Collisional Semiclassical Approximations in Phase-Space Representation

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Abstract

The Gaussian Wave-Packet phase-space representation is used to show that the expansion in powers of $\hbar$ of the quantum Liouville propagator leads, in the zeroth order term, to results close to those obtained in the statistical quasiclassical method of Lee and Scully in the Weyl-Wigner picture. It is also verified that propagating the Wigner distribution along the classical trajectories the amount of error is less than that coming from propagating the Gaussian distribution along classical trajectories.

PACS numbers: 34.10.+x, 03.65.Sq
I. INTRODUCTION

Nowadays, the advantages and difficulties for using the phase-space formulation of quantum mechanics are well known [1–3]. This formulation remains still very useful for studying the classical limit of quantum mechanics as well as for describing semiclassical approximations in collisional processes; for these purposes many authors use the Weyl-Wigner (WW) picture [1,4–6]. For the collisional problem it is often combined with the quasiclassical method of Ref. [7]. Following this approach Lee and Scully [1] have improved the accuracy of this method successfully with their Statistical Quasiclassical (SQC) method which was first suggested by Heller [8]. As we have shown in a previous paper [9], the approach of Lee and Scully corresponds to the zeroth order term of the expansion of the quantum Liouvillian in powers of $\hbar$ in the WW picture. So, their calculated transition probabilities could have higher order corrections.

The aim of this article is to show that the use of the Gaussian Wave Packet (GWP) phase-space representation [3,10,11] gives for the zeroth order term, which corresponds to what we call the Causal Approximation (CA), results similar to those obtained in the WW representation [1].

In the derivation of the expansion of the quantum Liouvillian in the GWP picture all orders of $\hbar$ are included; the first order term we shall call the Quasicausal Approximation (QCA). As it is shown in Refs. [10,11] one of the advantages of the GWP representation is that the quantum fluctuations of the mapped physical quantities become more evident; also the distribution function obtained when the density operator for a pure state is mapped into this representation is always non-negative.

Here we are also interested in verifying numerically, for the collisional problem, the statement put forward by Lee [3]: “the amount of error arising from propagating the Wigner distribution function (WDF) along the classical trajectories is usually considerably less than that coming from propagating other distributions along classical trajectories”. In our case the other distribution is the GWP distribution [10–12]. It is in agreement with Lee’s state-
ment the result we derive in Sec. II: first order corrections in \( h \) in the SQC method do not improve the numerical results of Lee and Scully [1].

In our comparison of the Weyl-Wigner formalism with the GWP approach we are going to work with a collinear non-reactive collision of an atom with a diatomic molecule, the interaction between them being an exponential repulsion, first used by Secrest and Johnson [13], of the form \( V = V_0 \exp[-\alpha(x - y)] \) where the constant \( V_0 \) is related to the classical turning point of the trajectory of the particle but its value does not have any effect on the results. In the WW and GWP formalisms we have taken this potential, the definition of the \( x \) and \( y \) coordinates, as well as the value of \( \alpha \) and \( V_0 \) from Ref. [13], the parameter \( \alpha \) is adjusted by published experimental data [13]. The mapped Hamiltonian in the GWP formalism has the constant \( V_0 \) renormalized.

In Sec. II we shall summarize our previous paper (Ref. [9]). In Sec. III we introduce the GWP representation and the CA and QCA. In Sec. IV we derive expressions for the transition probabilities and numerical results are presented in Sec. V.

**II. CAUSAL AND QUASICAUSAL APPROXIMATIONS IN THE WW FORMALISM**

In the first part of this section we are going to give a review of Ref. [9]. The quantum Liouville equation in the WW picture is [14]

\[
\frac{\partial W(q, p, t)}{\partial t} = -i \mathcal{L}_Q W(q, p, t),
\]

where \((q, p)\) is a point of phase-space and \(W(q, p, t)\) is the Wigner distribution function (WDF). We are using just one dimension. The quantum Liouvillian is

\[
\mathcal{L}_Q = H(q, p) \left[ \frac{2}{\hbar} \sin \frac{\hbar}{2} \Lambda \right],
\]

where \(H(q, p)\) being the Hamiltonian of the system and the operator

\[
\Lambda = \frac{\partial}{\partial q} \frac{\partial}{\partial p} - \frac{\partial}{\partial p} \frac{\partial}{\partial q}
\]
is the Poisson bracket, arrows indicate on which side the derivatives operate.

In Ref. [9] we show that from the formal solution of Eq. (1) given by

\[ W(q, p, t) = e^{-i\mathcal{L}_Q(t-t_0)}W_0(q, p), \]  

where \( W_0(q, p) \) is the WDF at the initial time \( t_0 \). Taking the classical limit of \( \mathcal{L}_Q \) in Eq. (2) we get

\[ \mathcal{L}_{cl} = iH(q, p) \hat{\Lambda}, \]  

and Eq. (4) becomes

\[ W^{(0)}(q, p, t) = e^{-i\mathcal{L}_{cl}(t-t_0)}W_0(q, p) = W_0(q(t_0 - t), p(t_0 - t)). \]  

Thus, each point \((q, p)\) of the phase space of the initial WDF evolves classically according to Hamilton’s equations, following a classical trajectory reversed in time. This we call the Causal Approximation (CA).

Still, according to Ref. [9], we can make an expansion of \( \mathcal{L}_Q \) in a power series of \( \hbar^2 \) which is substituted into Eq. (1) giving

\[ \frac{\partial W(q, p, t)}{\partial t} + i\mathcal{L}_0 W(q, p, t) = -i \sum_{n=1}^{\infty} \hbar^{2n} \mathcal{L}_{2n} W(q, p, t), \]  

where \( \mathcal{L}_0 = \mathcal{L}_{cl} \) and

\[ \mathcal{L}_{2n} = H(q, p) \left[ i \frac{(-1)^n}{2^{2n}(2n+1)!} \left( \hat{\Lambda} \right)^{2n+1} \right]. \]  

The integral equation corresponding to Eq. (7) is given by

\[ W(q, p, t) = e^{-i\mathcal{L}_0(t-t_0)}W_0(q, p) - i \sum_{n=1}^{\infty} \hbar^{2n} \int_{t_0}^{t} dt' e^{-i\mathcal{L}_0(t-t')} \mathcal{L}_{2n} W(q, p, t'). \]  

Solving this equation iteratively, we get in first order the Quasicausal Approximation (QCA)

\[ W_{QCA}(q, p, t) = e^{-i\mathcal{L}_0(t-t_0)}W_0(q, p) - i\hbar^{2} \int_{t_0}^{t} dt' e^{-i\mathcal{L}_0(t-t')} \mathcal{L}_2 e^{-i\mathcal{L}_0(t'-t_0)}W_0(q, p). \]  

In Eq. (10) the operator \(\exp[-i\mathcal{L}_0(t-t_0)]\) is responsible for the classical character of the evolution between different times.
This formalism is applied in Ref. [9] to a collisional process where a molecule suffers a collision from a pointlike projectile. As a result the molecule is transferred from the initial discrete energy level $|i\rangle$ to the final level $|f\rangle$, the total probability for this transition, in the limit $t \to \infty$ and $t_0 \to -\infty$, is given by

$$P_{i \to f} = 2\pi \hbar \int_{-\infty}^{\infty} dp_0 \int_{-\infty}^{\infty} dq_0 W_i(q_0, p_0) e^{iLQ(t-t_0)} W_f(q_0, p_0). \quad (11)$$

Eq. (11) is an exact result. Introducing now the QCA we get in the limit $t \to \infty$ and $t_0 \to -\infty$

$$P_{i \to f}^{\text{QCA}} = 2\pi \hbar \left[ \int_{-\infty}^{\infty} dp_0 \int_{-\infty}^{\infty} dq_0 W_i(q_0, p_0) W_f(q(t-t_0), p(t-t_0)) + i\hbar^2 \int_{-\infty}^{\infty} dp_0 \int_{-\infty}^{\infty} dq_0 W_i(q_0, p_0) \int_{t_0}^{t} dt' e^{iLQ(t-t')} L_2 W_f(q(t'-t_0), p(t'-t_0)) \right], \quad (12)$$

where the first term corresponds to the CA, while the second one is the QCA. The CA corresponds to the statistical quasiclassical (SQC) method of Lee and Scully given in Ref. [1]. Here as in Ref. [1] the $H_2 - He$ collision is considered, $H_2$ and $He$ being treated as an harmonic oscillator and a free particle respectively. The Hamiltonian in the Weyl-Wigner phase space is given by

$$H(Q, q, P, p) = \frac{P^2}{2M} + \frac{p^2}{2m} + \frac{1}{2} kq^2 + V_0 e^{-\alpha(Q-q)}, \quad (13)$$

where $Q$ and $q$ are the translational and vibrational coordinates respectively, $P$ and $p$ being their respective momenta. All the parameters appearing in Eq. (13), $M, m, V_0, \alpha$ and $k = m\omega^2$ (elastic constant of the oscillator) are taken from Ref. [13].

Following Lee and Scully (Refs. [1,3]) $Q, q, P, p$ obey Hamilton’s equations, so they describe classical trajectories, the initial state $W_i(q_0, p_0)$ in Eq. (12), is given by the WDF for the harmonic oscillator, the pair $(q_0, p_0)$ refers to the initial position and momentum of the harmonic oscillator and it belongs to a two-dimensional rectangular grid whose size and density depend on the desired accuracy.

Integrating numerically Hamilton’s equations for each $(q_0, p_0)$ of the grid for the harmonic oscillator and the appropriate initial $Q$ and $P$ of the particle, we get the set of final pairs
\((q,p)\) for the oscillator and final \((Q,P)\) for the particle, initial and final \(Q\) must be taken sufficiently large so that the particle can be considered free, which can be verified by using the fact that the total energy must be conserved along the trajectories.

In Eq.(12) the final state of the system is now given by the WDF, \(W_f(q,p)\) calculated for all final phase space points of the grid. Once initial and final WDF are calculated for each point, the CA can be obtained using the first term in Eq.(12).

In order to obtain the QCA, the second term in Eq.(12) must be calculated. This term can be approximated by \[C_{QCA} = BF_{if} \int_{t_0}^{t} dt' e^{-\alpha [Q(t'-t_0)-q(t'-t_0)]},\] (14)
with the constant \(B = \pi (\hbar \alpha)^3 V_0/12\) and
\[F_{if} = \int_{-\infty}^{\infty} dp_0 \int_{-\infty}^{\infty} dq_0 W_i(q_0,p_0) e^{i(t-t_0)E_0} \frac{\partial^3}{\partial p_0^3} W_f(q_0,p_0).\] (15)

Making \(y = 2E_{OH}/h\omega (E_{OH}(q_0,p_0)\) being the energy of the classical harmonic oscillator) we have
\[\frac{\partial^3}{\partial p_0^3} W_f(q_0,p_0) = A_0 p_0^3 + B_0 p_0,\] (16)
where
\[A_0 = \left(\frac{2}{\hbar \omega m}\right)^3 \frac{\partial^3 w_f(y)}{\partial y^3}, \quad \text{and} \quad B_0 = 3 \left(\frac{2}{\hbar \omega m}\right)^2 \frac{\partial^2 w_f(y)}{\partial y^2},\]
being \(w_f(y) = W_f(q_0,p_0)\).

Now we are going to show that this correction, given by Eq.(14) oscillates periodically in the time \(t\).

Let \(t_M\) be the time at which the atom is considered to be a free particle after colliding with the molecule. At this time the coordinate and momentum of the classical harmonic oscillator are given by
\[q_{0M} = A \cos(\omega t_M + \phi_0) \quad \text{and} \quad p_{0M} = -m\omega A \sin(\omega t_M + \phi_0).\]

At a later time \(t = t_M + \Delta t\), with \(\Delta t > 0\), the momentum \(p_0(t)\) of the harmonic oscillator will be
Thus, making \( a = p_0M \) and \( b = -m\omega q_0M \), one has

\[
p^3_0(t) = a^3 \cos^3 \omega \Delta t + b^3 \sin^3 \omega \Delta t + 3ab^2 \cos \omega \Delta t \sin^2 \omega \Delta t + 3a^2b \sin \omega \Delta t \cos^2 \omega \Delta t.
\]  

From Eq.\((17)\) and Eq.\((18)\) we obtain for Eq.\((16)\)

\[
A_0p_0^3(t) + B_0p_0(t) = a_3 \cos 3\omega \Delta t + b_3 \sin 3\omega \Delta t + a_1 \cos \omega \Delta t + b_1 \sin \omega \Delta t,
\]

where

\[
a_3 = A_0(\alpha^3 + \alpha^*3), \quad b_3 = iA_0(\alpha^3 - \alpha^*3),
\]

\[
a_1 = (3A_0\alpha\alpha^* + B_0)(\alpha + \alpha^*), \quad b_1 = i(3A_0\alpha\alpha^* + B_0)(\alpha - \alpha^*),
\]

and \( \alpha = (1/2)(a - ib) \). Eq.\((19)\) is a Fourier’s series, which substituted into Eq.\((15)\) shows that \( C_{QCA} \) in Eq.\((14)\) is a periodical function, since in this equation the integral in the time converges in the limit \( t \to \infty \). The average of this periodical function over one period of the oscillator will be zero. In this derivation we have used the approximate expression for the correction of the transition rate given by Eq.\((14)\). The exact demonstration, although more envolved, follows along similar lines.

\section*{III. CAUSAL AND QUASICAUSAL APPROXIMATIONS IN THE GWP FORMALISM}

In the GWP representation \([10–12]\), operators can be mapped both into a covariant (\(CV\)) and a contravariant (\(CTV\)) form and there are expressions which relate the \(CV\) with the \(CTV\) form as well as both of them with the corresponding \(WW\) representation.

The commutator of two operators of the Hilbert space \( A \) and \( B \) in the \(CV\) form is written \([3,10,11]\)

\[
\langle pq|[A, B]|pq\rangle = A^{CV}(q, p) \left( \mathcal{\Gamma}^{\uparrow} - \mathcal{\Gamma}^{\downarrow} \right) B^{CV}(q, p),
\]

\(8\)
where \((q, p)\) is a point in a phase-space, \(|pq\rangle\) represents the minimum uncertainty gaussian wave-packet or coherent state, \(A^{CV}(q, p)\) and \(B^{CV}(q, p)\) are the \(CV\) forms of operators \(A\) and \(B\) and \(\hat{\Gamma} = \exp[\hbar/2 \hat{D} \hat{D}^*]\), where \(D = (1/a_0)\partial/\partial q - ia_0 \partial/\partial p\). Arrows indicate on which side operators act and \(a_0\) is a constant with dimensions \(M^{-1} T^{-1}\).

The quantum Liouville equation in the \(CV\) representation for the density operator \(P^{CV}(q, p, t) = \langle pq|\Psi(t)\rangle\langle \Psi(t)|pq\rangle\) is given by

\[
\frac{\partial}{\partial t} P^{CV}(q, p, t) = -i \mathcal{L}^{CV} P^{CV}(q, p, t), \tag{21}
\]

\(\mathcal{L}^{CV}\) being the quantum Liouvillian in the \(CV\) form

\[
\mathcal{L}^{CV} = \frac{1}{\hbar} \mathcal{H}^{CV}(q, p) \left( \Gamma - \Gamma^* \right), \tag{22}
\]

and \(\mathcal{H}^{CV}(q, p) = \langle pq|H|pq\rangle\) the \(CV\) form of the hamiltonian \(H\) [11].

Now expanding \(\mathcal{L}^{CV}\) in a \(\hbar\) power series, \(\mathcal{L}^{CV} = \sum_{n=0}^{\infty} \hbar^n \mathcal{L}_n\), we identify

\[
\mathcal{L}_n = \frac{i}{2^n (n+1)!} \text{Im} \left[ \left( D^{n+1} \mathcal{H}^{CV} \right) \left( D^* \right)^{n+1} \right], \tag{23}
\]

where \(\mathcal{L}_0 = \mathcal{L}_{cl}\) is the classical Liouvillian.

One defines a Green’s function [11] by

\[
w(q, p, t|q_0, p_0, t_0) = e^{-i(t-t_0)\mathcal{L}^{CV}} w(q, p, t_0|q_0, p_0, t_0), \tag{24}
\]

with the condition

\[
\lim_{t \to t_0} w(q, p, t|q_0, p_0, t_0) = \delta(q - q_0)\delta(p - p_0). \tag{25}
\]

This Green’s function satisfies the Liouville equation

\[
\frac{\partial}{\partial t} w(q, p, t|q_0, p_0, t_0) = -i \mathcal{L}^{CV} w(q, p, t|q_0, p_0, t_0), \quad t > t_0 \tag{26}
\]

where the pairs \((q_0, p_0)\), and \((q, p)\) are the momenta and the coordinates at times \(t_0\) and \(t\) respectively. Here, as discussed in Ref. [9], classical causality is broken in the \(\hbar\) power series expansion of \(\mathcal{L}^{CV}\) when terms with \(n \geq 1\) are retained.
Because of Eq. (23), Eq. (26) can be written as follows

\[
\frac{\partial}{\partial t} w(t|t_0) + i\mathcal{L}_0 w(t|t_0) = \frac{2}{\hbar} \sum_{n=1}^{\infty} \frac{(\hbar n+1)}{(n+1)!} \text{Im} \left[ (D^{n+1}\mathcal{H}^{CV}) (D^*)^{n+1} w(t|t_0) \right].
\] (27)

In the GWP phase space the CV representation of the density operator, \( P^{CV}(q,p,t) \) is given by \([11]\)

\[
P^{CV}(q,p,t) = \int_{-\infty}^{\infty} dq_0 \int_{-\infty}^{\infty} dp_0 w(q,p,t|q_0,p_0,t_0) P^{CV}(q_0,p_0,t_0),
\] (28)

so, if a formal solution of Eq. (27)

\[
w(t|t_0) = e^{-i(t-t_0)\mathcal{L}_0} w(t_0|t_0) + \frac{2}{\hbar} \int_{t_0}^{t} dt' e^{-i(t-t')\mathcal{L}_0} \sum_{n=1}^{\infty} \frac{(\hbar n+1)}{(n+1)!} \text{Im} \left[ (D^{n+1}\mathcal{H}^{CV}) (D^*)^{n+1} w(t'|t_0) \right]
\] (29)

is substituted into Eq. (28), keeping in mind that \( w(t_0|t_0) = \delta(q-q_0)\delta(p-p_0) \), the first term gives for \( P^{CV}(q,p,t) \) the causal approximation (CA), while by including the lowest correction \( n = 1 \) term, the quasicausal approximation (QCA) is obtained.

**IV. TRANSITION PROBABILITIES FOR A COLLISIONAL PROCESS**

When we have a system in a given initial state \(|i\rangle\), at time \( t_0 \) and final state \(|f\rangle\) at time \( t \), with \( t > t_0 \), the transition probability \( \mathcal{P}_{i \rightarrow f} \) may be written \([11]\)

\[
\mathcal{P}_{i \rightarrow f} = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dq P^{CTV}_i(q,p,t_0) e^{i(t-t_0)\mathcal{L}^{CTV}} P^{CV}_f(q,p,t_0)
\]

\[
= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dq P^{CTV}_i(q,p,t_0) \tilde{P}^{CV}_f(q,p,t)
\] (30)

being \( P^{CTV}_i \) the CTV distribution function of the initial state and \( P^{CV}_f \) the CV distribution function of the final state.

For the CTV distribution function we have an equation \([11]\) analogous to Eq. (21) whose formal solution is given by

\[
P^{CTV}_i(q,p,t) = \exp \left[ -i(t-t_0)\mathcal{L}^{CTV} \right] P^{CTV}_i(q,p,t_0)
\]
with
\[ \mathcal{L}^{CTV} = \frac{1}{\hbar} \mathcal{H}^{CTV} \left[ \frac{\hat{r}^{CTV}}{\Gamma} - \left( \frac{\hat{r}^{CTV}}{\Gamma} \right)^* \right], \]
and
\[ \hat{r}^{CTV} = \exp \left( -\hbar \frac{D \mathcal{D}}{2} \right). \]

We use the model and method described by Lee and Scully \[43\] for the one-dimensional atom-molecule collinear collision, but in the GWP phase-space formulation. Here also in this non-reactive process the atom is treated like a free classical structureless particle while the molecule is represented by a harmonic oscillator. The interaction between the atom and the molecule \[13\] is the exponential repulsion described in Sec. I. The Hamiltonian for this system in the \(CV\) representation is
\[ \mathcal{H}^{CV} = \frac{P^2}{2M} + \frac{p^2}{2m} + \frac{1}{2k}q^2 + V_{eff}e^{-\alpha(Q-q)} + \frac{\hbar}{4} \left( \frac{a_0^2}{m} + \frac{k}{a_0^2} \right), \] (31)
where \(Q\) and \(q\) are the translational and vibrational coordinates respectively, \(P\) and \(p\) their respective momenta, \(V_{eff} = V_0 \exp(\alpha^2 \hbar/4a_0^2)\) and the parameters \(M, m, V_0, \alpha\) and \(k\) (elastic constant) are taken from Ref. \[13\], fitting the \(He-H_2\) system. The \(CTV\) form of the Hamiltonian is obtained from Eq. (31) by replacing \(a_0^2\) by \(-a_0^2\) \[11\].

In the \(\hbar\) power-series expansion of \(\mathcal{L}^{CV}\)
\[ \mathcal{L}^{CV} = \mathcal{L}_0 + \hbar \mathcal{L}_1 + \hbar^2 \mathcal{L}_2 + \cdots \] (32)
the contributions of the coordinates \(Q\) and \(P\) were neglected, except in the zeroth order term given by
\[ \mathcal{L}_0 = i \left( \frac{\partial \mathcal{H}^{CV}}{\partial Q} \frac{\partial}{\partial P} - \frac{\partial \mathcal{H}^{CV}}{\partial P} \frac{\partial}{\partial Q} + \frac{\partial \mathcal{H}^{CV}}{\partial q} \frac{\partial}{\partial p} - \frac{\partial \mathcal{H}^{CV}}{\partial p} \frac{\partial}{\partial q} \right) \] (33)
and which corresponds to classical motion.

In this approximation \(D^{n+1}\mathcal{H}^{CV} = (\alpha/a_0)^{n+1}V_{eff}\exp[-\alpha(Q-q)]\) for \(n \geq 1\), if one takes into account that \(a_0^2 = m\omega\). Eq. (29) can then be written
\[ w(t|t_0) = e^{-i(t-t_0)\mathcal{L}_0}w_0(t_0|t_0) + \frac{2V_{eff}}{\hbar} \int_{t_0}^{t} dt' e^{-i(t-t')\mathcal{L}_0} \text{Im} \left[ e^{-\alpha(Q-q)} \sum_{n=2}^{\infty} \left( \frac{\hbar \alpha D^*}{2a_0} \right)^n \frac{1}{n!} w(t'|t_0) \right]. \] (34)
Substituting Eq. (34) into Eq. (28) we have in first iteration

\[ P_{CV}(q, p, t) = e^{-i(t - t_0)\mathcal{L}_0} P_{CV}(q, p, t_0) + \frac{2V_{eff}}{h} \int_{t_0}^{t} dt' \left[ e^{-i(t-t')\mathcal{L}_0} e^{-\alpha(Q-q)} \right] e^{-i(t-t')\mathcal{L}_0} \text{Im} \sum_{n=2}^{\infty} \frac{(\frac{\hbar a}{2\mu_0} D^*)^n}{n!} e^{-i(t'-t_0)\mathcal{L}_0} P_{CV}(q, p, t_0). \]  

(35)

In order to obtain \( \tilde{P}_{CV}(q, p, t) = \exp[i(t - t_0)\mathcal{L}^CV] P_{f}^{CV}(q, p, t_0) \), which is the function appearing in Eq. (30), we proceed in the same fashion, but now as the Green’s function is given by \( \tilde{w}(t|t_0) = \exp[i(t - t_0)\mathcal{L}^{CV}] w(t_0|t_0) \), we get instead of Eq. (35)

\[ \tilde{P}_{CV}(q, p, t) = e^{i(t-t_0)\mathcal{L}_0} P_{CV}(q, p, t_0) - \frac{2V_{eff}}{h} \int_{t_0}^{t} dt' \left[ e^{i(t-t')\mathcal{L}_0} e^{-\alpha(Q-q)} \right] e^{i(t-t')\mathcal{L}_0} \text{Im} \sum_{n=2}^{\infty} \frac{(\frac{\hbar a}{2\mu_0} D^*)^n}{n!} e^{i(t'-t_0)\mathcal{L}_0} P_{CV}(q, p, t_0) \]  

(36)

since \( \tilde{P}_{CV}(q, p, t_0) = P_{CV}(q, p, t_0) \).

Substituting Eq. (36) into Eq. (31) we have, with quantum corrections in all orders of \( \hbar \)

\[ P_{i\rightarrow f} = \int \frac{dpdq}{2\pi h} P_{i}^{CTV}(q, p, t_0) e^{i(t-t_0)\mathcal{L}_0} P_{f}^{CV}(q, p, t_0) - \frac{\alpha V_{eff}}{a_0} \int \frac{dpdq}{2\pi h} P_{i}^{CTV}(q, p, t_0) \int_{t_0}^{t} dt' \left[ e^{i(t-t')\mathcal{L}_0} e^{-\alpha(Q-q)} \right] e^{i(t-t')\mathcal{L}_0} \text{Im} \left[ \left( \int_{0}^{1} d\xi \xi^{\frac{\hbar a}{\mu_0} D^*} - 1 \right) D^* e^{i(t'-t_0)\mathcal{L}_0} P_{f}^{CV}(q, p, t_0) \right], \]  

(37)

where we have used the property, valid for any operator \( A \)

\[ \int_{0}^{1} d\xi \xi^{A} = \sum_{n=0}^{\infty} \frac{A^n}{(n + 1)!}. \]  

(38)

The first term in Eq. (37) is the CA which is the zeroth order term of our \( \hbar \) power series-expansion, and corresponds to the expression of the Statistical Quasiclassical (SQC) method of Lee and Scully [1]. The difference between these two expressions lies in the distribution functions, while Lee and Scully work with the product of two Wigner Distribution Functions (WDF), in Eq. (37) we have the product of two Gaussian Distribution Functions (GDF), one of them in the \( CTV \) form and the other in the \( CV \) form.

Like in the SQC method, [1,2] here \( P_{i}^{CTV}(q, p, t_0) \) represents the initial vibrational state of the system, which we propagate along the classical trajectories. We also use the Lee and
Scully method [1] for constructing the two-dimensional rectangular grid in the \((q,p)\) plane. \(P_{i}^{CTV}(q_{n},p_{n},t_{0} = -\infty)\) is the weight carried by the point \((q_{n},p_{n})\) of the \(n\)th cell of the grid.

After integrating Hamilton’s equations for each point of the grid, the final GDF \((P_{f}^{CTV}(q,p,t = \infty))\) is calculated and then the transition probabilities are computed in the CA which corresponds to the first term in Eq. (37).

The GDF in the \(CV\) form is given by (see Appendix)
\[
P_{n}^{CV}(y) = \frac{1}{n!} y^{n} e^{-y},
\]  
where \(y = E/\hbar \omega\), \(E(q,p)\) being the energy of the classical harmonic oscillator, \(n\) is the quantum number which corresponds to the \(n\)th eigenstate of the harmonic oscillator. Introducing the new variable \(r^{2} = y\), the GDF in the \(CTV\) form is (see Appendix)
\[
P_{n}^{CTV}(r) = e^{-\frac{r^{2}}{4}} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} P_{n}^{CV}(r).
\]  

V. NUMERICAL RESULTS AND CONCLUSIONS

Using the mapped form of the quantum Liouville equation into the GWP phase-space we have derived expressions for the transition probabilities for semiclassical calculations of inelastic atom-molecule collisions which include also the quantum terms. These expressions are similar to those obtained in Ref. [9] for the WW formalism.

We show in Tables I and II the transition probabilities \(P_{i \rightarrow f}\) from the initial \((i)\) to the final \((f)\) state of the \(He-H_{2}\) system which were computed first by integrating numerically the Schrödinger equation, (these are the exact quantum mechanical results (QM) taken from Ref. [13]), second by using the Weyl-Wigner representation in the statistical quasiclassical (SQC) method taken from Ref. [1] and third by using the gaussian wave-packet representation in the causal approximation (GWP). The last ones are our results and they are given by the first term in Eq. (37). For more details on the system and models see the mentioned references.
The results in Tables I and II obtained using only the zeroth order term for both methods SQC and GWP should improve if quantum corrections were introduced.

The accuracy of the SQC and the GWP methods was checked by studying how well the transition probabilities obey microscopic reversibility; the results are presented in Table III. These results confirm that for the CA, the amount of error coming from propagating the WDF along classical trajectories is less than that coming from propagating the GWP distribution also along the classical trajectories, as stated in Ref. [3]. This agrees with the vanishing result found in Section II for the correction to the CA in the WW formalism. However, preliminary calculations of the first quantum correction (QCA) in the GWP formalism gave nonzero results.

Both methods (SQC and GWP) give nonvanishing results for classically forbidden processes. The numerical calculations, as far as the CA is concerned, for both formalisms present almost the same degree of difficulty for being performed.

ACKNOWLEDGMENTS

One of us (M. C. T.) would like to thank the Instituto de Física Teórica for the hospitality.

APPENDIX: DERIVATION OF THE CV FORM OF THE GDF

Let $|\varphi_n\rangle$, with $n = 0, 1, 2,...$ be the eigenstates of the harmonic oscillator and $|\alpha\rangle = |pq\rangle$ a coherent state, the CV form for the density operator [10,15] $\langle pq|\varphi_n\rangle\langle\varphi_n|pq\rangle$ is given by

$$P_n^{CV}(r) = \frac{r^{2n}}{n!}e^{-r^2},$$

where $\alpha = (a_0^2/2\hbar)^{1/2}q + i(1/2\hbar a_0^2)^{1/2}p = re^{i\theta}$. If $E$ represents the energy of the classical harmonic oscillator and $r^2 = \frac{E}{\hbar\omega} = y$, we may write

$$P_n^{CV}(y) = \frac{1}{n!}y^ne^{-y}.$$  \hspace{1cm} (A1)

We see that this CV form of the GDF depends only on the energy of the harmonic oscillator.
In order to obtain the CTV form of the GDF we use the property of the coherent states \[15\] which relates the normal (NO) and antinormal (AO) ordering of a function \(f\) of \(\alpha\) and \(\alpha^*\)

\[f^{(AO)}(\alpha, \alpha^*) = e^{\frac{\alpha^2}{2}} f^{(NO)}(\alpha, \alpha^*).\]  \((A2)\)

In polar coordinates \(r\) and \(\theta\), we have

\[\frac{\partial^2}{\partial \alpha \partial \alpha^*} = \frac{1}{4r} \left( \frac{\partial}{\partial r} r \frac{\partial}{\partial r} + \frac{1}{r} \frac{\partial^2}{\partial \theta^2} \right),\]  \((A3)\)

and Eq. (A2) in the GWP representation is written \[10\]

\[P_{CTV}^n(r, \theta) = e^{-\frac{1}{4r} \left( \frac{\partial}{\partial r} r \frac{\partial}{\partial r} + \frac{1}{r} \frac{\partial^2}{\partial \theta^2} \right)} P_{CV}^n(r, \theta).\]  \((A4)\)

For any positive integer \(n\) we have derived the formula

\[\left( \frac{1}{4r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} \right)^n e^{-r^2} = (-1)^n n! L_n(r^2) e^{-r^2},\]  \((A5)\)

where \(L_n\) are the Laguerre polynomials.

Since \(P_{CV}^n(r)\) for the harmonic oscillator do not depend on \(\theta\), Eq. (A4) can be written as

\[P_{CTV}^n(r) = e^{-\frac{1}{4r} \left( \frac{\partial}{\partial r} r \frac{\partial}{\partial r} \right)} P_{CV}^n(r).\]  \((A6)\)

Using Eqs. (A6), Eq. (A1) and Eq. (A5) we obtain for \(n = 0\)

\[P_{CTV}^0(r) = \sum_{n=0}^{\infty} L_n(r^2) e^{-r^2}.\]  \((A7)\)

For \(n = 1\) we get, similarly,

\[P_{CTV}^1(r) = \sum_{n=0}^{\infty} (1 - n) L_n(r^2) e^{-r^2},\]  \((A8)\)

because

\[\left( \frac{1}{4r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} \right)^n (r^2 e^{-r^2}) = (-1)^{n+1} n! \left[ (n + 1) L_{n+1}(r^2) - L_n(r^2) \right] e^{-r^2}.\]  \((A9)\)

For \(n = 2\)

\[P_{CTV}^2(r) = \frac{1}{2!} r^4 e^{-r^2} + \left[ \sum_{n=3}^{\infty} \frac{n(n-1)}{2} L_n(r^2) - 2 \sum_{n=2}^{\infty} n L_n(r^2) + \sum_{n=1}^{\infty} L_n(r^2) \right] e^{-r^2}.\]  \((A10)\)
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Table Captions

**Table I.** Transition probability $P_{0\rightarrow f}$ for a collinear He-$H_2$ collision calculated by the quantum mechanical (QM) method (Ref. [13]), statistical quasiclassical (SQC) method (Ref. [1]) and gaussian wave-packet (GWP) method in the CA (first term in Eq. (37)). The total initial energy $E$ is measured in units of $\hbar \omega/2$, where $\omega$ is the vibrational frequency of the $H_2$ molecule. In the calculation of $P_{0}^{CTV}$ at least 100 Laguerre polynomials were used, although only about 10 polynomials are required in order to obtain convergence. Numbers inside brackets give the upper limit of the transition probability and $*$ means that the transition is prohibited classically.

**Table II.** Similar to Table I; except that the oscillator goes from the first exited state to the final state $f$.

**Table III.** Similar to Table I; results of Table I and Table II are compared in order to test microscopic reversibility.
| E | $\mathcal{P}_{0 \rightarrow f}$ | QM   | SQC  | GWP |
|---|-----------------|------|------|-----|
| 8 | 0 → 0           | (0.892) | 0.893 | 0.830 |
|   | 0 → 1           | 0.108 | 0.107 | 0.156 |
|   | 0 → 2           | 0.001 | -     | 0.014 |
| 12| 0 → 0           | (0.538) | 0.529 | 0.501 |
|   | 0 → 1           | 0.394 | 0.412 | 0.349 |
|   | 0 → 2           | 0.068 | 0.068 | 0.122 |
|   | 0 → 3           | -     | -     | 0.028 |
| 16| 0 → 0           | (0.204) | 0.187 | 0.229 |
|   | 0 → 1           | 0.434 | 0.422 | 0.339 |
|   | 0 → 2           | 0.291 | 0.314 | 0.250 |
|   | 0 → 3           | 0.071 | 0.077 | 0.124 |
|   | 0 → 4           | -     | -     | 0.045 |
|   | 0 → 5           | -     | -     | 0.013 |
| 20| 0 → 0           | (0.060)* | 0.046* | 0.090* |
|   | 0 → 1           | 0.128 | 0.202 | 0.221 |
|   | 0 → 2           | 0.366 | 0.351 | 0.270 |
|   | 0 → 3           | 0.267 | 0.294 | 0.220 |
|   | 0 → 4           | 0.089 | 0.106 | 0.134 |
|   | 0 → 5           | -     | -     | 0.66  |

**TABLE I.**
|      | \( \mathcal{P}_{1 \rightarrow f} \) | QM | SQC | GWP |
|------|----------------------------------|----|-----|-----|
| 8    | 1 \( \rightarrow \) 0           | 0.108 | 0.106 | 0.135 |
|      | 1 \( \rightarrow \) 1           | (0.850) | 0.863 | 0.780 |
|      | 1 \( \rightarrow \) 2           | 0.042  | 0.031 | 0.085 |
| 12   | 1 \( \rightarrow \) 0           | 0.394  | 0.411 | 0.396 |
|      | 1 \( \rightarrow \) 1           | (0.244) | 0.176 | 0.250 |
|      | 1 \( \rightarrow \) 2           | 0.345  | 0.385 | 0.272 |
|      | 1 \( \rightarrow \) 3           | 0.037* | 0.028* | 0.082* |
| 16   | 1 \( \rightarrow \) 0           | 0.434  | 0.420 | 0.377 |
|      | 1 \( \rightarrow \) 1           | (0.034) | 0.065 | 0.137 |
|      | 1 \( \rightarrow \) 2           | 0.220  | 0.151 | 0.176 |
|      | 1 \( \rightarrow \) 3           | 0.261  | 0.302 | 0.181 |
|      | 1 \( \rightarrow \) 4           | 0.051  | 0.061 | 0.098 |
|      | 1 \( \rightarrow \) 5           | -      | -     | 0.031 |
| 20   | 1 \( \rightarrow \) 0           | 0.218  | 0.199 | 0.230 |
|      | 1 \( \rightarrow \) 1           | (0.286) | 0.285 | 0.233 |
|      | 1 \( \rightarrow \) 2           | 0.009  | 0.042 | 0.143 |
|      | 1 \( \rightarrow \) 3           | 0.170  | 0.090 | 0.149 |
|      | 1 \( \rightarrow \) 4           | 0.240  | 0.262 | 0.149 |
|      | 1 \( \rightarrow \) 5           | 0.077  | 0.121 | 0.105 |

**TABLE II.**
| E  | $P_{i \rightarrow f}$ | QM  | SQC  | GWP |
|----|----------------------|-----|------|-----|
| 8  | 0 → 1                | 0.108 | 0.107 | 0.156 |
|    | 1 → 0                | 0.108 | 0.106 | 0.135 |
| 12 | 0 → 1                | 0.394 | 0.412 | 0.349 |
|    | 1 → 0                | 0.394 | 0.411 | 0.396 |
| 16 | 0 → 1                | 0.424 | 0.422 | 0.339 |
|    | 1 → 0                | 0.434 | 0.420 | 0.377 |
| 20 | 0 → 1                | 0.218 | 0.202 | 0.221 |
|    | 1 → 0                | 0.218 | 0.199 | 0.230 |

**TABLE III.**