qualities of CMD. We apply the method to the calculation of structure, diffusion, and vibrational IR spectra of liquid water.

The method has as its underlying approximations two basic elements. The first is the so-called linearization approximation, common to several recently proposed dynamics methods (13–16). This approximation essentially assumes that the amplitude of those nuclear paths that constructively add to produce the final result come from that set of paths that connect the initial and final state that differ only slightly from one another. This is a linearized path integral (LPI) approximation. This first element can be justified by considerations of coherence loss for systems in which the dynamics of many degrees of freedom are relatively well coupled to the degree of freedom that is of interest (15). The second element is that which actually allows the computation of the results for the restricted set of important paths: The quantum mechanical distribution of momenta and coordinates is approximated by that for a potential surface that uses an optimally chosen harmonic potential locally around each point in space. This variational local harmonic approximation was introduced by Feynman and Kleinert (FK) (17), and independently by Giachetti and Tognetti (18), and allows the impact of these quantum fluctuations to be prescribed analytically. That this can be done analytically is critical to obtaining a practical approach. This approach has the advantage, first, that the formulation is rigorous independent of whether the operators involved in the method are linear, and, second, the derivation makes it clear when the method should be accurate. Further, for this FK-LPI approach, it is only in the generation of initial conditions that an effective potential appears; the dynamics is computed by classical mechanics on the bare underlying potential exactly as in ordinary classical mechanical simulations, and in contrast to CMD. As with CMD, the quantization of some degrees of freedom and not others is completely straightforward to implement.

The claim (15) that the LPI, or classical Wigner, approximation is an ideal tool for obtaining approximate quantum CFs in condensed phase has been verified not only for some challenging model system problems (19–22), but more importantly, also for real liquids. Thus within the last 2 years, the LPI approximation to CFs has been successfully applied for determining (i) vibrational relaxation rates of oxygen in liquid oxygen, determined by the golden rule force-force CF (23), (ii) diffusion coefficients through the Kubo velocity CF (VCF) for liquid para-hydrogen at 17 and 25 K (2), and (iii) the spectrum of density fluctuations (Van Hove CF) of liquid He(4) at 27 K (1).

There have been earlier attacks on the quantum dynamics of liquid water, by Lobaugh and Voth (24) using CMD for an intramolecularly flexible water model, and by Hernandez de la Penia and Kusalik (25) using CMD for a rigid model of water. It is not our purpose here to show that our method is an improvement over those methods for these properties, but rather to demonstrate that the method is sufficiently readily implemented that one can readily address a general model of water with reasonable accuracy. In the next section, we very briefly describe the methods and their implementation in the present context. Then, we describe results for the quantum liquid structure, nuclear velocity, and IR spectrum, compared with both the predictions of classical mechanics and the experimental result. We conclude with a summary of observations and some comments on the outlook for future applications of the method.

Theory and Implementation

In this section we present the basic equations of the LPI or classical Wigner method and discuss how they are implemented in the FK-LPI water simulation.

The Classical Wigner Approach. The subject of this article concerns the application and implementation of probably the simplest approach to the dynamics of large quantum systems, namely the so-called classical Wigner or, equivalently, the LPI or linearized semiclassical-initial value representation approach (14, 15). The precise expression that is derived from the linearization approximation seems to have appeared first in the work of Hernandez and Voth (13). Although it is not a precise statement, the LPI method can be thought of as corresponding to the calculation of statistical dynamical properties by averaging over trajectories with initial conditions consistent with quantum mechanical position and momenta distributions (the Wigner phase space distribution), but with dynamics propagated with only classical dynamics. In its formal representation, it can be summarized as follows. To obtain the CF $\langle \hat{A}(0)\hat{B}(t) \rangle$ (the brackets indicate an average over statistical conditions at time 0, and $\hat{A}$ and $\hat{B}$ are operators), one makes use of the approximate classical Wigner expression:

$$\langle \hat{A}(0)\hat{B}(t) \rangle \approx \frac{1}{(2\pi\hbar)^{3N}} \int dq dp \frac{Z}{\pi \hbar} \exp(-\beta\hbar\hat{A}) w(q, p) \cdot (\hat{B}) w(q, p).$$

[1]

The interpretation/implementation of Eq. 1 goes as follows: phase-space points $(q, p)$ are sampled from the Wigner transform of $\exp(-\beta\hbar\hat{A})$, the transform being defined for an arbitrary operator $\hat{C}$ by:

$$(\hat{C}) w[q, p] = \int_{-\infty}^{+\infty} d\eta \exp(-i\eta q / \hbar) \left( x + \frac{1}{2} \eta |\hat{C}| x - \frac{1}{2} \eta \right).$$

[2]

$(q, p)$ are evolved classically to $(q_\tau, p_\tau)$, which serves as the phase-space arguments of $(\hat{B}) w[q, p]$. $3N$ is the dimensionality of the problem.

FK Wigner Transform. Recently, we suggested a route to the Wigner transform of the $\exp(-\beta\hbar\hat{A})$ operator, as required by LPI (15). This approach was based on combining the novel effective frequency variational theory of FK (17) with the quasi-density operator formalism of Jang and Voth (9). The resulting CF approach, called FK-LPI, can be conceptually understood as follows. The sampling of the quantum distribution is divided into two stages. In the first stage, phase-space points are chosen based on a classical-like probability distribution that is computationally accessible. These initial points are the so-called centroids. In the second stage, a quantum distribution is sampled around each centroid, representing the quantum fluctuations around this classical-like point. This procedure for generating a quantum distribution can be formulated exactly. However, to make evaluation of this distribution of fluctuations analytically accessible, and therefore make the CF calculation possible, one uses a local harmonic description for the potential in the vicinity of the centroid. Further, the effective harmonic description introduced by FK is used. The effective frequencies of the local normal modes are chosen variationally, optimizing the prediction of the system free energy compared with the exact result. The local harmonic description is not the same as that given simply by the curvature of the local potential, but rather accounts for the part of the potential actually sampled at the thermodynamic state. We have shown in model studies (15) that this difference is, in fact, important to the accuracy of the approach. For further details of the effective frequency approach, we refer to ref. 15.
Implementation. Potential. The liquid water model is constructed by adopting the framework of the simple point charge (SPC) model of Berendsen et al. (26). In this model, the water interactions are described by Lennard-Jones interactions between oxygen atoms \( \epsilon = 78.22 \text{ K} \) \( \sigma = 3.165 \) \( \text{Å} \) and an electrostatic Coulomb potential between all atoms on different molecules, the latter defined by charges \( 0.41e \) and \( -0.82e \) on hydrogen and oxygen, respectively. To allow for a flexible water model, we adopt the harmonic part of the local mode intramolecular water potential of Reimers and Watts (27). The water monomer equilibrium geometry is chosen to match the one prescribed by the original rigid SPC model: an angle of 109.5° and a bond length of 1.0 Å. In the following, we will refer to the model as SPCf (f for flexible).

To handle the long-range electrostatic interactions, the Ewald summation method is used, with conducting tin foil boundary conditions (28, 29). In the real space part, we use the standard approximation of retaining only the central box in the summation. A total of 337 reciprocal space vectors corresponding to \( k = 2\pi(n_x, n_y, n_z)/L, n_x + n_y + n_z \leq 27 \), are used in the Ewald reciprocal space sum and the Gaussian charge distribution parameter \( \alpha \) is set to \( 5.37 \) \( \text{Å} \), with \( L = 18.6359 \) bohr being the length of the simulation box. We consider 32 water molecules equivalent to a density of 0.99 g \( \text{cm}^3 \). The minimum image convention together with a spherical cut-off at half the box length is used for the short-ranged part of the potential. A time step of 1 fs is used for dynamics, and all VCFs are calculated up to 2.5 ps.

Generation of Boltzmann Wigner distribution. To obtain the FK centroid potential, effective frequencies, and quasi-density operator Wigner transform, the FK equations must be solved self-consistently (17, 30). These involve Gaussian smears of both the classical potential and its Hessian around specified centroid positions and they are implemented as follows. First, it is noted that the whole SPCf Ewald water potential is pairwise except for the Reimers-Watts intramolecular bending mode term, which is a function of all three water monomer atoms. Thus we may express the oxygen Lennard-Jones interactions, the Ewald real space term, the Ewald molecular self-interaction, and the Reimers-Watts OH intramolecular term accurately by a sum over Gaussian functions for computational efficiency (see ref. 31 for details). Moreover, because the Ewald reciprocal space potential is a function of only pairwise particle distances, it follows that the smearing of this and the Gaussian potential terms and their corresponding smeared Hessians all can be evaluated analytically. Here, also for efficiency, the remaining bending mode smeared Hessian and potential are obtained by approximating (i) the smeared Hessian by the classical Hessian, evaluated at the centroid geometry, and (ii) Taylor-expanding the smeared bending potential to first order in the so-called FK smearings width (17, 30).

We use eight cycles of the FK iterative equations (more than required for convergence); for each iteration, the 288 \( \times \) 288 effective frequency matrix is diagonalized. After self-consistency has been reached, the centroid potential and quasi-density operator are obtained (see ref. 15 for more details). The temperature is set to 296 K.

The integration over centroid positions is done by Metropolis Monte Carlo (MC) (29), using the centroid density as weighting function. The trial moves involve simultaneous displacements of all atoms. These are composed of the following sequential operations: (i) a uniform random translation of each atom, (ii) a uniform random rotation of each molecule, (iii) a uniform random translation of each molecule, and finally, (iv) again a uniform random translation of each atom. Thus, the transition probability for trial configurational moves is manifestly symmetric in configurational state, and we can use the usual Metropolis criterion for acceptance (see page 121 of ref. 29). The step parameters are 0.0196 bohr, 0.0334 rad, and 0.0033 bohr for center-of-mass translation, rotation, and atomic translation, respectively.

A total of 50,000 centroid MC steps are performed, and for every 20th configuration, the corresponding Wigner-transformed quasi-density operator is constructed and 10 sets of position and momenta are sampled for subsequent classical dynamics. For the classical simulation 300,000 MC samplings are used for generating initial conditions for the classical dynamics. To estimate the uncertainties in the calculated quantities, the calculations were repeated by using four different equilibrated initial water configurations.

Results

In this section, we describe the structural and dynamic results of the simulations.

Equilibrium Properties. Fig. 1 shows the distribution of the FK effective frequencies and, for comparison, the density of classical frequencies. As is conventional, the imaginary frequencies are plotted as their magnitude on the negative frequency axis. It can be seen that these extend to about \( \approx 700 \) cm\(^{-1} \). However, in the context of the FK Wigner transform, this fact does not cause any problem. The \((q, p)\) sampling is well defined as long as \( h \Omega(r, i) \leq \pi k_B T = 646 \) cm\(^{-1} \) (15). Hence only a very small portion of the effective frequency normal modes do not allow for momentum sampling in their direction. In the unusual cases that this inequality is violated, we adopt the natural convention that the momenta sampled along these modes are given by their limiting value, approaching the cut-off \( mk_B T \) from the origin, namely the momentum value zero (15). It is notable that the effective frequency distribution is significantly different from the classical frequency distribution, so the procedure is not simply equivalent to using a harmonic approximation based on instantaneous normal modes.

The classical, FK Wigner-based, and experimental (32) radial distribution functions (RDF) for O—H and O—O atom pairs gOH(r) and gOO(r) are shown in Figs. 2 and 3, respectively. Although these results can be obtained essentially exactly via equilibrium time-independent quantum simulation (see, for example, ref. 33), here, these calculations test the effective frequency of local harmonic approximation to the exact quantum distribution. The comparison to the two cases of classical mechanics and experiment provides an illustration of the size of the uncertainties inherent in parameterizing an empirical potential by fitting classical structural results for model potentials.
to the (necessarily quantum) experimental data. As can be seen, the general trend is that expected: the quantum water RDFs are less structured and the peaks are shifted to longer distances as compared with the classical RDFs. Starting with $g_{\text{OH}}(r)$, we see that the Wigner-based $g_{\text{OH}}(r)$ is in good agreement with the experimental $g_{\text{OH}}(r)$. Not only are the Wigner and experimental intramolecular distributions (at $\sim 1$ Å) in good agreement with each other, so are the peak heights of the following two peaks, corresponding to the two hydrogen atoms in one water molecule in the first solvation shell. In particular, classically, the first intermolecular peak is higher than the second, whereas both the quantum and experimental RDFs predict the reverse order for amplitudes. The closer, hydrogen-bonded H at $\sim 2$ Å is broadened substantially by zero-point effects. In Fig. 3, $g_{\text{OO}}(r)$ is seen to match reasonably with the height of the experimental first peak. On the other hand, the classical RDF is seen to exaggerate the liquid structure. We note that the FK Wigner-based RDFs are in good accord with the RDFs of Lobaugh and Voth (24), obtained by direct path integral MC calculations on a similar flexible water model. It is also instructive to compare the FK average quantum potential energy with that reported by Lobaugh and Voth (24). Our calculated potential energy of $-13.9 \pm 0.35$ kJ/mol compares well with $-14.69$ kJ/mol from ref. 24.

**Dynamical Results. Diffusion.** An important dynamical quantity is the diffusion coefficient $D$ of liquid water. This quantity can be extracted from the oxygen or hydrogen VCF through the standard transport coefficient expression

$$D = \frac{1}{3} \int_0^\infty dt \langle \hat{v}(t)\hat{v}(0) \rangle.$$  \[3\]

In Fig. 4, we report the oxygen atom VCF obtained by both classical MD and directly from the FK-LPI approximation. We also show the so-called Kubo-transformed VCF as calculated by FK-LPI (2). The Kubo VCF is a related CF that is as similar as possible to the classical CF. It is real-valued, and it shares the same initial value, namely the classical mean-squared velocity, simply related to the temperature. Nevertheless, the integrated Kubo-transformed VCF yields the quantum, not the classical, diffusion coefficient, see e.g., refs. 2 and 34. From Fig. 4, we note the larger initial amplitude of the FK-LPI normal VCF as compared with the classical and Kubo FK-LPI VCF. This initial value is proportional to the kinetic energy of the oxygen atom, which is evidently larger because of quantum confinement effects. Also, the intramolecular motion is much more visible in the FK-LPI normal VCF as compared with the classical and Kubo FK-LPI VCF. This initial value is proportional to the kinetic energy of the oxygen atom, which is evidently larger because of quantum confinement effects. Also, the intramolecular motion is much more visible in the FK-LPI normal VCF, a fact also owing to zero-point motion. In Table 1, we present the values for $D$ obtained by classical MD, FK-LPI, and FK Kubo VCF. We include the value of $D$ reported by Lobaugh and Voth (24), computed by CMD with a similar flexible SPC potential, and by Hernandez de la Pena and Kusalik (25), using rigid body CMD with the TIP4P potential. We note the required consistent agreement between the two FK-LPI predictions, which are also completely consistent with the values obtained from

<table>
<thead>
<tr>
<th>Model</th>
<th>$D_{QM}$</th>
<th>$D_{CI}$</th>
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<tbody>
<tr>
<td>This work</td>
<td>$0.49 \pm 0.06$</td>
<td>$0.25 \pm 0.06$</td>
</tr>
<tr>
<td>SPC-F (24)</td>
<td>$0.42$ (CMD)</td>
<td>$0.30 \pm 0.02$</td>
</tr>
<tr>
<td>TIP4P (25)</td>
<td>$0.548 \pm 0.005$ (CMD)</td>
<td>$0.358 \pm 0.004$</td>
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Units are Å²/ps. The values $0.49 \pm 0.06$, $0.47 \pm 0.06$ are the values obtained from FK-LPI Kubo and normal VCF, respectively.
integration of the hydrogen atom VCF (discussed below). One should be cautious, however, when comparing these FK-LPI and CMD values for several reasons. First, as is evident from Table 1, the classical Ds depend, not surprisingly, on the chosen water potential. Second, it is not well established how much D should depend on the change in system size from 32 used here, to, say, 125 molecules. Third, we do not know the uncertainty associated with the CMD D from Lobau and Voth (24). Finally, in that CMD calculation, only the hydrogen nuclei were quantized in the simulation. It is not clear what influence the quantization of the oxygen atom would have on the Ds, but as noted above, the initial value does display quantum effects. Nevertheless, the Ds obtained by FK-LPI and reported by CMD on similar models differ by only \( \pm \sim 15\% \).

**Spectrum of hydrogen VCF and dipole moment quantum correction factor (QCF).** The hydrogen atom VCF can be invoked as mimicking the total system dipole moment VCF for water (35), which is, in turn, directly related to the liquid IR absorption spectrum (24, 36). Implementation of this approximate relationship provides a simple route to developing a quantitative estimate of quantum corrections to the IR spectrum by the FK-LPI hydrogen VCF. Fig. 5 shows the classical, FK-LPI, and FK-LPI Kubo-transformed hydrogen VCFs. As in Fig. 4, we observe pronounced quantum effects in the FK-LPI VCF, now even more extreme because of the lower hydrogen mass. The Kubo VCF and classical results are rather close to each other. A comparison of the Fourier transform of the quantum hydrogen VCF (data not shown) as predicted by the FK-LPI VCF and the FK-LPI Kubo-transformed VCF is informative. A standard relation yields the normal VCF spectrum from the FK-LPI Kubo VCF spectrum (37). For an exact theory, these two spectra would be identical. Here, the consistency is an important internal test of the theory. We, in fact, find generally good agreement between the two FK-LPI spectra, especially at higher frequencies. The two FK-LPI spectra agree completely in the bending and OH stretching regions of the spectrum, a result that can be traced to the fact that the underlying FK-LPI theory is exact for harmonic potentials.

From the ratio between the classical and FK-LPI hydrogen VCF spectrum, one may define a FK-LPI-derived QCF, \( Q_{FK-LPI}(\omega) \). Because it can be shown that the single-atom hydrogen VCF represents a significant part of the total dipole moment VCF for liquid water (35), it is then reasonable to apply \( Q_{FK-LPI}(\omega) \) as a correction to the IR spectrum obtained simply from classical molecular dynamics. We apply \( Q_{FK-LPI}(\omega) \), obtained by using the Kubo VCF for H, to the IR spectrum reported by Jeon et al. (38) who considered a common variant of a SPCf model, often referred to as SPC/F (39). In Fig. 6, we show the experimental IR spectrum and compare it with the IR spectra obtained by applying (i) no QCF, (ii) the QCF of Oxtoby (40), and (iii) \( Q_{FK-LPI}(\omega) \) to the purely classical spectrum, reported by Jeon et al. (38), obtained from the fluctuating net dipole moment of their SPC/F liquid simulation. We clearly see a very significant improvement over the other approaches, compared with experiment, using the FK-LPI QCF. We emphasize that the FK-LPI QCF is computed \( ab\ initio \) and is determined only by the potential model chosen for water.

**Conclusion and Outlook**

We have reported the results of an application of the variational FK-LPI local harmonic approximation to a flexible model of liquid water. The structural results agree reasonably well with experimental data for water, and the quantum diffusion coefficients agree fairly well with CMD simulations of similar water models. It is important to note that the diffusion coefficients obtained from a direct calculation of the hydrogen or the oxygen atom VCFs agree very well with the values derived from a calculation of the Kubo-transformed CFs, providing some confidence that the values derived are accurate. The values must only be the same for an exact theory. These results provide considerable support for the view that the method is accurate.

The FK-LPI methodology is sufficiently readily applied so that a development of models that are designed to reproduce both structural and dynamic properties of the (quantum) liquid suggests itself. Further, applications to reaction dynamics involving light atom transfer in solution should be readily accessible, particularly if a limited number of degrees of freedom are quantized. At the same time, it is interesting to explore the degree to which the linearization approximation is satisfactory as one reduces the size of the system. Molecular clusters appear to be a useful proving ground from this perspective.

Finally, we note that it is the diagonalization of the Hessian for sampling of initial conditions that is the computationally demanding step here. There are various approximations to the Wigner distribution that one can formalize that can make the method far more computationally rapid, and exploration of these compared with the full theory may lead to an even more readily implemented approach.

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