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Spin effects and the Pauli principle in semiclassical electron dynamics

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Several approaches to the semiclassical dynamics of fermions have been proposed in the past. The main subject under discussion was the inclusion of the Pauli principle, i.e., the fact that two electrons with parallel spins must be in orthogonal states. In the past, this was sometimes achieved by adding repulsive Pauli potentials or by using antisymmetric trial states. In this article we show that (a) the use of semiclassical propagators based on classical trajectories is sufficient to account for the Pauli principle, but (b) a semiclassical wave-function approach is not satisfactory.

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I. INTRODUCTION

Recent advances in attosecond physics have renewed the interest in the theoretical description of electron dynamics at ultrafast time scales. Especially when high-energy phenomena are of interest, such as strong-field ionization, it should be reasonable to approximate the dynamics using a semiclassical approach. However, for more than one electron one has to take the spin symmetry into account and, as a consequence, the Pauli exclusion principle. Electrons, or more generally fermions, with parallel spins have to be in orthogonal states. The first dynamical treatment of fermions (especially nucleons) was made using completely classical dynamics, with an additional momentum-dependent Pauli potential, to keep the fermions apart [1–4]. Boal and Glosli [3] stated that classical dynamics "incorporates antisymmetrization effects through a momentum dependent potential." As an exemplary case, we report here their choice for the Pauli potential between particles i and j, although various other forms have been used in the literature: Defining the phase-space distance (with fitting parameter α)

$$X = \tfrac{1}{2}[\alpha^2(q_i - q_j)^2 + (p_i - p_j)^2/(\hbar^2\alpha^2)], \tag{1}$$

a Pauli potential can then be written as

$$V_p(X) = \frac{\alpha^2\hbar^2}{2m}\frac{X}{e^X - 1}. \tag{2}$$

Already here it should be noted that a Pauli potential based on phase-space distance cannot account for all spin effects, because, e.g., the electrons in an atomic 1s and a 2s orbital have zero distance.

A short time afterwards, a step from classical dynamics to semiclassical Gaussian wave-packet (GWP) dynamics was made, so as to include Heisenberg's uncertainty principle. (This approach was often termed quantum molecular dynamics, which is somewhat misleading.) The nuclear matter community kept the Pauli potential [5] or introduced a Pauli blocking [6,7] for this revised approach. The presence of the Pauli potential led to artifacts in the simulations; e.g., wrong thermodynamic properties were predicted. This brought about the development of yet another semiclassical approach. Usually, Hartree products of GWPs are propagated in semiclassical approaches. Instead, one could also antisymmetrize these products to obtain determinants and rederive equations of motion for this ansatz. One then arrives at fermionic molecular dynamics (FMD) or antisymmetric molecular dynamics (AMD) [8–11], which, despite their names, are semiclassical methods. The basic idea is as follows: Let $|\Psi(\{q_i, p_i\})\rangle$ be a determinant made of GWPs and spin. One then calculates a "classical" Lagrangian,

$$\mathcal{L} = \langle\Psi|i\hbar\frac{d}{dt} - \hat{H}|\Psi\rangle, \tag{3}$$

and obtains the equations of motion for $\{q_i, p_i\}$ from the Lagrange equations. The main difference between this approach and the usual semiclassical dynamics is that in Eq. (3) the first step is an integration over position and spin variables. This ansatz obeys automatically the Pauli and the uncertainty principles. However, the resulting equations of motion are very different from the classical ones, and much more complicated.

On the other hand, people have treated electrons semiclassically, without a Pauli potential, and with simple Hartree products of Gaussians, with some success. For example, Harabati and Kay [12] used the Herman-Kluk (HK) propagator [13,14] to describe "collinear helium" in one dimension (1D). They obtained very good results for the binding energies of singlet and triplet states. Similar good agreement has been found for a harmonium system [15] (and for singlet states in Ref. [16]). A different trajectory guided method led to similar success for electrons in a hydrogen molecule [17] and in Ref. [18] the cross section for (Mott) scattering of identical particles was shown to be semiclassically exact. These developments have led to several open questions about what the necessary ingredients for a semiclassical description of electron dynamics really are. Is a Pauli potential necessary? Does one have to propagate determinants? How accurate can semiclassical propagators be when the equations of motion do not contain information about the spin?

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II. THEORY

The system we use to study these questions contains two scattering electrons. Depending on their spin, they will approach each other to different degrees, thus revealing the effect of the Pauli principle. Additionally, many-electron systems are governed by the pairwise interaction of electrons, so that, if the interaction of one pair is described accurately, it is reasonable to believe that this remains the case for more particles. Our test system is described by a Hamiltonian of two interacting but otherwise free electrons in one dimension (atomic units will be used throughout):

$$\hat{H} = \frac{\hat{p}_1^2}{2} + \frac{\hat{p}_2^2}{2} + \frac{1}{\sqrt{(x_1 - x_2)^2 + c}}. \tag{4}$$

The smoothing parameter $c = 0.55$ has often been used for electron dynamics before (see, e.g., Ref. [19]).

The process we describe is the scattering of the two electrons, as a function of their total spin, comparing different semiclassical methods with exact quantum mechanical propagation. Initially, the two electrons are far apart, as expressed by the two spatial orbitals:

$$\varphi_1(x) = \left(\frac{\gamma}{\pi}\right)^{1/4} e^{-\gamma x^2/2}, \tag{5}$$

$$\varphi_2(x) = \left(\frac{\gamma}{\pi}\right)^{1/4} e^{-\gamma(x-15)^2/2 + ip_0 x}. \tag{6}$$

We choose $\gamma = 1/4$ as a compromise between well-localized electrons and a limited amount of spreading during the propagation. The first orbital describes an electron at rest, and the second an electron with momentum $p_0 = -2$ moving towards the first electron. These spatial orbitals can be combined to create either a singlet,

$$\Psi_s(x_1,x_2) = \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1\uparrow} & \varphi_{1\uparrow}\\ \varphi_{2\downarrow} & \varphi_{2\downarrow}\end{vmatrix} - \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1\downarrow} & \varphi_{1\downarrow}\\ \varphi_{2\uparrow} & \varphi_{2\uparrow}\end{vmatrix}\right) \tag{7}$$

$$= \frac{1}{2}[\varphi_1(x_1)\varphi_2(x_2) + \varphi_2(x_1)\varphi_1(x_2)](|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle), \tag{8}$$

or a triplet,

$$\Psi_t(x_1,x_2) = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1\uparrow} & \varphi_{1\uparrow}\\ \varphi_{2\uparrow} & \varphi_{2\uparrow}\end{vmatrix} \tag{9}$$

$$= \frac{1}{\sqrt{2}}[\varphi_1(x_1)\varphi_2(x_2) - \varphi_2(x_1)\varphi_1(x_2)]|\uparrow\uparrow\rangle, \tag{10}$$

wave function. The energy of the two states is identical, since at $t = 0$ the electrons are far apart and the total energy is conserved. An exact quantum mechanical propagation leads to a time-dependent electron density, $\rho_s(x,t)$, for the singlet state, which illustrates the scattering (see Fig. 1). If the same calculation is repeated for the triplet state, we obtain a different density, $\rho_t(x,t)$. To emphasize the difference between the two, we show the difference density $\Delta\rho(x,t) = \rho_t(x,t) - \rho_s(x,t)$ in Fig. 2. In the blue area $\rho_s > \rho_t$ (Fermi hole), while in the red 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. This result is independent of the S_z eigenvalue: If a triplet with two determinants and $(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$ is used in Eq. (10), the result remains the same. The case of a more general wave function, where different spatial parts belong to different spin states, can always be reduced to the factorizable case, if the Hamiltonian is not spin dependent, because different spin states are orthogonal.

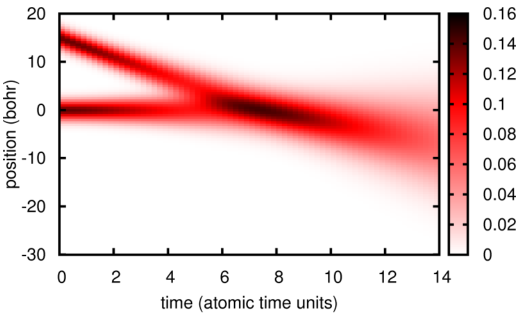

FIG. 1. (Color online) Time-dependent electron density from an exact quantum dynamical simulation for the singlet state.

III. RESULTS

Given the numerically exact quantum results we can address the question of whether the Pauli repulsion can be reproduced by semiclassical methods and, if so, what the necessary conditions are (Pauli potential, determinants instead of Hartree products, etc.). First, we note that both spatial orbitals in Eqs. (5) and (6) are chosen to be Gaussians. In the following, we employ different propagation techniques for those Gaussians, based on work by Heller [20,21] and Herman and Kluk [13]. In all cases we have renormalized the numerical results by calculating

$$N_{s/t}(t) = \langle\Psi_{s/t}(t)|\Psi_{s/t}(t)\rangle \tag{11}$$

and dividing the wave function by $\sqrt{N_{s,t}}$ at each time step [14,22]. As a first test we consider the frozen and thawed Gaussian propagation of the wave function [20], whereby only a single trajectory per Gaussian is necessary. The observable used to show the effect of the Pauli repulsion is $\langle(\hat{x}_1 - \hat{x}_2)^2\rangle^{1/2}$ (the distance between the two electrons). Results are shown in Fig. 3. One notes that the quantum mechanical expectation values agree initially, with a larger distance for the triplet at later times, as expected from the previous considerations.

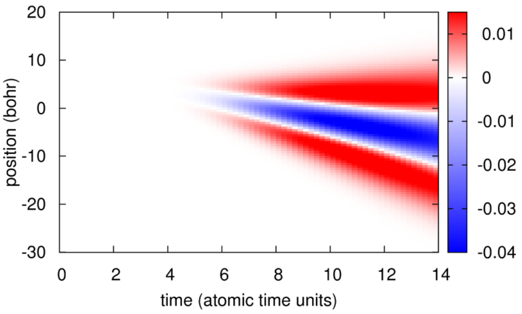

FIG. 2. (Color online) Difference density $\Delta\rho(x,t) = \rho_t(x,t) - \rho_s(x,t)$. In the triplet case, the electrons keep a larger distance because of Pauli repulsion.

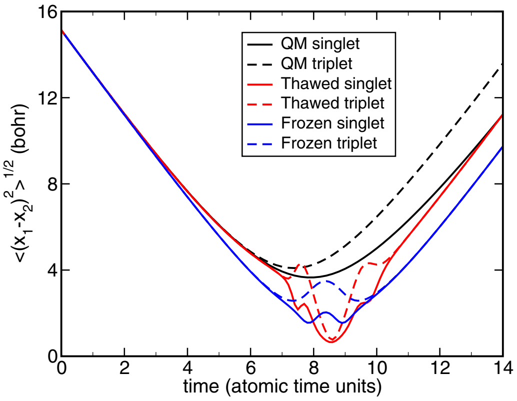

FIG. 3. (Color online) Expectation values $\langle (x_1 - x_2)^2\rangle^{1/2}$ for the exact propagation and the frozen and thawed Gaussian wave-packet propagations.

While the two electrons are close to each other, the triplet experiences a stronger repulsive force, so that the triplet-singlet difference approaches a constant value at long times. (The final kinetic energies must be the same.) In contrast, the frozen and thawed Gaussian results show almost no difference between singlet and triplet, except for a very short time during the collision. This can be understood using the analytic results shown in Appendix. Using the relative coordinate $\hat{y} = \hat{x}_1 - \hat{x}_2$ we find for the triplet-singlet difference

$$\Delta y^2 = \frac{\epsilon_t}{\mathrm{Re}\gamma_t \sinh(\epsilon_t)} \geqslant 0, \tag{12}$$

with

$$\epsilon_t = \mathrm{Re}\gamma_t \left(q_t^2 + \frac{1}{\mathrm{Re}\gamma_t}(p_t + \mathrm{Im}\gamma_t q_t)^2 \right). \tag{13}$$

The difference Δy^2 is largest for $\epsilon_t = 0$ and approaches zero for large values of ϵ_t. From Eq. (13) it follows that ϵ_t is small during the collision, but grows quadratically with the distance q_t. Therefore, the semiclassical approximations to the wave function cannot reproduce the long time difference between the two spin states. Only if ϵ_t is small, i.e., when the wave packets overlap and interference becomes possible, can a difference occur. The different sign of the spatial superposition then leads to the difference in the expectation value. However, Eq. (12) tells us also that the distance between singlets can never be smaller than the distance between triplets, in agreement with the exact calculation.

After the semiclassical approximation to the wave function, we consider semiclassical approximations to the propagator and here especially the HK propagator, which has been developed in Refs. [13,14]; for an early review see Ref. [23]. The HK time-evolution operator (for two electrons in 1D) which approximates the exact quantum time evolution is given by

$$K_{\mathrm{HK}}(t) = \int R_{\mathbf{qp}t} e^{iS_{\mathbf{qp}t}} \prod_{k=1}^{2} |g(q_k,p_k,t)\rangle\langle g(q_k,p_k,0)| \frac{dq_k dp_k}{2\pi\hbar}, \tag{14}$$

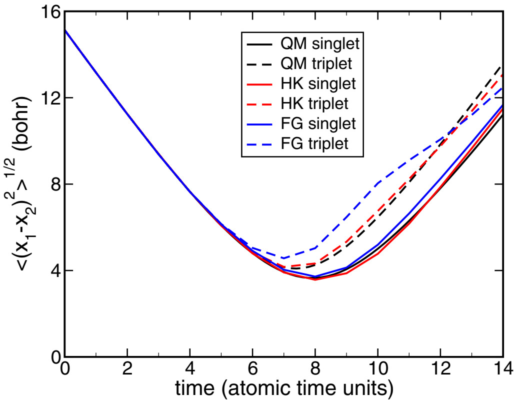

FIG. 4. (Color online) Comparison of exact quantum mechanical expectation values with semiclassical results from the semiclassical HK propagation and prefactor-free frozen Gaussian (FG) propagation. Both semiclassical methods show noticeable differences between parallel and antiparallel spins.

with $\mathbf{q} = (q_1,q_2), \mathbf{p} = (p_1,p_2)$, and the bare potential in the expression for the action $S_{\mathbf{qp}t}$. Furthermore, it contains a prefactor, $R_{\mathbf{qp}t}$, which is dependent on the so-called stability or monodromy matrix and accounts among others for approximate normalization of the dynamics [14,24]. It differs in a fundamental way from the single trajectory approaches used before by containing an integral over phase space.

As shown in Fig. 4 (see black and red lines), HK semiclassical dynamics using 10^5 trajectories reproduces the quantum results and the difference between the singlet and triplet states extremely well. In order to understand if the phase-space integration is responsible for the good results of HK, we repeated the calculation (using 10^5 trajectories) with the prefactor set to 1, see blue lines in Fig. 4. In both cases, the wave function has been renormalized [22]. Apart from the renormalization, this is similar to the conventional frozen Gaussian approach [21]. In this case too, the difference between singlet and triplet states is well reproduced, although some of the accuracy is lost. From these results we conclude that for the distinction of singlets and triplets it is sufficient to allow interference of trajectories, creating "collective correlation," in the nomenclature of E. Heller [21]. The semiclassical time-evolution operator is similar to its exact quantum counterpart $\exp(-i\hat{H}t)$, which also acts only on the spatial part of the initial state and does not depend on the spin degrees of freedom. We note that all four semiclassical propagation methods discussed are symmetric with respect to exchange of electrons, so that the antisymmetry of the initial state is preserved.

Finally, we also studied the time evolution of the distance using what is known as classical Wigner dynamics [25,26] or, equivalently, the linearized semiclassical initial value representation [27,28] developed in the Miller group. Here, a phase-space integration is performed, but no phase information is used during the propagation. As a consequence, the difference between the singlet and triplet states, as might have been expected, is lost.

In the simulations described above, only a single observable was discussed. However, we would like to point out that, if the time-dependent distance is correctly reproduced, then also the velocities or momenta must be correct and also, at least substantially, the kinetic and potential energies.

To summarize, we have shown that neither Pauli potentials nor symmetry adapted trial states are needed to capture the difference between the interactions of electrons with parallel and antiparallel spin. Both the frozen Gaussian approach of Heller and the HK propagator reproduce the dynamics correctly. In contrast, neither of the single trajectory approaches gives correct results. For both spins, the electrons come far too close together. The semiclassical propagators can reproduce the singlet or triplet difference well since they are acting on the spatial part of the wave function only. The difference between the singlet, Eq. (8), and the triplet, Eq. (10), wave functions is the change of sign between the Hartree products. As long as this phase difference is propagated in time correctly, all observables will have the correct time dependence. The present study however cannot answer the question of whether the propagation of determinants instead of Hartree products, i.e., FMD, might be more efficient. A study by Shalashilin [29] found that the description of double ionization using FMD is considerably easier than that using coupled coherent states. A systematic comparison of FMD with semiclassical initial value representation and HK, with regard to the number of trajectories and the complexity of the equations of motion, has to be left for the future.

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APPENDIX: ANALYTIC RESULTS FOR SINGLE TRAJECTORY PROPAGATIONS

If the semiclassical approximation is made to the wave functions (8) and (10), it is possible to derive some analytic expressions for the difference between the singlet result and the triplet result. To do so, we first introduce the difference coordinate $y = x_1 - x_2$. The propagation in the center-of-mass coordinate is trivial and can therefore be ignored here. The spatial part of the wave packet in the relative coordinate is then

$$\langle y|\Phi_{\pm,t}(p,q)\rangle = N\big(e^{-\gamma_t(y-q_t)^2/2+ip_t(y-q_t)} \pm e^{-\gamma_t(y+q_t)^2/2-ip_t(y+q_t)}\big), \qquad (A1)$$

with q_t and p_t being the position and momenta propagated according to the classical equations of motion, and γ_t being the (possibly time-dependent) inverse width of the wave packet, which obeys the equation of motion

$$\frac{d\gamma_t}{dt} = -2i\gamma_t^2 + i\frac{d^2V}{dy^2}. \qquad (A2)$$

In the wave function the $+$ corresponds to the singlet wave function (antisymmetric in spin) and the $-$ to the triplet wave function (antisymmetric in space). We can now calculate the expectation value for the relative coordinate using only Gaussian integration,

$$\langle\Phi_{\pm,t}|\hat{y}^2|\Phi_{\pm,t}\rangle = \frac{1}{2\mathrm{Re}\gamma_t} + q_t^2 \mp \frac{\epsilon_t \exp(-\epsilon_t)}{\mathrm{Re}\gamma_t[1 \pm \exp(-\epsilon_t)]}, \qquad (A3)$$

and the difference between triplet and singlet,

$$\Delta y^2 = \langle\Phi_{-,t}|\hat{y}^2|\Phi_{-,t}\rangle - \langle\Phi_{+,t}|\hat{y}^2|\Phi_{+,t}\rangle = \frac{\epsilon_t}{\mathrm{Re}\gamma_t \sinh(\epsilon_t)} \geqslant 0, \qquad (A4)$$

with

$$\epsilon_t = \mathrm{Re}\gamma_t\left(q_t^2 + \frac{1}{\mathrm{Re}\gamma_t}(p_t + \mathrm{Im}\gamma_t q_t)^2\right). \qquad (A5)$$

The interpretation of these results is given in the main text.

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