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COMMENT

Comment on 'Semiclassical approximations in phase space with coherent states'

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Abstract

The semiclassical Herman–Kluk initial value approximation of the quantum-mechanical propagator, which is heavily used in dynamical studies of atomic and molecular systems, takes into account nonlinearity of the underlying classical dynamics by using multiple classical initial value solutions. In applications to the propagation of Gaussian wavepackets non-Gaussian distortions in the course of time and therefore a realistic description of the quantum dynamics are possible. This is in contrast to the single-trajectory approximations investigated in a recent paper by Baranger *et al*, one of which was erroneously termed Herman–Kluk approximation.

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1. Introduction

The importance of Gaussian wavepackets for the transition from 'micro-' to 'macro-mechanics' has been pointed out in the heyday of quantum theory by Schrödinger [1]. Also in modern applications of semiclassical time-dependent methodology Gaussian wavefunctions play a dominant role. Heller's early work on Gaussian wavepacket dynamics (GWD), e.g., was built on a single so-called 'thawed Gaussian' [2] whereas in a later work, multiple 'frozen Gaussians' [3] have been used in the so-called frozen Gaussian approximation (FGA). In 1984, Herman and Kluk (HK) improved the FGA by deriving its semiclassically correct prefactor [4]. Since then a number of researchers have successfully built on this semiclassical approximation by using it in applications to atomic and molecular problems [5–7].

Recently, however, there appeared a misconception of the term Herman–Kluk approximation in the literature [8], where a one-trajectory result (the kernel of the full expression) for a mixed matrix element of the time-evolution operator was termed HK formula. The flaws attributed to the HK approximation in section 5 of the paper by Baranger *et al* are therefore due to a misinterpretation of the full result. In this comment we point to the correct usage of the term.

2. The Herman–Kluk propagator

The standard form of the HK propagator in the coordinate representation [4, 9–12] is given by[3]

$$K^{\mathrm{HK}}(\mathbf{x}'', t; \mathbf{x}', 0) = \int \frac{\mathrm{d}^N \mathbf{p}'\, \mathrm{d}^N \mathbf{q}'}{(2\pi\hbar)^N} \langle \mathbf{x}''|\mathbf{z}_t\rangle R(\mathbf{p}', \mathbf{q}', t)\, \mathrm{e}^{\mathrm{i}S(\mathbf{p}',\mathbf{q}',t)/\hbar} \langle \mathbf{z}'|\mathbf{x}'\rangle. \tag{1}$$

The abbreviations used are (bold face indicating vectors and matrices, N being the spatial dimension)

$$R(\mathbf{p}', \mathbf{q}', t) = \left| \frac{1}{2}\left(\mathbf{m}_{11} + \mathbf{m}_{22} - \mathrm{i}\hbar\gamma \mathbf{m}_{21} - \frac{1}{\mathrm{i}\hbar\gamma}\mathbf{m}_{12}\right)\right|^{1/2} \tag{2}$$

with the definition of the classical stability (or monodromy) matrix

$$\mathbf{M} = \begin{pmatrix} \mathbf{m}_{11} & \mathbf{m}_{12} \\ \mathbf{m}_{21} & \mathbf{m}_{22} \end{pmatrix} \equiv \begin{pmatrix} \dfrac{\partial \mathbf{p}_t}{\partial \mathbf{p}'} & \dfrac{\partial \mathbf{p}_t}{\partial \mathbf{q}'} \\ \dfrac{\partial \mathbf{q}_t}{\partial \mathbf{p}'} & \dfrac{\partial \mathbf{q}_t}{\partial \mathbf{q}'} \end{pmatrix} \tag{3}$$

and the time-dependent (real) classical action

$$S \equiv \int_0^t [\mathbf{p}_{t'} \cdot \dot{\mathbf{q}}_{t'} - H]\, \mathrm{d}t' \tag{4}$$

with the Hamiltonian H. The coherent states, which in the coordinate space representation are given by Gaussian wavepackets centred around $\mathbf{z} = (\mathbf{q}, \mathbf{p})$ in phase space

$$\langle \mathbf{x}|\mathbf{z}\rangle \equiv \left(\frac{\gamma}{\pi}\right)^{N/4} \mathrm{e}^{-\gamma(\mathbf{x}-\mathbf{q})^2/2 + \mathrm{i}\mathbf{p}(\mathbf{x}-\mathbf{q})/\hbar} \tag{5}$$

play a central role in the expression above and their width parameter γ also enters the prefactor (2).

Some remarks are helpful here. Firstly, the final Gaussians are centred around classical trajectories $\{\mathbf{p}_t(\mathbf{p}', \mathbf{q}'), \mathbf{q}_t(\mathbf{p}', \mathbf{q}')\}$ starting at the initial phase space points $(\mathbf{p}', \mathbf{q}')$ to be integrated over. The HK method is therefore also called an initial value representation of the propagator. Secondly, the square root in equation (2) has to be taken in such a fashion that the expression is a continuous function of time, thus taking into account all problems posed by the calculation of the Maslov index in other semiclassical approaches. Thirdly, the stationary phase approximation (SPA) to the phase space integral in (1) leads to the well-known VVG propagator. Finally, it has been shown that the HK propagator is unitary in the SPA [13]. This is in contrast to the misleading statement after equation (5.3) of [8], based on using only the kernel instead of the full HK approximation.

3. Semiclassical propagation of Gaussian wavepackets

In the following we concentrate on the semiclassical propagation of a Gaussian wavepacket, which can be viewed as a 'mixed matrix element' of the time-evolution operator. This object has also been the focus of interest in sections 4 and 5 of the paper of Baranger *et al* [8]. For

[3] The original derivation of Herman and Kluk was performed for the mixed matrix element of the time-evolution operator to be considered below.

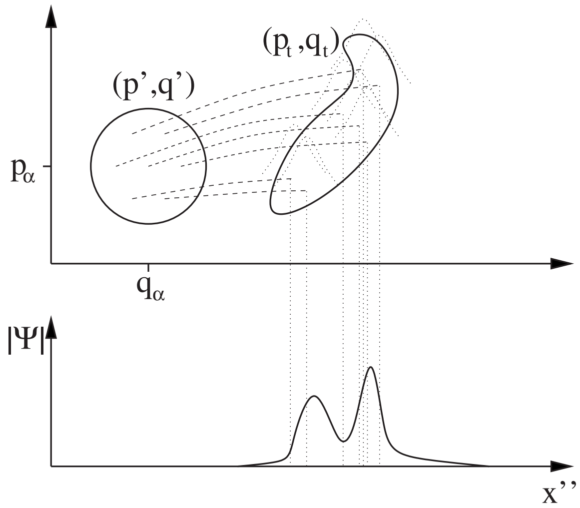

Figure 1. Schematic representation of the HK propagator applied to a Gaussian wavepacket $\langle x'|\mathbf{z}_\alpha\rangle$ for a fictitious nonlinear dynamics: the final wavepacket $\langle x''|\Psi\rangle$ is given as a sum over many Gaussians represented by their envelope at the final point (p_t, q_t), which started at a point (p', q') around the centre (p_α, q_α) of the initial Gaussian. Each (complex) Gaussian is 'weighted' by a product of the pre-exponential factor times an exponential $R\exp\{\mathrm{i}S/\hbar\}\langle\mathbf{z}'|\mathbf{z}_\alpha\rangle$ to give the final complex wavefunction.

the HK approximation to this mixed matrix element of the evolution operator between a final position state and an initial coherent state

$$K(\mathbf{x}'', t; \mathbf{z}_\alpha, 0) \equiv \langle\mathbf{x}''|\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}|\mathbf{z}_\alpha\rangle = \int \mathrm{d}\mathbf{x}' K(\mathbf{x}'', t; \mathbf{x}', 0)\langle\mathbf{x}'|\mathbf{z}_\alpha\rangle \tag{6}$$

one uses the semiclassical propagator $K^{\mathrm{HK}}(\mathbf{x}'', t; \mathbf{x}', 0)$ of equation (1). If one now performs the integration over $\mathbf{x}'$ analytically after having inserted the initial Gaussian $\langle\mathbf{x}'|\mathbf{z}_\alpha\rangle$ with centre parameters $(\mathbf{q}_\alpha, \mathbf{p}_\alpha)$ and (for the reason of simplicity) the same width parameter γ as used for the basic functions in equation (1), one finds the HK FGA

$$K^{\mathrm{HK}}(\mathbf{x}'', t; \mathbf{z}_\alpha, 0) = \int \frac{\mathrm{d}^N\mathbf{p}'\,\mathrm{d}^N\mathbf{q}'}{(2\pi\hbar)^N}\langle\mathbf{x}''|\mathbf{z}_t\rangle R(\mathbf{p}', \mathbf{q}', t)\,\mathrm{e}^{\mathrm{i}S(\mathbf{p}',\mathbf{q}',t)/\hbar}\langle\mathbf{z}'|\mathbf{z}_\alpha\rangle \tag{7}$$

with the overlap

$$\langle\mathbf{z}'|\mathbf{z}_\alpha\rangle = \mathrm{e}^{-\gamma(\mathbf{q}'-\mathbf{q}_\alpha)^2/4+\mathrm{i}(\mathbf{q}'-\mathbf{q}_\alpha)(\mathbf{p}'+\mathbf{p}_\alpha)/(2\hbar)-(\mathbf{p}'-\mathbf{p}_\alpha)^2/(4\gamma\hbar^2)}. \tag{8}$$

The integration over initial phase space is still left over in equation (7), but it is cut off by a bell-shaped weight function (the overlap between the two Gaussians). One can perform this integration using Monte Carlo methods [9] leading to a very powerful numerical semiclassical procedure used routinely by many research groups nowadays.

Graphically, the HK propagator applied to a Gaussian can be represented in the way shown in figure 1. We want to emphasize that the integration over many trajectories (i.e. over initial phase space) is crucial for general Hamiltonian problems. A true HK-like expression (in any, possibly mixed basis[4]) must consist of an integration over initial phase space coming from the coordinate space expression (1), which may not be treated in any additional approximation.

[4] For other integral representations of mixed (e.g., momentum coordinate) semiclassical time-evolution operator matrix elements, see, e.g., [10].

This is the standard nomenclature in the literature, in contrast to [8], where part of the integrand of equation (7) (the so-called kernel (5.1) in [8]) is termed HK approximation. However, in this case one would not sum over multiple trajectories, and the wavepacket would stay Gaussian forever, in contrast to the situation depicted in figure 1.

One can derive also single-trajectory approximations *from* the HK expression. These are not to be equated with the original formula, because they involve additional approximations. It has been shown in [6] that by a quadratic expansion of the exponent around the phase space centre of the initial wavepacket, Heller's thawed GWD [2] can be derived analytically from equation (7). It is well known that this gives the exact quantum result for the time-dependent wavefunction if one considers maximally quadratic potentials, that is if the classical dynamics is linear. For a numerical calculation of the nonlinear dynamics of a one-dimensional Morse oscillator we refer to the literature [6, 9]. In [6], a comparison is made between HK and GWD results, revealing that the first method does account for the fine (interference related) details of the numerically exact quantum curve, whereas the GWD only gives the overall envelope of the dynamics correctly.

4. Final remarks

An (incomplete) history of applications of the HK approximation up to 1998 has been given in [6]. Additional references can be found in the recent publications of the Miller group (see, e.g., [7]). All these show that the HK propagator is being put to good use in the literature. Besides the many applications to multi-nuclear (or electronic) degree of freedom Hamiltonian systems, the simultaneous semiclassical treatment of nuclear *and* electronic degrees of freedom through the classical electron analogue model (or equivalently the mapping method) are noteworthy [7, 14]. Finally, we also want to mention the so-called forward–backward technique, which after using the propagator of equation (1) and under additional approximations leads to the classical Husimi model [7].

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