Semiclassical Electron Correlation in Density-Matrix Time Propagation

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Lack of memory (locality in time) is a major limitation of almost all present time-dependent density-functional approximations. By using semiclassical dynamics to compute correlation effects in the time propagation of the density matrix, we incorporate memory, including initial-state dependence, as well as changing occupation numbers, and predict more observables in strong-field applications.

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The impact of time-dependent density-functional theory (TDDFT) [1,2] on calculations of excitation spectra and response in molecules and solids is evident in its increasing use. A weak perturbation is applied to the system beginning in its ground state, and usually the exchange-correlation (xc) effects are treated with a ground-state (adiabatic) approximation. Generally the results are usefully accurate, but specific cases (e.g., charge-transfer excitations, optical response of solids, etc.) require improved approximations undergoing intense research.

In principle, TDDFT also applies beyond the linear-response regime, but success has been slower. There are three main reasons. First, many observables of interest are not simply related to the time-dependent one-body density: in addition to the approximation for the xc functional, new approximate "observable functionals" are needed to extract the quantity of interest from the Kohn-Sham (KS) system. Even with an exact xc potential, they would remain elusive. These include double-ionization probabilities and momentum-densities, and naive approximations to these generally fail [3,4]. Second, lack of memory dependence in the usual xc approximations has been shown to be often far more problematic than in the linear-response regime [5,6]. The exact functional depends on the history of the density as well as on the initial state. Different initial states lead to fundamentally different xc potentials [6]. But no approximation today has initial-state dependence, almost all neglect history dependence, and all violate an exact condition on memory dependence, derived in Ref. [7]. Third, a particularly severe difficulty is encountered when a system starting in a wave function dominated by a single Slater determinant (SSD), evolves to a state that fundamentally needs at least two SSDs to describe it. This is the time-dependent (TD) analog of ground-state static correlation, and arises in electronic quantum-control problems [7,8], in ionization [4], and in coupled electron-ion dynamics [9]. The TD KS system evolves the occupied orbitals under a one-body Hamiltonian, remaining in an SSD: the KS one-body density matrix is always idempotent (even with exact functionals), while, in contrast, that of the true system develops eigenvalues [natural occupation numbers (ONs)] far from 0 or 1 in these applications. The exact xc potential and observable functionals consequently develop complicated structure that is difficult to capture in approximations. For example, in Ref. [4], a simple model of ionization in two-electron systems showed that the momentum distribution computed directly from the exact KS system contains spurious oscillations due to using a single, necessarily delocalized orbital, a nonclassical description of the essentially classical two-electron dynamics. Ref. [7] discussed the unusual and nonintuitive xc potentials that arise in certain electronic quantum-control problems, e.g., He $1s^2 \rightarrow 1s2p$. If the overlap between the initial and final states is targeted, the maximum that can be achieved is 0.5 [8], while close to 0.98 is achieved for the true interacting problem.

Recent pioneering strides in TD density-matrix functional theory (TDDMFT) show this alternative approach can overcome some of the challenges of adiabatic TDDFT in linear response [10], e.g., adiabatic TDDMFT functionals were shown to capture charge-transfer excitations well. All one-body observables are directly obtained. However, adiabatic functionals bootstrapped from the usual ground-state DMFT disappointingly cannot change ONs [11] unless some unusual structural changes are made in the functional form [10]. The first real-time TDDMFT calculations [12], use an extra energy-minimizing procedure at each time that results in time-dependent ONs.

In this Letter, we present a new approach to correlation in electron dynamics that makes a significant step in solving all the problems mentioned above. We work directly with the one-body density matrix in real time and use a semiclassical approximation for the correlation term in the equation of motion while evaluating the other terms exactly quantum-mechanically. All one-body observables are obtained directly. It is the first density-matrix (or density-) functional approach that has initial-state dependence, with memory naturally carried along by the classical trajectories, and the first real-time approach that can change ONs significantly away from the adiabatic limit. A heirarchy of semiclassical approximations for the correlation term is discussed, decreasing in accuracy but also in computational cost. On the first level, correlation is obtained exactly to

$O(\hbar)$, while at the lowest level quantum mechanics enters only in the determination of the initial state, with the dynamical correlation obtained via pure classical evolution. Despite its simplicity, we demonstrate via a simple example that this latter approach yields time-dependent ONs.

Semiclassics lies at the very foundations of the earliest density-functional theories that predate the rigorous DFT of Refs. [13]. Recently, its semiclassical origins have been reawakened [14]. Until now, semiclassical methods have not been applied to functional development in TDDFT nor in TDDMFT, although mean-field semiclassical methods have been used to approximate KS dynamics, e.g., [15]. TDDMFT may equally be viewed as a "phase-space-density-functional theory", as reflected, for example, in the relation between the one-body Wigner function $w(\mathbf{r}, \mathbf{p}, t)$ and the spin-summed one-body density matrix $\rho_1(\mathbf{r}', \mathbf{r}, t) = N\sum_{\sigma_1\ldots\sigma_N} \int d^3r_2 \ldots d^3r_N \times \Psi^*(\mathbf{r}'\sigma_1, x_2 \ldots x_N, t)\Psi(\mathbf{r}\sigma_1, x_2 \ldots x_N, t)$: $w(\mathbf{r}, \mathbf{p}, t) = \int d^3y \rho_1(\mathbf{r}\text{-}\mathbf{y}/2, \mathbf{r} + \mathbf{y}/2, t)e^{i\mathbf{p}\cdot\mathbf{y}}/(2\pi)^3$. [Here $x_i = (\mathbf{r}_i, \sigma_i)$ indicates spatial and spin coordinates, and atomic units are used throughout]. This observation suggests the utility of semiclassical approaches, as we shall see shortly.

All the one-body terms in the equation of motion for ρ_1 can be treated exactly, and for spin-unpolarized systems:

$$\begin{aligned} i\dot{\rho}_1(\mathbf{r}', \mathbf{r}, t) = {} & (-\nabla^2/2 + v(\mathbf{r}, t) + \nabla'^2/2 \\ & - v(\mathbf{r}', t))\rho_1(\mathbf{r}', \mathbf{r}, t) + \int d^3r_2 f_{\mathrm{ee}}(\mathbf{r}, \mathbf{r}', \mathbf{r}_2) \\ & \times\left(n(\mathbf{r}_2, t)\rho_1(\mathbf{r}', \mathbf{r}, t) - \frac{1}{2}\rho_1(\mathbf{r}', \mathbf{r}_2, t)\rho_1(\mathbf{r}_2, \mathbf{r}, t)\right) \\ & + \int d^3r_2 f_{\mathrm{ee}}(\mathbf{r}, \mathbf{r}', \mathbf{r}_2)\rho_{2\mathrm{C}}(\mathbf{r}', \mathbf{r}_2, \mathbf{r}, \mathbf{r}_2, t), \end{aligned} \tag{1}$$

where we have decomposed the second-order density matrix, $\rho_2(\mathbf{r}', \mathbf{r}_2', \mathbf{r}, \mathbf{r}_2, t) = N(N-1)\sum_{\sigma_1\ldots\sigma_N} \int d^3r_3 \ldots d^3r_N$ $\Psi^*(\mathbf{r}'\sigma_1, \mathbf{r}_2'\sigma_2, x_3 \ldots x_N, t)\Psi(\mathbf{r}\sigma_1, \mathbf{r}_2\sigma_2, x_3 \ldots x_N, t) = \rho_1(\mathbf{r}_1', \mathbf{r}_1, t)\rho_1(\mathbf{r}_2', \mathbf{r}_2, t) - \rho_1(\mathbf{r}_1', \mathbf{r}_2, t)\rho_1(\mathbf{r}_2', \mathbf{r}_1, t)/2 + \rho_{2\mathrm{C}}(\mathbf{r}_1', \mathbf{r}_2', \mathbf{r}_1, \mathbf{r}_2, t)$: the first term is the noninteracting, uncorrelated product, the second term takes care of the Pauli principle at the uncorrelated level, and the third term is the correlation component, whose functional dependence on ρ_1 is unknown. In TDDMFT, $\rho_2(\mathbf{r}', \mathbf{r}_2, \mathbf{r}, \mathbf{r}_2, t)$ is to be approximated as a functional of ρ_1 and the initial interacting state Ψ_0, $\rho_2[\rho_1, \Psi_0]$. We have defined the electron-interaction kernel $f_{\mathrm{ee}}(\mathbf{r}, \mathbf{r}', \mathbf{r}_2) = 1/|\mathbf{r} - \mathbf{r}_2| - 1/|\mathbf{r}' - \mathbf{r}_2|$. There is a one-to-one mapping between $v(\mathbf{r}, t)$ and ρ_1 (or $w(\mathbf{r}, \mathbf{p}, t)$) for a given initial state $\Psi_0(\mathbf{r}_1 \ldots \mathbf{r}_N)$ provided the TD external potential $v(\mathbf{r}, t)$ that the N-electron system evolves in is local (multiplicative) [16]. This follows directly from the Runge-Gross theorem, and also a 1-1 mapping holds for external vector potentials [4], but we will focus on scalar potentials at present. An immediate advantage of replacing the coordinate-space density with the density matrix as basic variable is that it directly gives the expectation value of *any* one-body operator: no additional observable functionals are needed for momentum distributions or kinetic energies, for example. There is no KS equivalent: because of idempotency of noninteracting density matrices, it is impossible for a noninteracting system of electrons to have the same phase-space density as a system of interacting electrons.

Ideally, the approximation made for $\rho_2[\rho_1, \Psi_0]$ captures correlation, memory-dependence including initial-state dependence, and, most importantly for the quantum-control and ionization applications mentioned earlier, yield time-dependent ONs, $f_i(t)$, defined via the natural orbital decomposition $\rho_1(\mathbf{r}, \mathbf{r}', t) = \sum_i f_i(t)\psi_i(\mathbf{r}, t)\psi_i^*(\mathbf{r}', t)$.

The TDDMFT developments have so far been predominantly within linear response [10], investigating adiabatic functionals for ρ_2. Our approach computes the correlation component of ρ_2 semiclassically, focusing on full dynamics (not linear response). We propagate Eq. (1) treating all terms except the last exactly quantum-mechanically. The last term is treated as a driving term: we approximate $\rho_{2\mathrm{C}} \approx \rho_{2\mathrm{C}}^{\mathrm{SC}}$, evaluated separately via semiclassical dynamics, calculated from running classical trajectories in the N-body interacting phase-space.

Semiclassical methods construct an approximate quantum propagator utilizing classical trajectory information alone. Although there are a variety of forms, the essential structure is a sum over classical trajectories $\sum_{\mathrm{cl.traj.}} C_i(t)e^{iS_i(t)/\hbar}$, where $S_i(t)$ is the classical action along the ith trajectory, and the prefactor $C_i(t)$ captures fluctuations around the classical path. Semiclassical approaches capture quantum effects such as interference, zero-point energy, tunneling (to some extent), while generally scaling favorably with system size. Based on classical trajectories, intuition about the physical mechanisms underlying the dynamics can be gained. Although mostly applied to nuclear dynamics in molecules, there have been applications to electrons [17].

Semiclassical formulae have been derived both from largely intuitive arguments (e.g., Ref. [18]), as well as from careful rigorous asymptotic analyses of the quantum propagator (see, e.g., Refs. [19]) that satisfy TDSE to order $\hbar$. Miller [20] showed the equivalence of different semiclassical representations within stationary-phase evaluation of the transformations. The most popular is the Heller-Herman-Kluk-Kay [18,21,22], which is a "semiclassical rigorization" of Heller's frozen Gaussian approach, uniformly solving the TDSE to $O(\hbar)$. It is a sum over initial points in (N body) phase space, $\underline{\mathbf{z}}_0 \equiv (\underline{\mathbf{r}}_0, \underline{\mathbf{p}}_0) \equiv ([\mathbf{r}_1(0), \mathbf{p}_1(0)] \ldots [\mathbf{r}_N(0), \mathbf{p}_N(0)])$:

$$(e^{-i\hat{H}t})^{\mathrm{SC}} = (2\pi)^{-M} \int d^{2M}\underline{\mathbf{z}}_0 |\underline{\mathbf{z}}_t\rangle C_t(\underline{\mathbf{z}}_0)e^{iS_t(\underline{\mathbf{z}}_0)}\langle\underline{\mathbf{z}}_0|, \tag{2}$$

where: $\underline{\mathbf{z}}_t = [\underline{\mathbf{r}}(t), \underline{\mathbf{p}}(t)]$ obeys Hamilton's equations

$$\dot{\underline{\mathbf{r}}} = \underline{\mathbf{p}}(t), \dot{\underline{\mathbf{p}}} = -\nabla H(\underline{\mathbf{r}}, \underline{\mathbf{p}}, t), \tag{3}$$

$M = 3N$ is the dimensionality of configuration space, and $S(\underline{\mathbf{z}}_0, t)$ is the classical action, $\int^t (T - V)dt$, for a trajectory which begins at the phase space point ($\underline{\mathbf{r}}_0$, $\underline{\mathbf{p}}_0$), reaching point ($\underline{\mathbf{r}}_t$, $\underline{\mathbf{p}}_t$) at time t. The state $|\underline{\mathbf{z}}\rangle$ is a product of coherent states for each coordinate, labeled by their centers in phase-space: $\langle x|q,p\rangle = (\frac{\gamma}{\pi})^{1/4}\exp(-\gamma(x-q)^2/(2) + ip(x-q))$, where γ is a chosen width parameter. The preexponential determinant $C_t(\underline{\mathbf{z}}_0)$ accounts for fluctuations about the classical paths: when γ is chosen identical for all particles, $C_t(\underline{\mathbf{z}}_0) = |\frac{1}{2}(\frac{\partial \mathbf{r}_t}{\partial \mathbf{r}_0} + \frac{\partial \mathbf{p}_t}{\partial \mathbf{p}_0} - i2\gamma\frac{\partial \mathbf{r}_t}{\partial \mathbf{p}_0} + \frac{i}{2\gamma}\frac{\partial \mathbf{p}_t}{\partial \mathbf{r}_0})|^{1/2}$.

Typically, the phase-space integral is performed via Monte-Carlo integration, with initial conditions weighted by the initial wave packet $\langle\underline{\mathbf{z}}_0|\Psi_0\rangle$. Because of the evaluation of the prefactor C, the numerical effort per trajectory scales as N^3; methods which neglect this scale as N but at the cost of losing accuracy and semiclassical rigor. While Monte-Carlo integration scales as $\sqrt{N}$ for positive integrands, the phase-space integral can be difficult to converge due to its oscillatory nature, especially for many degrees of freedom and chaotic dynamics, and so various sophisticated integral-filtering techniques, or "forward-backward" (FB) methods [23] have been formulated, allowing calculations for up to 100 degrees of freedom [24].

Applying Eq. (2) to propagate Ψ, then computing $\rho_2^{\rm SC}$ via integration constitutes our highest level of semiclassical heirarchy for correlation. We compute

$$\rho_1^{\rm SC}(\mathbf{r}',\mathbf{r},t) = \frac{1}{N-1}\int \rho_2^{\rm SC}(\mathbf{r}',\mathbf{r}_2,\mathbf{r},\mathbf{r}_2,t)d^3r_2 \tag{4}$$

and

$$\begin{aligned}\rho_{2\rm C}^{\rm SC}(\mathbf{r}',\mathbf{r}_2,\mathbf{r},\mathbf{r}_2,t) = {}&\rho_2^{\rm SC}(\mathbf{r}',\mathbf{r}_2,\mathbf{r},\mathbf{r}_2,t)\\ &-\rho_1^{\rm SC}(\mathbf{r}',\mathbf{r},t)n^{\rm SC}(\mathbf{r}_2,t)\\ &+\rho_1^{\rm SC}(\mathbf{r}',\mathbf{r}_2,t)\rho_1^{\rm SC}(\mathbf{r}_2,\mathbf{r},t)/2,\end{aligned} \tag{5}$$

where $n^{\rm SC}(\mathbf{r}_2,t)$ is the one-body density, the diagonal of Eq. (4). Finally, this $\rho_{2\rm C}^{\rm SC}$ is input into Eq. (1) as a driving term. At this level, correlation effects are exact to $O(\hbar)$, while all other effects are quantum-mechanically exact. Difficulties with converging the highly-oscillatory integral in Eq. (2), and the N^3 scaling of the prefactor, render this impractical for more than a few electrons, to the point where, for many cases, little computational benefit is gained over running the full quantum mechanics.

Instead, in a FB fashion, we can take advantage of significant phase cancellation between the propagation of Ψ^* and that of Ψ in calculating $\rho_2^{\rm SC}$. Applying the semiclassical propagator Eq. (2) to both the Ψ and Ψ^* appearing in ρ_2, and doing some intermediate integrations via stationary phase, the second level in our heirarchy is

$$\begin{aligned}\rho_2^{\rm SC}(\mathbf{r}',\mathbf{r}_2,\mathbf{r},\mathbf{r}_2,t) = \frac{N(N-1)}{(2\pi)^{3N+2}}&\int d^{2M}\underline{\mathbf{z}}_0 d^3z'_{1,t}d^3z'_{2,t}\\ &\times e^{i(S(t)-S'(t))}\mathcal{G}(\mathbf{r}',\mathbf{r},\mathbf{r}_2;\mathbf{z}'_{1,t}\mathbf{z}'_{2,t}\mathbf{z}_{1,t}\mathbf{z}_{2,t})\\ &\times\langle\Psi_0|\underline{\mathbf{z}}'_0\rangle\langle\underline{\mathbf{z}}_0|\Psi_0\rangle,\end{aligned} \tag{6}$$

where $\underline{\mathbf{z}}'_0 = (\mathbf{q}'_{1,t}(-t),\mathbf{p}'_{1,t}(-t),\mathbf{q}'_{2,t}(-t),\mathbf{p}'_{2,t}(-t),\mathbf{r}_{3,0},\mathbf{p}_{3,0}\ldots\mathbf{r}_{N,0},\mathbf{p}_{N,0})$ and $\mathcal{G}(\mathbf{r}',\mathbf{r},\mathbf{r}_2;\mathbf{z}'_{1,t}\mathbf{z}'_{2,t}\mathbf{z}_{1,t}\mathbf{z}_{2,t}) = \langle\mathbf{r}'|\mathbf{z}'_{1,t}\rangle^*\langle\mathbf{r}_2|\mathbf{z}'_{2,t}\rangle^*\langle\mathbf{r}|\mathbf{z}_{1,t}\rangle\langle\mathbf{r}_2|\mathbf{z}_{2,t}\rangle$. That is, an initial phase-space point $\underline{\mathbf{q}}_0$, $\underline{\mathbf{p}}_0$ is classically evolved for time t, when the phase-space points of the first two particles are shifted to $(\mathbf{q}'_{t1},\mathbf{p}'_{t1},\mathbf{q}'_{t2},\mathbf{p}'_{t2})$, before all particles evolve back to time zero. There is therefore significant cancellation of phase $(S(t)-S'(t))$, that would generally result in good convergence of Monte Carlo evaluation of this phase-space integral, even for many electrons. Further, the product of the numerically expensive prefactors has been reasonably approximated to 1 for many electrons. The true initial state appearing in Eq. (6) is in practise approximated by a few (KS) SSD's, or by a high-level wave function calculation, if a stationary state. Equations (4) and (5) are then used to extract the semiclassical correlation component $\rho_{2\rm C}^{\rm SC}$, capturing interference and zero-point energy effects, that is then input into Eq. (1) as a driving term.

An even more simple prescription is obtained by neglecting the phase and prefactor altogether: this yields the quasiclassical Wigner method [25], and can also be shown to result from a linearization of the FB [23]:

$$w_N^{\rm QC}(\underline{\mathbf{r}},\underline{\mathbf{p}},t) = w_N(\underline{\mathbf{r}}(-t),\underline{\mathbf{p}}(-t),t=0) \tag{7}$$

from which, by integration, a quasiclassical approximation to the correlation component of ρ_2 is obtained, and inserted as a driving term into Eq. (1). This represents the lowest level of our semiclassical heirarchy: in computing the correlation, while scaling classically with the system size, all interference is lost, quantum mechanics enters only in determining the initial Wigner function, and when the wave function becomes delocalized, this approximation degrades. Nevertheless quasiclassical methods (even of the entire dynamics) have proven useful in analyzing electron ionization distributions [26].

Our prescription thus results in a semiclassical approximation for the correlation component to ρ_2 in the equation of motion Eq. (1) for ρ_1, all other terms of which are treated exactly quantum mechanically. But can our approach lead to time-dependent ONs? To illustrate this, we consider a simple model system, the two-electron Moshinsky atom [27]: $\hat{H} = -\frac{1}{2}(\nabla_1^2+\nabla_2^2) + \frac{k(t)}{2}\times(r_1^2+r_2^2)+\lambda(r_1-r_2)^2$. Although a poor model of a real atom, its purpose here is simply to demonstrate that even the lowest level quasiclassical approximation to correlation is able to capture changing ONs. Its harmonic nature makes it exactly solvable, and we apply a simple sinusoidal force constant, $k(t) = 1 - 0.05\sin(2t)$, that encourages population transfer to the first accessible excited state (an excitation in the center of mass coordinate), from the initial ground state, a spin singlet. Moreover, due to its harmonic nature, the quasiclassical and semiclassical propagations equal the exact quantum propagation [25]. Figure 1 plots the ONs, $f_i(t)$, of the spatial natural orbitals, obtained from diagonalizing $\rho_1(\mathbf{r},\mathbf{r}',t)$ at each time t. In striking contrast, TDDMFT, with the usual adiabatic approximations would yield constant occupation numbers. Aside from the significance in quantum-control problems, lack of time-dependent ONs impacts observables; e.g., the momentum

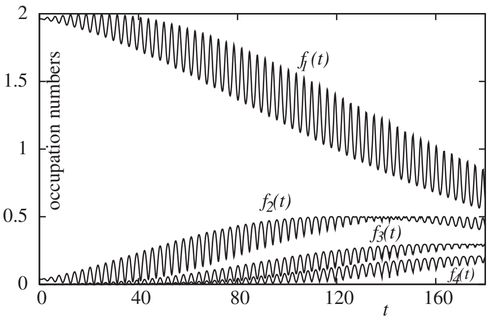

FIG. 1. Occupation numbers for the model system: quasiclassical correlation shown is exact, while the usual adiabatic TDDMFT approximations yield constant straight lines.

distributions are qualitatively incorrect [4]. How well our approach works for realistic systems is currently being tested; this example, however, illustrates that it certainly does not suffer from the inability to change ONs as existing schemes do. In our scheme, ONs generally will change correctly in the quasiclassical or semiclassical sense, depending on the level in the heirarchy used; in the latter, they will be correct to order $\hbar$.

In summary, we have presented a semiclassical approach to correlation in TDDMFT, that (i) naturally captures history-dependence and initial-state dependence (for the first time) at the semiclassical level, as memory is carried along with the classical trajectories composing ρ_2^{SC}, (ii) directly yields all one-body observables, and (iii) changes occupation numbers. Correlation is treated semiclassically, while all other terms determining the density matrix are exact. The highest semiclassical level yields correlation exactly to $O(\hbar)$, but will be impractical in many cases; the approximate semiclassical treatment [Eq. (6)] will still capture quantum many-body effects in a computationally efficient way. The simplest approximation [Eq. (7)] scales classically, so is well worth investigating, especially since the other terms in the equation of motion for ρ_1 are treated exactly. As there is no guarantee of N representability of ρ_1 being preserved in the semiclassical dynamics [at least beyond $O(\hbar)$], tests on realistic systems are necessary. Treating many of the challenging aspects of approximate density-functional methods described earlier, it is a promising approach to study electron dynamics in strong fields.

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