

# Exact-exchange optimized effective potential and memory effect in time-dependent density functional theory<sup>\*</sup>

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**Abstract.** The memory effect in time-dependent density functional theory (TDDFT) is important in simulating many time-dependent physical processes, and its implementation in real time has been a longstanding challenge, thus limiting most of TDDFT applications to either adiabatic or linear-response regime. In this paper, we conduct the non-adiabatic calculations for a one-dimensional two-electron Helium model in a triplet state using the recently formulated Sturm-Liouville-type *time-local* equation for the time-dependent optimized effective potential (TDOEP) with the exact exchange functional, and the results agree with the exact time-dependent Schrödinger equation solutions. It is also found that the time-dependent dipole moment and probability density calculated from the TDOEP approach are more accurate than those from the adiabatic time-dependent Krieger-Li-Iafrate (TDKLI) approximation and the adiabatic local spin density approximation. Specifically, the non-adiabatic and memory-dependent terms in the time-local TDOEP equation correctly describe the time-dependent structure of exchange-correlation potential and yield the probability density evolution. These findings should provide important insights toward future studies on memory effects in TDDFT.

## 1 Introduction

Time-dependent density functional theory (TDDFT) [1] is formally exact, however, the exact form of the crucial exchange-correlation (xc) potential is not known. Thus far, most time-dependent xc potentials for real-time TDDFT simulations of dynamic systems were based on the adiabatic extension of approximate ground-state xc functionals that only depend on the instantaneous density, which lacks memory effects. The inclusion of the memory effects is essential to prevent many errors due to the adiabatic approximation [2–12]. For example, the TDDFT calculation based on the adiabatic approximation could not produce the correct time-dependent density for a system driven by a near resonant external field, even though the corresponding time-dependent dipole exhibits Rabi-type oscillations [6]. It has been shown that no adiabatic approximation of xc potential can adequately describe such nonlinear dynamics that involves a large temporal change in charge density [7]. In addition, it was found that the xc potential derived from the adiabatic

approximation does not possess the inherent dynamical steps appearing in the exact time-dependent xc potential [9,10]. Moreover, it was demonstrated that standard xc functionals with the adiabatic approximation are unable to describe the population inversion from the ground state to the second excited state of LiCN in real-time TDDFT [13]. Also, studies of gold clusters showed that memory effects can significantly broaden the absorption lines of the surface plasmon and redshift emission lines of high-harmonic generation [14]. Last but not least, it was shown that the step and peak features of the xc potential due to memory effects is crucial to describe the highly correlated dynamics for autoionization process [15].

To alleviate the unwanted errors arising from the adiabatic approximation, it has been suggested to impose the exact conditions in TDDFT [16–18] to regain the temporally nonlocal effects [19,20]. However, these conditions not only can hinder a straightforward extension of approximate xc potentials from the ground-state DFT studies but also makes impossible a systematic means to construct more accurate xc functionals. In general, given an initial state at time  $t_0$ , it is very demanding to compute the corresponding time-dependent xc potential  $v_{xc}(\mathbf{r}, t)$  that depends on the density  $\rho(\mathbf{r}', t')$  at all spatial points  $\mathbf{r}'$  and at all times  $t'$  between  $t_0$  and  $t$ .

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In the past two decades, several approaches to go beyond the adiabatic approximation have been made, including the time-dependent current density functional theory (TDCDFT) [19–25], time-dependent deformation functional theory (TDDefFT) [25–27], and the time-dependent optimized effective potential (TDOEP) based on orbital-dependent xc functionals [28,29]. Currently, commonly used xc functionals in TDCDFT and TDDefFT are based on the homogeneous electron liquid assumption, as the extension of the local density approximation (LDA). However, applications of these two approaches have been limited to extended systems and suffer from spurious damping when dealing with few-electron systems [25,30]. By contrast, the orbital-dependent xc functionals are amenable to finite systems [31–33]. Most importantly, the TDOEP equation provides a general, rigorous framework for the construction of memory-dependent xc potentials [8,12,28,33,34], and the exact TDOEP satisfies the zero-force theorem in TDDFT [35]. It has been adapted for systematic construction of the exact exchange-correlation potential via the Keldysh perturbation expansion [36] and the time-dependent generalization of the Görling-Levy perturbation expansion [37]. Moreover, the orbital-dependent functional approach can avoid electronic self-interaction by including the exact exchange [38] or self-interaction correction [39], and generates derivative discontinuities for the energy functionals [40,41].

Nevertheless, the extreme complexity involved in the nonlinear TDOEP integral equation renders a direct solution of TDOEP formidable [34,42,43], and the utility of the TDOEP is still largely unexplored. Thus far the exact TDOEP in the context of the exact-exchange (EXX) functional has only been successfully implemented in two distinct cases, by Wijewardane and Ullrich for a quasi-one-dimensional quantum well [34] and more recently by Liao et al. for a one-dimensional hydrogen chain [35]. Specifically, in the former a global self-consistency scheme was applied to solving the nonlinear TDOEP integral equation iteratively, which requires all dynamical information about the time-dependent KS orbitals and xc potential in every global iteration cycle. Whereas, in the latter case an equivalent Sturm-Liouville-type *time-local* TDOEP equation has been formulated (see Sect. 2) to enable a step-by-step solution in real time.

In this paper, we consider a one-dimensional two-electron helium model in a triplet state, which can be solved exactly by propagating the exact time-dependent Schrödinger wavefunction. We have performed the real-time TDDFT simulations based on the newly formulated time-local TDOEP equation to compute the memory-dependent xc potential [35]. It is shown that the non-adiabatic and memory dependent terms in the time-local TDOEP equation correctly describe the shape of the time-dependent xc potential, which yields accurate time-dependent density evolution consistent with the exact time-dependent Schrödinger equation (TDSE) solution. For comparisons, we have also solved the time-dependent KS equation with the time-dependent Krieger-Li-Iafrate (TDKLI) approximation [28,44] and the adiabatic local spin-density approximation (ALSDA) [45], respectively.

The remaining parts of this paper are arranged as follows. Section 2 reviews the derivation of the time-local TDOEP equation. Section 3 describes the one-dimensional two-electron helium model and the setup for TDSE and TDDFT. Section 4 presents the results and discusses the memory effects obtained in the TDOEP-based calculations. Finally, a short summary is given in Section 5. Atomic unit ( $m_e = e = \hbar = 1$ ) is used throughout the paper and the abbreviated notation  $\varphi_{j\sigma} = \varphi_{j\sigma}(\mathbf{r}, t)$ ,  $\chi_{j\sigma} = \chi_{j\sigma}(\mathbf{r}, t)$ ,  $v_{xc\sigma} = v_{xc\sigma}(\mathbf{r}, t)$ , and  $u_{xcj\sigma} = u_{xcj\sigma}(\mathbf{r}, t)$  is adopted whenever it is unambiguous.

## 2 Time-local TDOEP approach

For TDDFT calculations in real time, the time-dependent KS orbital  $\varphi_{j\sigma}(\mathbf{r}, t)$  is propagated according to the time-dependent KS equation,

$$\left[ i \frac{\partial}{\partial t} - \hat{H}_\sigma \right] \varphi_{j\sigma}(\mathbf{r}, t) = 0, \quad (1)$$

where  $\hat{H}_\sigma = -\frac{\nabla^2}{2} + v(\mathbf{r}, t) + v_H(\mathbf{r}, t) + v_{xc\sigma}(\mathbf{r}, t)$  is the time-dependent KS Hamiltonian consisting of the external potential  $v(\mathbf{r}, t)$ , Hartree potential  $v_H(\mathbf{r}, t)$ , and xc potential  $v_{xc\sigma}(\mathbf{r}, t)$  with the subscript  $\sigma$  denoting the electron spin degree of freedom. The implementation of the time-dependent xc potential  $v_{xc\sigma}(\mathbf{r}, t)$  in the context of TDOEP requires that the time-dependent KS orbitals simultaneously satisfy the TDOEP integral equation [28,42],

$$\sum_{j=1}^{N_\sigma} \varphi_{j\sigma}^*(\mathbf{r}, t) \chi_{j\sigma}(\mathbf{r}, t) + c.c. = g_\sigma(\mathbf{r}, t), \quad (2)$$

where the time-dependent *effective memory* (EM) orbital  $\chi_{j\sigma}(\mathbf{r}, t)$  is defined as

$$\begin{aligned} \chi_{j\sigma}(\mathbf{r}, t) \equiv & -i \int_{-\infty}^t dt' \int d^3r' \sum_{k=1}^{\infty} \varphi_{k\sigma}(\mathbf{r}, t) \varphi_{k\sigma}^*(\mathbf{r}', t') \\ & \times \left\{ v_{xc\sigma}(\mathbf{r}', t') - u_{xcj\sigma}^*(\mathbf{r}', t') \right. \\ & \left. - [\bar{v}_{xcj\sigma}(t') - \bar{u}_{xcj\sigma}^*(t')] \right\} \varphi_{j\sigma}(\mathbf{r}', t'), \end{aligned} \quad (3)$$

and  $u_{xcj\sigma}(\mathbf{r}, t)$  involves the functional derivative of the exchange-correlation action functional  $A_{xc}$  with respect to  $\varphi_{j\sigma}(\mathbf{r}, t)$ ,

$$u_{xcj\sigma}(\mathbf{r}, t) = \frac{1}{\varphi_{j\sigma}^*(\mathbf{r}, t)} \frac{A_{xc}[\{\varphi_{i\sigma}\}]}{\delta \varphi_{j\sigma}(\mathbf{r}, t)}, \quad (4)$$

with

$$\bar{v}_{xcj\sigma}(t) = \int \varphi_{j\sigma}^*(\mathbf{r}, t) v_{xc\sigma}(\mathbf{r}, t) \varphi_{j\sigma}(\mathbf{r}, t) d^3r, \quad (5)$$

$$\bar{u}_{xcj\sigma}^*(t) = \int \varphi_{j\sigma}^*(\mathbf{r}, t) u_{xcj\sigma}^*(\mathbf{r}, t) \varphi_{j\sigma}(\mathbf{r}, t) d^3r, \quad (6)$$

and

$$g_\sigma(\mathbf{r}, t) = i \sum_{j=1}^{N_\sigma} |\varphi_{j\sigma}(\mathbf{r}, t)|^2 \times \int_{-\infty}^t [\bar{u}_{xcj\sigma}(t') - \bar{u}_{xcj\sigma}^*(t')] dt'. \quad (7)$$

It can be readily seen that each EM orbital  $\chi_{j\sigma}(\mathbf{r}, t)$  satisfies the time-dependent EM orbital equation [42],

$$\left[ i \frac{\partial}{\partial t} - \hat{H}_\sigma \right] \chi_{j\sigma}(\mathbf{r}, t) = \left\{ v_{xc\sigma}(\mathbf{r}, t) - u_{xcj\sigma}^*(\mathbf{r}, t) - [\bar{v}_{xcj\sigma}(t) - \bar{u}_{xcj\sigma}^*(t)] \right\} \varphi_{j\sigma}(\mathbf{r}, t). \quad (8)$$

It can also be shown that the function  $g_\sigma(\mathbf{r}, t)$  in equation (2) vanishes for a large class of the orbital-dependent xc functionals [46]. Following reference [35], we define a function

$$\mathcal{S}_\sigma(\mathbf{r}, t) \equiv \sum_{j=1}^{N_\sigma} \varphi_{j\sigma}^*(\mathbf{r}, t) \chi_{j\sigma}(\mathbf{r}, t) + c.c., \quad (9)$$

which possesses a zero value, i.e.,

$$\mathcal{S}_\sigma(\mathbf{r}, t) = 0 \quad \forall t. \quad (10)$$

By taking the first-order time-derivative of equation (9), we obtain the relation

$$\begin{aligned} \frac{\partial}{\partial t} \mathcal{S}_\sigma(\mathbf{r}, t) &= \frac{\partial}{\partial t} \left[ \sum_{j=1}^{N_\sigma} \varphi_{j\sigma}^*(\mathbf{r}, t) \chi_{j\sigma}(\mathbf{r}, t) + c.c. \right] \\ &= \sum_{j=1}^{N_\sigma} i \left\{ [\Delta \varphi_{j\sigma}^*(\mathbf{r}, t)] \chi_{j\sigma}(\mathbf{r}, t) - \varphi_{j\sigma}^*(\mathbf{r}, t) [\Delta \chi_{j\sigma}(\mathbf{r}, t)] \right\} + c.c. \\ &= -\nabla \cdot \vec{\mathcal{J}}_\sigma(\mathbf{r}, t), \end{aligned} \quad (11)$$

where  $\vec{\mathcal{J}}_\sigma$ , analogous to the probability current, is defined as

$$\vec{\mathcal{J}}_\sigma = \sum_{j=1}^{N_\sigma} \frac{i}{2} [(\nabla \varphi_{j\sigma}^*) \chi_{j\sigma} - \varphi_{j\sigma}^* (\nabla \chi_{j\sigma})] + c.c., \quad (12)$$

with  $\Delta = -\frac{\nabla^2}{2}$ . Subsequently, the second-order time-derivate of equation (9) yields the relation

$$\begin{aligned} \frac{\partial^2}{\partial t^2} \mathcal{S}_\sigma &= -\frac{\partial}{\partial t} (\nabla \cdot \vec{\mathcal{J}}_\sigma) \\ &= -\frac{\partial}{\partial t} \left\{ \nabla \cdot \sum_{j=1}^{N_\sigma} \frac{i}{2} [(\nabla \varphi_{j\sigma}^*) \chi_{j\sigma} - \varphi_{j\sigma}^* (\nabla \chi_{j\sigma})] + c.c. \right\} \\ &= \nabla \cdot (\mathbf{F}_\sigma^{(w)} + \mathbf{F}_\sigma^{(t)}) + \nabla \cdot [\rho_\sigma \nabla v_{xc\sigma}], \end{aligned} \quad (13)$$

where

$$\mathbf{F}_{\sigma\mu}^{(w)} = \sum_{j=1}^{N_\sigma} i \mathbf{j}_{j\sigma\mu} (u_{xcj\sigma} - c.c.) - \frac{|\varphi_{j\sigma}|^2}{2} \partial_\mu (u_{xcj\sigma} + c.c.), \quad (14)$$

$$\mathbf{F}_{\sigma\mu}^{(t)} = \sum_{\nu=1,2,3} \partial_\nu \tau_{\sigma\mu\nu}, \quad (15)$$

$$\mathbf{j}_{j\sigma\mu} = \frac{i}{2} [(\partial_\mu \varphi_{j\sigma}^*) \varphi_{j\sigma} - \varphi_{j\sigma}^* (\partial_\mu \varphi_{j\sigma})], \quad (16)$$

and

$$\tau_{\sigma\mu\nu} = \sum_{j=1}^{N_\sigma} \frac{1}{2} [(\partial_\mu \varphi_{j\sigma}^*) (\partial_\nu \chi_{j\sigma}) + (\partial_\nu \varphi_{j\sigma}^*) (\partial_\mu \chi_{j\sigma}) + c.c.], \quad (17)$$

with  $\mu, \nu = 1, 2, 3$  indexing each vector component in three dimensional Cartesian coordinates, e.g.,  $\mathbf{j}_{j\sigma} = (j_{j\sigma 1}, j_{j\sigma 2}, j_{j\sigma 3})$ , and  $\partial_1, \partial_2, \partial_3$  being the partial derivative  $\partial/\partial x, \partial/\partial y, \partial/\partial z$  respectively. By invoking equation (10), which stipulates that  $\mathcal{S}_\sigma(\mathbf{r}, t)$  and its high order time derivatives are zero for all time  $t$ , it is immediately seen that equation (13) reduces to the Sturm-Liouville-type time-local TDOEP equation,

$$\nabla \cdot [\rho_\sigma \nabla v_{xc\sigma}] = -\nabla \cdot (\mathbf{F}_\sigma^{(w)} + \mathbf{F}_\sigma^{(t)}), \quad (18)$$

which is the working equation for computing the xc potential  $v_{xc\sigma}$ . In our numerical implementations, equation (18) is posed as a linear algebraic inverse problem via discretization in the spatial coordinate and then solved accordingly, see Appendix A for details. It is noticed that the Sturm-Liouville type EXX TDOEP equation, equation (18), is similar to that for the exact time-dependent xc potential, which can be conveniently partitioned into a kinetic-like term consisting of one-body density matrix and an interaction term depending on the xc hole [11,47]. However, in the former the kinetic-like term,  $\mathbf{F}_\sigma^{(t)}$ , is composed of the KS and EM orbitals, and the interaction component  $\mathbf{F}_\sigma^{(w)}$ , is solely dependent on KS orbital, whereas in the latter the exact TDSE wavefunction is used to derive the exact one-body density matrix and xc hole.

### 3 Driven one-dimensional model of the helium atom and TDDFT approach

As an illustration, we consider a one-dimensional helium model in the presence of an external sine-square pulse, using a Hamiltonian with the soft-Coulomb interaction [6,10]. The two-electron wavefunction obeys

the time-dependent Schrödinger equation,

$$i \frac{\partial}{\partial t} \Psi(x_1, x_2, t) = \left[ -\frac{1}{2} \frac{\partial^2}{\partial x_1^2} - \frac{1}{2} \frac{\partial^2}{\partial x_2^2} + v_{ext}(x_1) + v_{ext}(x_2) + v_{int}(x_1, x_2, t) \right] \Psi(x_1, x_2, t), \quad (19)$$

where

$$v_{int}(x_1, x_2, t) = -\frac{1}{\sqrt{(x_1 - x_2)^2 + a^2}},$$

and

$$v_{ext}(x_i, t) = -\frac{2}{\sqrt{x_i^2 + a^2}} + x_i E(t), \text{ for } i = 1, 2,$$

with time-dependent external field

$$E(t) = F \sin^2 \left( \frac{\pi t}{T} \right) \sin(\omega t).$$

Here, the notation  $x$  denotes the spatial coordinate, and the subscripts of  $x_1$  and  $x_2$  are used to index the two electrons. The parameter  $a$  is introduced to avoid the singularity of Coulomb interaction. Also, the parameters  $F$ ,  $T$ , and  $\omega$  describe time-dependent external field. To mitigate the correlation effect in a two-electron system, the two electrons are prepared in the triplet ground state, so that the underlying initial wavefunction  $\Psi(x_1, x_2)$  changes sign upon the exchange of electron's spatial coordinates, i.e.,  $\Psi(x_1, x_2) = -\Psi(x_2, x_1)$  at  $t = 0$ .

To explore the memory effects within the time-local TDOEP with the EXX functional, both TDSE and TDDFT calculations are performed to examine the evolution of the time-dependent density, which manifests the most essential features of many-electron dynamics. For the TDDFT simulations, the time-dependent KS equation, equation (1), is solved, and the lowest two orbitals ( $j\sigma = 1\uparrow, 2\uparrow$ ) are propagated for the antisymmetric state, of which  $N_\uparrow = 2$  and  $N_\downarrow = 0$ . For comparison, additional TDDFT simulations were also carried out based on (1) the TDKLI approximation [28,44],

$$v_{xc\sigma}^{\text{TDKLI}}(x, t) \equiv \frac{1}{2\rho_\sigma(x, t)} \sum_{j=1}^{N_\sigma} \left\{ |\varphi_{j\sigma}(x, t)|^2 \left[ u_{xcj\sigma}(x, t) + (\bar{v}_{xcj\sigma}(t) - \bar{u}_{xcj\sigma}(t)) \right] + c.c. \right\}, \quad (20)$$

and (2) the adiabatic local spin-density approximation (ALSDA) [45],

$$v_{xc\sigma}^{\text{ALSDA}}(x, t) \equiv - \left[ \frac{6}{\pi} \rho_\sigma(x, t) \right]^{1/3}. \quad (21)$$

In the following calculations, we consider the excitation of the helium model by two sine-square pulses, respectively, with frequencies equal to 0.1 and 0.172 (a.u.), of which the second frequency 0.172 is the resonance frequency of the excitation from the triplet ground state to the first triplet excitation state. In addition, we set  $F = 0.005$ ,  $T = 200$ , and  $a = 1$ .

## 4 Results and discussions

Figure 1 shows that the dipole oscillation obtained by the exact TDSE solution is in phase with the external field for non-resonant dynamics (with the pulse frequency  $\omega = 0.1$ ), however, it is out of phase, with a phase shift and an increasing amplitude, for the resonant process (with the pulse frequency  $\omega = 0.172$ ). In both cases, the ALSDA does not reproduce the desired oscillation amplitude, and it does not possess the energy absorbing feature characterizing the resonance. By contrast, both TDOEP and TDKLI approaches yield time-dependent dipole oscillation quantitatively close to those obtained by the TDSE. Unlike ALSDA, both TDKLI and TDOEP explicitly employ the single Slater determinant for constructing the exact-exchange functional, which is crucial to describe the exact wavefunction of the triplet state. Here TDOEP performed only slightly better than TDKLI since in these simulations the major contribution to the xc potential is the orbital-dependent potential  $u_{xcj\sigma}$ , rather than the kinetic-like term involving EM orbital  $\chi_{j\sigma}$ . Moreover, by projecting the TDSE wavefunction on the ground-state wavefunction, i.e.,  $|c_0(t)|^2 = |\langle \Psi_0 | \Psi(t) \rangle|^2$ , it was seen that for the non-resonant case, see Figure 1a, both electrons primarily remain in the ground-state, however, for the resonant case, see Figure 1b, the excitation of electrons was evident such that TDOEP is more accurate than TDKLI. Note that for a one-electron system, an exact xc potential exactly cancels the Hartree potential, i.e.,  $\chi_{j\sigma} = 0$ , such that time-dependent KS equation reduces to TDSE, however, ALSDA does not satisfy this condition because of the non-vanishing self-interaction.

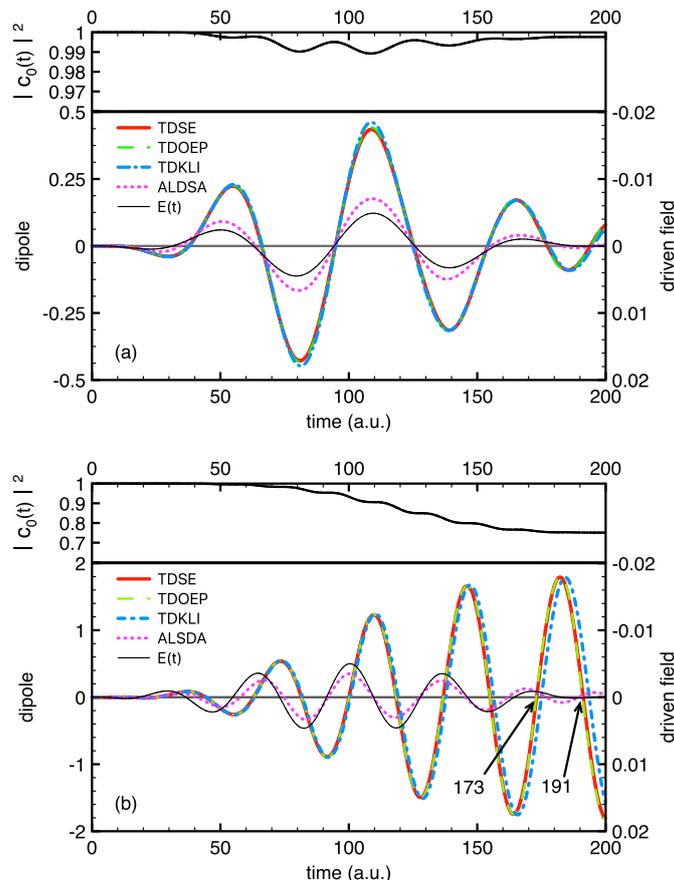
To investigate the memory effect associated to EM orbitals, we decompose the time-local TDOEP equation in one dimension, c.f. equation (18), into two equivalent equations,

$$\frac{\partial}{\partial x} \left[ \rho_\sigma(x, t) \frac{\partial}{\partial x} v_{xc\sigma}^{(w)}(x, t) \right] = -\frac{\partial}{\partial x} F_\sigma^{(w)}(x, t), \quad (22)$$

$$\frac{\partial}{\partial x} \left[ \rho_\sigma(x, t) \frac{\partial}{\partial x} v_{xc\sigma}^{(t)}(x, t) \right] = -\frac{\partial}{\partial x} F_\sigma^{(t)}(x, t), \quad (23)$$

where  $v_{xc\sigma}(x, t) = v_{xc\sigma}^{(w)}(x, t) + v_{xc\sigma}^{(t)}(x, t)$ . We emphasize that the non-adiabatic dynamics is manifested in the time-dependent kinetic-like stress tensor  $\tau_\sigma$  of equation (15) and the orbital-dependent stress current density  $\mathbf{j}_{j\sigma}$  of equation (14), but EM orbitals only contribute to  $v_{xc\sigma}^{(t)}$  through the kinetic-like stress tensor.

Figure 2 shows the probability density and xc potential at times  $t = 173$  and 191, corresponding to two instants when the dipole moment of the exact TDSE solution



**Fig. 1.** In both (a) and (b), the upper panels depict the coefficient of the projection calculated from TDSE wavefunction, i.e.,  $|c_0(t)|^2 = |\langle \Psi_0 | \Psi(t) \rangle|^2$  with  $\Psi_0$  being the two-electron ground-state wavefunction, and the lower panels show the computed time-dependent dipole through solving TDSE (solid red), TDOEP (dashed green), TDKLI (dot-dashed blue), and ALSDA (dotted pink). The frequencies of the external fields (thin solid black) are (a) 0.1 in the off-resonance case and (b) 0.172 in the resonance case. The two arrows in the panel (b) indicate two successive instants,  $t = 173$  and  $191$ , when the dipole moment of the exact TDSE solution is nearly zero.

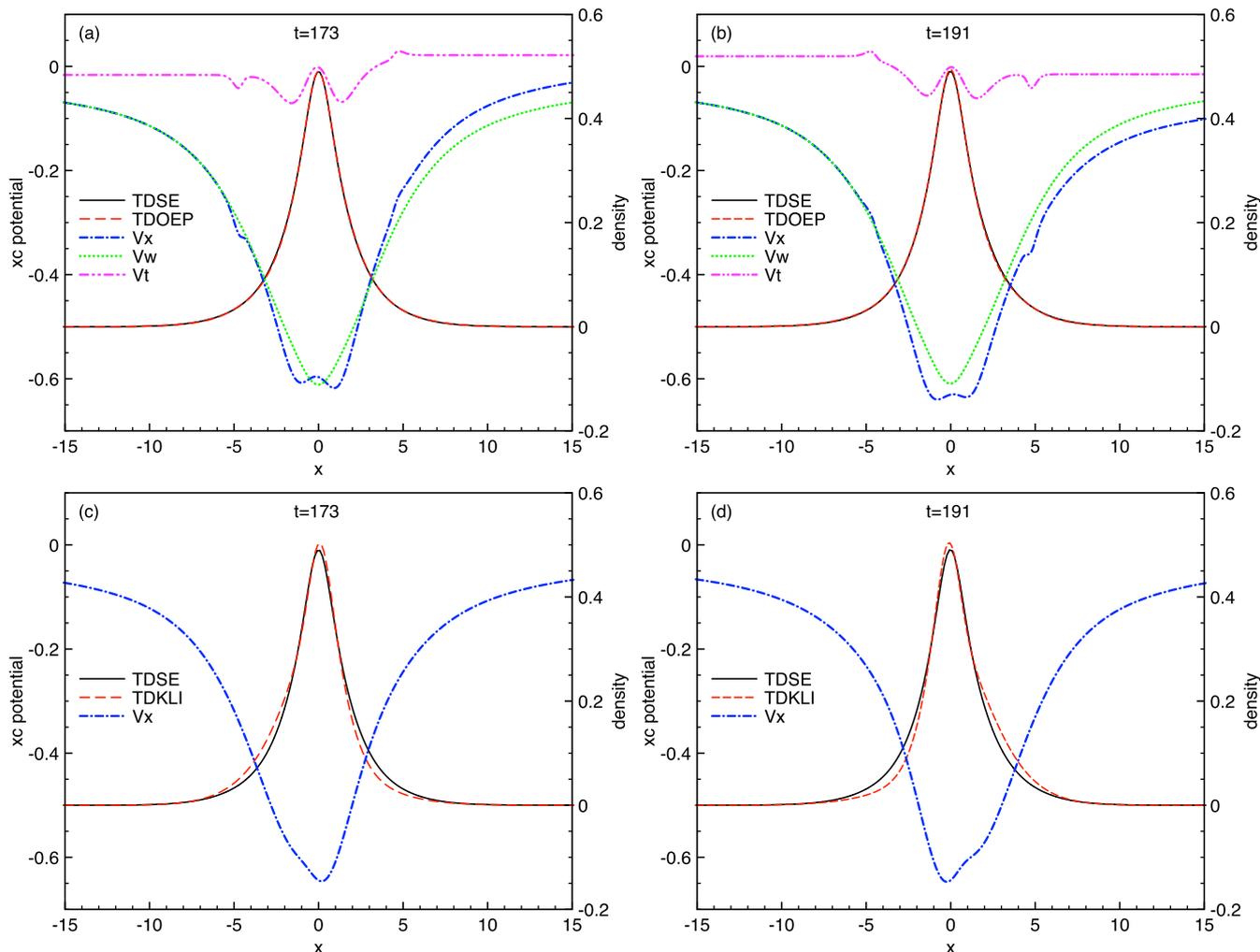
is very close to zero, see Figure 1b. Figures 2a and 2b show that  $v_{xc\sigma}^{(t)}$  of the TDOEP has two distinct local minima, which are missing in the TDKLI approximation in Figures 2c and 2d. These unique local minimum structures make the resultant time-dependent density and dipole oscillation agree with the exact TDSE solution. Furthermore, time-dependent xc potential of the TDOEP reveals a very different asymptotic behavior from those in the ground-state DFT and in the adiabatic approximation. Specifically, instead of  $v_{xc\sigma}(x) \rightarrow -1/|x|$  as  $|x| \rightarrow \infty$ , Figures 2a and 2b show steps in  $v_{xc\sigma}$  at large  $x$  due to the non-adiabatic and memory effects. This highly nonlocal feature has been observed by the exact time-dependent xc potential calculated from the TDSE density [9,10]. Figures 2a and 2b show that the time-local TDOEP equation, equation (18), is capable of capturing this important asymptotic feature, which is missing in the adiabatic approximation.

## 5 Summary

We have considered the excitation of a model one-dimensional helium atom in a triplet electronic

state in the presence of a time-dependent sine-square pulse and applied the newly formulated time-local equation for the full EXX TDOEP to explore the memory effect in real-time TDDFT. The memory-dependent xc potential beyond the adiabatic approximation has been computed in each time step, in conjunction with propagating the KS and EM orbitals in real time. In addition, we have calculated the time-dependent dipole oscillation and time-dependent probability density using the TDKLI approximation and the ALSDA. The results of the time-local TDOEP approach and TDKLI approximation, to a lesser degree, were shown to closely agree with the exact TDSE solution, whereas the ALDA was inadequate, especially failing to describe the dynamics induced by a resonant field. Our TDOEP calculations clearly demonstrate that the unique structure of the xc potential, especially for  $v_{xc\sigma}^{(t)}$  attributed to the EM orbitals, improves the accuracy beyond the TDKLI approximation.

The memory effect is a fundamental but elusive feature of TDDFT. Even though it is, in principle, possible to numerically extract the exact time-dependent xc potential from the exact TDSE solution (which has been only



**Fig. 2.** The xc potential and the probability density  $\rho(x, t)$  computed through solving TDSE, TDOEP, TDKLI: panels (a) and (c) are for  $t = 173$ ; panels (b) and (d) are for  $t = 191$ . In all panels, the solid black lines represent the density computed from the exact TDSE solution, and the dashed red lines represent the density based on TDOEP, (a) and (b), and TDKLI, (c) and (d). The dot-dashed blue lines show the exchange potential  $V_x = v_{xc\sigma}(x, t)$ , and  $V_w = v_{xc\sigma}^{(w)}(x, t)$  and  $V_t = v_{xc\sigma}^{(t)}(x, t)$  are defined in equations (22) and (23), respectively.

feasible for a two-electron system thus far), for example, by invoking the density-potential mapping algorithm [48]. The prime difficulty is to correctly construct xc functionals once the physical features of the memory-dependent xc potential are resolved [10,11,15,49]. This paper not only investigates memory effects in the EXX functional, but also presents a practical numerical scheme to compute the memory-dependent xc potential in real time, without *a priori* knowledge of the exact solution of the corresponding TDSE. To this end, we remark that there are still open issues in the TDOEP approach. For example, it is still difficult to construct the correlation part, including all the higher-order terms in xc functional, both analytically and numerically. This is especially true when the complexity of computing exact TDOEP involving unoccupied KS orbitals is greatly increased. In addition, the solution of time-dependent xc potential may become unstable over long time due to either lack of information in memory loss or errors in the EM orbitals.

Moreover, the EXX corresponds to the first-order term of the exact xc potential in time-dependent DFT perturbation theory [37], thus, the resultant EXX TDOEP may not be adequate for the strong-field or long-time propagation dynamics. Notwithstanding, the time-local TDOEP equation is generic, independent of any assumed orbital-dependent xc functionals, and the aforementioned issues may be resolved by implementing an appropriate correlation functional in the near future.

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## Author contribution statement

The authors are all responsible for the whole content of the paper.

## Appendix A: Numerical implementation of solving TDOEP

Here, instead of solving equation (18) directly, which may become numerically unstable, we impose a temporal preconditioning scheme, in conjunction of the Tikhonov regularization in the coordinate space, to improve the numerical stability. Recall that equation (10) implies the zero equality relations,

$$\mathcal{S}_\sigma(x, t) = \frac{\partial}{\partial t} \mathcal{S}_\sigma(x, t) = \frac{\partial^2}{\partial t^2} \mathcal{S}_\sigma(x, t) = 0 \quad \forall t. \quad (\text{A.1})$$

The main issue when solving equation (18) is dealing with  $\mathcal{S}(x, t)$ , as its time-derivatives may greatly deviate from zero over long time due to the instability of the equation, thus, signaling serious errors in the implemented numerical calculations. To resolve this problem, we consider the following Taylor's expansion (to second order):

$$\begin{aligned} \mathcal{S}_\sigma(x, t + \Delta\tau) &= \mathcal{S}_\sigma(x, t) + \frac{\partial \mathcal{S}_\sigma(x, t)}{\partial t} \Delta\tau \\ &\quad + \frac{\partial^2 \mathcal{S}_\sigma(x, t)}{\partial t^2} \frac{\Delta\tau^2}{2} + \mathcal{O}(\Delta\tau^3) \\ &= \mathcal{S}_\sigma(x, t) - \left[ \frac{\partial}{\partial x} \mathbb{J}(x, t) \right] \Delta\tau \\ &\quad + \left\{ \frac{\partial}{\partial x} \left[ \mathbf{F}_\sigma^{(t)}(x, t) + \mathbf{F}_\sigma^{(w)}(x, t) \right] \right. \\ &\quad \left. + \frac{\partial}{\partial x} \left[ \rho_\sigma(x, t) \frac{\partial}{\partial x} v_{xc\sigma}(x, t) \right] \right\} \frac{\Delta\tau^2}{2} \\ &\quad + \mathcal{O}(\Delta\tau^3), \end{aligned} \quad (\text{A.2})$$

and enforce a temporal preconditioning criterion such that  $\mathcal{S}(x, t + \Delta\tau) = 0$ , where the preconditioning time step  $\Delta\tau$  is a sufficiently small number to keep errors under control over long time. As a result, equation (A.2) may be rearranged to yield the relation

$$\begin{aligned} \frac{\partial}{\partial x} \left[ \rho_\sigma(x, t) \frac{\partial}{\partial x} v_{xc\sigma}(x, t) \right] &= - \frac{\partial}{\partial x} \left[ \mathbf{F}_\sigma^{(t)}(x, t) - \mathbf{F}_\sigma^{(w)}(x, t) \right] \\ &\quad - \frac{2\mathcal{S}_\sigma(x, t)}{\Delta\tau^2} + \frac{2 \left[ \frac{\partial}{\partial x} \mathbb{J}_\sigma(x, t) \right]}{\Delta\tau}, \end{aligned} \quad (\text{A.3})$$

which is formally equivalent to equation (18) as long as  $\mathcal{S}_\sigma(x, t) = \mathbb{J}_\sigma(x, t) = 0$  throughout the calculations. The last two terms in equation (A.3) are zero, in principle, but kept to check and control the stability likely to arise from

numerical errors. To this end, it was sufficient to choose  $\Delta\tau = 0.05$  for all the TDOEP simulations demonstrated in this paper,

Equation (A.3) becomes unstable (ill-posed) when the underlying density  $\rho_\sigma(x, t)$  is very close to zero, which can be seen by casting equation (A.3) into a linear algebraic inverse equation

$$Av_{xc\sigma} - b = 0, \quad A \in \mathbb{R}^{n \times n}, \quad v_{xc\sigma}, b \in \mathbb{R}^n, \quad (\text{A.4})$$

via spatial discretization and finite differencing, where the matrix  $A$  is defined as  $D \times \text{diag}(\rho) \times D$  with the differential operator  $D \equiv \partial/\partial x$  expressed with the finite difference method and the diagonal matrix  $\text{diag}(\rho)$  containing values of  $\rho_\sigma(x)$  on a grid. Similarly, the value of the vector  $b$  can be directly derived from the right-hand side of equation (A.3) on the grid. In the situation of a very small density, i.e.,  $\rho_\sigma(x, t) \rightarrow 0$ , a rank-deficient matrix  $A$  results in an ill-conditioned linear system of equations. To deal with the ill-conditioned problem, the Tikhonov regularization and the singular value decomposition (SVD) are applied [50,51]. Specifically, the xc potential  $v_{xc\sigma}(x, t)$  is written as a sum  $v_{xc\sigma}(x, t) = v_{xc\sigma}^{(w)}(x, t) + v_{xc\sigma}^{(t)}(x, t)$ , and the solution to the linear inverse problem in equation (A.4) is recast as two separate minimization problems, i.e.,

$$\min_{v_{xc\sigma}^{(w)}} \left\| Av_{xc\sigma}^{(w)} - b^{(w)} \right\|^2 + \underbrace{\alpha^2 \left\| D(v_{xc\sigma}^{(w)} - \tilde{v}_{xc\sigma}^{(w)}) \right\|^2}_{\text{regularization}}, \quad (\text{A.5})$$

and

$$\min_{v_{xc\sigma}^{(t)}} \left\| [\rho_\sigma(x, t)]^\gamma \left( Av_{xc\sigma}^{(t)} - b^{(t)} \right) \right\|^2 + \underbrace{\beta^2 \left\| D v_{xc\sigma}^{(t)} \right\|^2}_{\text{regularization}}, \quad (\text{A.6})$$

where the regularization parameters  $\alpha$  and  $\beta$  are judiciously chosen to balance the residual (i.e., the first term) and the smoothness constraint (i.e., the second term) in each minimization problem, with  $\|\cdot\|^2$  denoting the Euclidean norm. In the context of the Tikhonov regularization method, the differential operator  $D$  in equations (A.5) and (A.6) controls the smoothness of the solutions, and the choice of  $b^{(w)}$ ,  $\tilde{v}_{xc\sigma}^{(w)}$ ,  $\gamma$ , and  $b^{(t)}$  determine the outcome of the regularization. In order to successfully solve equation (A.4), on the one hand, we choose

$$b^{(w)} = - \frac{\partial}{\partial x} \left[ \mathbf{F}_\sigma^{(w)}(x, t) \right], \quad (\text{A.7})$$

and

$$\tilde{v}_{xc\sigma}^{(w)}(x, t) = - \frac{V_H(x, t)}{N_\uparrow + N_\downarrow}, \quad (\text{A.8})$$

for equation (A.5). It is easily seen that

$$\frac{\partial}{\partial x} \left[ v_{xc\sigma}^{(w)}(x, t) \right] \rightarrow \frac{\partial}{\partial x} \left[ - \frac{V_H(x, t)}{N_\uparrow + N_\downarrow} \right] \text{ for } |x| \rightarrow \infty, \quad (\text{A.9})$$

thus,  $\frac{\partial}{\partial x} v_{xc\sigma}^{(w)}(x, t) \rightarrow 1/|x|^2$  for  $|x| \rightarrow \infty$ , which correctly accounts for Coulomb force. On the other hand, recalling equation (A.3), we choose

$$\begin{aligned} b^{(t)}(x, t) &= b(x, t) - b^{(w)}(x, t) \\ &= -\frac{\partial}{\partial x} \left[ \mathbf{F}_{\sigma}^{(t)}(x, t) \right] - \frac{2\mathcal{S}(x, t)}{\Delta T^2} + \frac{\left[ \frac{\partial}{\partial x} \mathbb{J}(x, t) \right]}{\Delta T}, \end{aligned} \quad (\text{A.10})$$

for  $v_{xc\sigma}^{(t)}$  in equation (A.6), and assume that

$$\frac{\partial}{\partial x} \left[ v_{xc\sigma}^{(t)}(x, t) \right] \rightarrow 0 \text{ for } |x| \rightarrow \infty, \quad (\text{A.11})$$

to account for the vanishing memory effect at large distance. In addition, we multiply the factor  $[\rho_{\sigma}(x, t)]^{\gamma}$ , with  $\gamma \geq 1$ , on both  $Av_{xc\sigma}^{(t)}$  and  $b^{(t)}$  to reduce the influence of the noise.

Appropriate values of  $\gamma$ ,  $\alpha$ , and  $\beta$  are set to stabilize the TDOEP without significant loss of accuracy. All the TDOEP calculations demonstrated in this paper are computed via equations (A.5) and (A.6) using the SVD, with the parameters  $\gamma = 4$  and  $\alpha = \beta = 10^{-6}$ .

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