Interference in semiclassical electron dynamics

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Abstract. We further strengthen the hypothesis that the difference between singlet and triplet initial states in the scattering of two electrons is an interference effect. This is achieved by comparing semiclassical results based on multiple classical trajectories à la Herman and Kluk published previously [Phys. Rev. A 89, 032104 (2014)] with classical Wigner (LSC-IVR) results based on a similar set of trajectories but not taking into account their phases (classical action divided by $\hbar$).

1. Introduction
Electronic many particle dynamics in the time-domain in atoms and quantum dots with or without magnetic fields has been investigated semiclassically only recently [1, 2, 3]. In addition, the scattering of two electrons without any external potential has been studied in [4], to answer the question if the Pauli principle is accounted for semiclassically. It was found out that the multi-trajectory Herman-Kluk method does account for the differences in the triplet versus the singlet state without the need for additional, artificial terms in the Hamiltonian [5], enforcing this difference. Single trajectory-based semiclassical approaches like the thawed Gaussian approximation of Heller [6] are not capable of displaying this difference in the asymptotic limit, however. This fact has been taken as a first indication that interference effects between different trajectories might be responsible for the difference between singlet and triplet scattering.

Here we further strengthen this hypothesis, by contrasting again the Herman-Kluk results from [4], but this time against multi-trajectory results without interference effects that have been gained from an application of the linearized semiclassical initial value approach, which is also referred to as classical Wigner method and uses a similar set of trajectories as the true semiclassical method.

To this end, in Section 2, we first recapitulate the semiclassical initial value representation of the quantum propagator à la Herman and Kluk and then the linearized version of the semiclassical approximation in the case of arbitrary correlation functions. In Section 3, we review a fully quantum treatment with a focus on the difference between the initial triplet and singlet states. In Section 4 we then apply both trajectory based approaches to describe the dynamics of scattering of two electrons, initially in the two different states. Conclusions and an outlook are given in Section 5.
2. Semiclassical and classical initial value representations

The solution of the time-dependent Schrödinger equation in terms of classical trajectories has a long history and is intimately connected to the semiclassical approximation to the Feynman path integral representation of the propagator [7]. An early review of different semiclassical approximations with a focus on the Herman-Kluk (HK) propagator is given in [8].

The computational advantage of the semiclassical HK propagator is its dependence on the solution of classical initial value problems. In their terms and for two degrees of freedom (DOF), which we will focus on later, it is given by

\[ K(x, t; x', 0) = \int \frac{d^2p d^2q}{(2\pi \hbar)^2} R(p, q, t) e^{iS(p, q, t)}/\hbar \langle x|g_{\gamma}(p, q)\rangle \langle g_{\gamma}(p, q)|x'\rangle, \]

(1)

with \( x^T = (x, y) \), \( q^T = (q_x, q_y) \), \( p^T = (p_x, p_y) \), \( p_t = p(p, q, t) \), \( q_t = q(p, q, t) \),

\[ g_{\gamma}(q, p) = \left( \frac{\det \gamma}{\pi^2} \right)^{1/4} e^{-\frac{1}{2}(x-q)^T \gamma (x-q) + \frac{1}{\hbar} p^T (x-q)} \]

(2)

denoting a normalized Gaussian wavefunction, and the classical action

\[ S(p, q, t) = \int_0^t dt' (T - V) \]

(3)

for the motion of a system governed by a potential energy \( V \). Furthermore, it contains a prefactor

\[ R(q, p, t) = \sqrt{\det \left[ \frac{1}{2} \left( m_{11} + \gamma m_{22} \gamma^{-1} - i\hbar \gamma m_{21} - \frac{1}{i\hbar} m_{12} \gamma^{-1} \right) \right]}, \]

(4)

which is dependent on the so-called stability or monodromy matrix [9] and has been derived by Herman and Kluk [10] following up on earlier ground-breaking work by Heller [11]. The matrices \( \gamma \), appearing in the prefactor as well as in the Gaussians, are usually chosen diagonal. Over a wide range of reasonable parameters, the final result does not depend on their value. For diagonal elements of \( \gamma \) that go to infinity, the semiclassical van Vleck-Gutzwiller propagator is recovered [9]. This formulation is based on the solution of classical boundary value problems, however, and therefore has not found such a widespread acceptance in numerical work as the HK propagator that is based on classical initial value problems, i.e., is a semiclassical initial value representation of the propagator.

Due to the presence of the phase factor in the propagator, different trajectories can “interfere” constructively or destructively and a lot of quantum effects, like plateau formation in high-order harmonic generation [12, 13], energy quantization in Bose-Hubbard systems [14] and breather oscillation [15] can be described properly by the HK propagator. A review of semiclassical initial value representations with a focus on applications in chemistry can be found in [16] and a semiclassical hybrid approach combining Heller’s thawed Gaussians [6] with Herman-Kluk propagation for a limited number of degrees of freedom is laid out in [17]. This latter approach allows the semiclassical treatment of dissipative quantum systems. Deep tunneling effects, however, seem to be out of reach in a formulation with real trajectories and in real time [18].

In correlation functions of the form

\[ C_{AB}(t) = \text{tr}[\hat{A}\hat{e}^{i\hat{H}t/\hbar} \hat{B}\hat{e}^{-i\hat{H}t/\hbar}], \]

(5)

two time-evolution operators do appear and therefore a double Herman-Kluk expression emerges in a semiclassical description. For a sizable number of degrees of freedom, this might impose an
unsurmountable numerical wall for the evaluation of such expressions. Simplifications are thus sought for and a linear expansion of the action difference leads to a purely classical expression with no quantum interference effects. The final result

\[ C_{AB}^W(t) = \int \frac{d^2p d^2q}{(2\pi\hbar)^2} A^W(q, p) B^W(q_t, p_t) \]

is given in terms of a single (multi-dimensional) phase space integral, where \( A^W \) is the Wigner transform \( A^W(q, p) = \int d^2s e^{-ip \cdot s/\hbar} \langle q + s/2 | \hat{A} | q - s/2 \rangle \)

of the operator \( \hat{A} \), and an analogous relation holds for the operator \( \hat{B} \). Heller had written down the final expression for the correlation function intuitively [19]. Semiclassical derivations have been given by Miller and coworkers [20, 21] as well as by Herman and Coker [22] and for dipole-dipole correlation functions in [23, 24]. In the latter cases, the starting point was a double HK expression and the mathematics involved is straightforward but tedious.

Obviously the correlation function (6) does not contain time-dependent oscillatory integrands (initial states that are not single Gaussians may induce “static” negativities, however, as can be seen below) and interference effects are not described any more. The method is therefore also referred to as the classical Wigner method. It has a long history of analysis and applications [19, 25, 26, 27] and is known under different pseudonyms, as, e.g., linearized semiclassical initial value representation (LSC-IVR) or truncated Wigner approximation. The reason for the latter naming convention is that the approximation is analogous to the truncation of the Moyal bracket in the equation of motion for the Wigner function at the lowest (classical) order [28].

If one is interested in the time-dependent (pure state) density of the system of interest, \( \hat{A} \) and \( \hat{B} \) are the projection operators representing the initial state and position space, according to

\[ \hat{A} = |\Psi_\alpha(0)\rangle \langle \Psi_\alpha(0)|, \]
\[ \hat{B} = |x\rangle \langle x|. \]

For an initial wavefunction

\[ \Psi_\alpha(x, 0) = \exp\left[ -\frac{1}{2} (x - q_\alpha)^T \gamma (x - q_\alpha) + \frac{1}{\hbar} P_\alpha^T (x - q_\alpha) \right], \]

centered around \( (q_\alpha, p_\alpha) \), the diagonal elements of the density matrix in position representation in LSC-IVR thus are given by

\[ \rho(x, t) = \int \frac{d^2p d^2q}{(\pi\hbar)^2} \delta[q_t - x] \]
\[ \times \exp\left[ -\frac{1}{\hbar^2} (p - p_\alpha)^T \gamma^{-1} (p - p_\alpha) - (q - q_\alpha)^T \gamma (q - q_\alpha) \right], \]

which contains the classical trajectories \( \mathbf{q}_t \) as the only dynamical input.

3. Scattering of two electrons

Depending on their spin, two electrons will approach each other to different degrees, thus revealing the effect of the Pauli principle. Our test system is described by a Hamiltonian of two
interacting electrons that are not subject to any external potential in one dimension (atomic units (a.u.) will be used throughout the rest of this work)

\[
\hat{H} = \frac{p_x^2}{2} + \frac{p_y^2}{2} + V = \frac{p_x^2}{2} + \frac{p_y^2}{2} + \frac{1}{\sqrt{(x-y)^2 + c}}.
\]

We use the smoothing parameter \(c = 0.55\) for the repulsive Coulomb interaction that has often been used for electron dynamics before, because it closely reproduces the ground state of the 3D Helium atom [29].

In the following, we investigate the scattering of two electrons as a function of their total spin, comparing the semiclassical HK method with exact quantum mechanical propagation and the classical (truncated) Wigner approach. A similar comparison has been made before in [4], where HK results have been compared to the quantum ones and the ones from a thawed Gaussian approximation. Initially, the two electrons are assumed to be far apart, occupying the two spatial orbitals

\[
\varphi_1(x) = \left(\frac{\gamma_x}{\pi}\right)^{1/4} e^{-\frac{\gamma_x}{2}(x-q_{x,a})^2 + ip_{x,a}(x-q_{x,a})},
\]

\[
\varphi_2(y) = \left(\frac{\gamma_y}{\pi}\right)^{1/4} e^{-\frac{\gamma_y}{2}(y-q_{y,a})^2 + ip_{y,a}(y-q_{y,a})},
\]

with \(q_{x,a} = 0, p_{x,a} = 0\) and \(q_{y,a} = 15, p_{y,a} = -2\). The first orbital initially describes an electron at rest and at the origin, and the second a far away electron, moving towards the first electron. These spatial orbitals can be combined either to create a singlet

\[
\Psi_s(x,y) = \frac{1}{\sqrt{2}} \begin{pmatrix} \varphi_1 \uparrow & \varphi_1 \uparrow & \varphi_2 \downarrow & \varphi_2 \downarrow \end{pmatrix} = \frac{1}{2} (\varphi_1(x)\varphi_2(y) + \varphi_2(x)\varphi_1(y)) (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)
\]

or a triplet

\[
\Psi_t(x,y) = \frac{1}{\sqrt{2}} \begin{pmatrix} \varphi_1 \uparrow & \varphi_1 \uparrow & \varphi_2 \uparrow & \varphi_2 \uparrow \end{pmatrix} = \frac{1}{\sqrt{2}} (\varphi_1(x)\varphi_2(y) - \varphi_2(x)\varphi_1(y)) |\uparrow\uparrow\rangle
\]

wave function. The energy of the two states is identical at all times, since at \(t = 0\) the electrons are far apart, and the total energy is conserved. A graphical display of the real part of the spatial part of the two initial states is given in Fig. 1. The structure in the upper left corner of both figures is identical, whereas the one in the lower right corner has opposite sign.

An exact quantum mechanical propagation leads to a time-dependent one particle electron density

\[
\rho_s(x,t) = \int dy \rho_s(x,y)
\]

for the singlet, which illustrates the scattering, see Fig. 2. If the same calculation is repeated for the triplet state, we obtain a different time-dependent density \(\rho_t(x,t)\), where the non-zero blue area at the end is notably wider. To emphasize the difference between the two, we show the difference density \(\Delta \rho(x,t) = \rho_t(x,t) - \rho_s(x,t)\) as a function of time in the third panel of Fig. 2. In the magenta area, \(\rho_s > \rho_t\) (Fermi hole), while in the green area \(\rho_s < \rho_t\). This demonstrates the Pauli principle: Two electrons in a triplet cannot come as close to each other as two electrons in a singlet.
Figure 1. Real part of the initial spatial part of the two-electron wavefunction in the singlet (left panel) triplet (right panel) case.

Figure 2. Time dependent singlet (left panel), triplet (middle panel), and difference (right panel) one particle electron density from an exact quantum dynamical calculation.

4. Semiclassical and classical numerical results

After having set the stage with the full quantum results, which can still be calculated easily for just two degrees of freedom, we now show the numerical results of a full semiclassical calculation as well as of an LSC-IVR calculation of the observable

\[
\langle (\hat{x} - \hat{y})^2 \rangle^{1/2} = \sqrt{\int d^2 x \Psi^*(x,t)(x-y)^2 \Psi(x,t)} = \sqrt{\text{Tr}[\hat{\rho}(\hat{x} - \hat{y})^2]},
\]

based on the Herman-Kluk propagator and its linearized approximation, respectively. Here the abbreviation \( d^2 x = dx dy \) has been used. For the pure initial states that we propagate, the full semiclassical calculations have been performed on the wavefunction level, according to

\[
\Psi(x,t) = \int d^2 x' K(x,t; x',0) \Psi(x',0).
\]

The overlap between the initial wavefunction and the Gaussian that appears in the propagator is given by (see, e.g., [17] for the single Gaussian case)
The two distinct contributions to the wavefunction corresponding to the two classes of trajectories for the triplet case. The vectors appearing in the exponent are defined by the wavefunction given in Eqs. (15, 16), however. Because the initial density (looking only at the spatial part of the wavefunction) allows for different indices of the Gaussian wavepackets, \( i, j = 1, 2 \), we have to generalize the projection operator from (8). For a single one out of the four contributions to the dynamics of the initial density

\[
\rho(x, y, 0) = \Psi^*(x, y)\Psi(x, y)
\]

\[
= \frac{1}{4} \left[ \varphi_1^*(x)\varphi_2^*(y) \pm \varphi_2^*(x)\varphi_1^*(y) \right] \left[ \varphi_1(x)\varphi_2(y) \pm \varphi_2(x)\varphi_1(y) \right]
\]

allows for different indices of the Gaussian wavepackets, \( i, j = 1, 2 \), we have to generalize the projection operator from (8). For a single one out of the four contributions to the dynamics of the initial density

\[
\rho_{i,j}(x, y, 0) = \varphi_i(x)\varphi_j^*(x)\varphi_j(y)\varphi_j^*(y),
\]

we then get the final Wigner expression

\[
\rho_{i,i',j,j'}(x, y, t) = \int dx dy dq_x dq_y \left( \delta(x - q_x, t) \delta(y - q_y, t) \right)
\]

\[
\times e^{-\frac{\gamma}{2} \left[ (q_x - (q_x)_i)^2 + (q_x - (q_x)_i')^2 \right] + \frac{\gamma}{2} \left[ (q_y - (q_y)_j)^2 + (q_y - (q_y)_j')^2 \right]}
\]

\[
\times e^{\frac{\gamma}{2} \left[ \left( (q_x)_i - (q_x)_i', q_y - (q_y)_j \right) - \left( (q_x)_j - (q_x)_j', q_y - (q_y)_i \right) \right] - \left( (q_x)_i - (q_x)_i', q_y - (q_y)_j \right) - \left( (q_x)_j - (q_x)_j', q_y - (q_y)_i \right)]}
\]

\[
\times e^{\frac{\gamma}{2} \left[ \left( (q_y)_i - (q_y)_i', q_x - (q_x)_j \right) - \left( (q_y)_j - (q_y)_j', q_x - (q_x)_i \right) \right] - \left( (q_y)_i - (q_y)_i', q_x - (q_x)_j \right) - \left( (q_y)_j - (q_y)_j', q_x - (q_x)_i \right)]}
\]

\[
\times e^{\frac{\gamma}{2} \left[ \left( (q_x)_i - (q_x)_i', q_y - (q_y)_j \right) - \left( (q_x)_j - (q_x)_j', q_y - (q_y)_i \right) \right] - \left( (q_x)_i - (q_x)_i', q_y - (q_y)_j \right) - \left( (q_x)_j - (q_x)_j', q_y - (q_y)_i \right)]}
\]

\[
\times e^{\frac{\gamma}{2} \left[ \left( (q_y)_i - (q_y)_i', q_x - (q_x)_j \right) - \left( (q_y)_j - (q_y)_j', q_x - (q_x)_i \right) \right] - \left( (q_y)_i - (q_y)_i', q_x - (q_x)_j \right) - \left( (q_y)_j - (q_y)_j', q_x - (q_x)_i \right)]}
\]

\[
\times e^{\frac{\gamma}{2} \left[ \left( (q_x)_i - (q_x)_i', q_y - (q_y)_j \right) - \left( (q_x)_j - (q_x)_j', q_y - (q_y)_i \right) \right] - \left( (q_x)_i - (q_x)_i', q_y - (q_y)_j \right) - \left( (q_x)_j - (q_x)_j', q_y - (q_y)_i \right)]}
\]
which (in principle) contains negativities due to the phase terms. The two “off-diagonal” terms with $i \neq i'$ and $j \neq j'$ that could in principle account for a difference between singlet and triplet, are vanishingly small, however. This can be seen as follows: Consider the case where $i = 1$ and $i' = 2$. Then in order for the exponent to be close to zero and therefore the contribution to the integral to be large, $q_x$ would have to be around zero as well as around 15 at the same time, which is impossible. The off diagonal terms can therefore be safely neglected. This also immediately leads to the observation that there is no difference to be expected between singlet and triplet in the LSC-IVR results. We will have just two finite contributions to the LSC-IVR result, that are the same in both the singlet as well as the triplet case and each of these contributions is in the form given by (11), one with initial phase space center $(q_\alpha, p_\alpha)$ and the other one with the center $(\tilde{q}_\alpha, \tilde{p}_\alpha)$.

Let us now come to a comparison of the numerical results. The HK results have been obtained by propagating the wavefunction in grid representation, which emerges by analytical integration over $d^2x'$ in Eq. (19). The remaining phase space integration was performed numerically, using $10^5$ trajectories for converged results. The expectation values were then found in the usual way according to Eq. (18). In the LSC-IVR case, we employed the density from Eq. (28) and calculated the expectation value grid free, by performing the integration over $d^2x$ analytically, which is very easy as it only amounts to evaluating the delta-functions. The phase space integration was then performed numerically, using $10^4$ trajectories for converged results. As can be seen in Fig. 3, by a comparison to full quantum calculations, the HK results do account for the difference between singlet and triplet to a very high degree, see also [4]. The classical Wigner results for the same quantity, however, do not show any difference between the two cases [32]. They are both identical and lie right in-between the singlet and triplet quantum results as can be seen in Fig. 4. The set of trajectories used to calculate the (converged) classical results is a subset of the ones used for the HK results. Due to the neglect of the phase information
Figure 4. Multiple trajectory classical Wigner result for the distance between two electrons starting in a singlet state (solid green line) and a triplet state (dashed green line). The two results are on top of each other. For a comparison, full quantum results are displayed in black.

by working with the density, the classical results show no difference between singlet and triplet, however!

5. Conclusions and Outlook
We have worked out that the difference between singlet and triplet initial state scattering of two electrons cannot be accounted for by a classical (truncated) Wigner method based on multiple trajectories. Both cases, singlet and triplet, lead to the same result for all times, and especially to the same long-time limit. This is in stark contrast to the HK result presented previously in [4] and repeated here for convenience. We are therefore led to the conclusion that the difference between singlet and triplet scattering is an interference effect. This conclusion had been made before by a comparison to the single trajectory Gaussian wavepacket results, but is even more convincing now that we have used a similar set of trajectories as in the HK calculation, without taking into account the phase information. We also stress that there was no need in the semiclassical HK calculation to invoke a fermionic molecular dynamics extension [33] or use Grassmann variable path integrals [34]. The symmetrization/antisymmetrization of the wavefunction is at the heart of the difference in interference in the HK approach and was also used successfully for the extraction of spectra of the different “species” of Helium [35]. In the classical (truncated Wigner) approach it was shown that the symmetrization on the level of the density is not leading to any observable difference between singlet and triplet.

An interesting project for future investigations will be the semiclassical investigation of the dynamics of more than two electrons. A recent study related to this generalization deals with the leading correction due to symmetrization in a quantum (Bohmian) trajectory setup [36].
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