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Time-local equation for the exact optimized effective potential in time-dependent density functional theory

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Abstract

A longstanding challenge in time-dependent density functional theory is to efficiently solve the exact time-dependent optimized effective potential (TDOEP) integral equation derived from orbital-dependent functionals, especially for the study of non-adiabatic dynamics in time-dependent external fields. In this letter, we formulate a completely equivalent time-local TDOEP equation that admits a unique real-time solution in terms of time-dependent Kohn-Sham and effective memory orbitals. The time-local formulation is numerically implemented, with incorporation of exponential memory loss to address the unaccounted for correlation component in the exact-exchange only functional, to enable study of the many-electron dynamics of a one-dimensional hydrogen chain. It is shown that the long time behavior of the electric dipole converges correctly and the zero-force theorem is fulfilled in the current implementation.

Time-dependent density functional theory (TDDFT) introduced in 1984 [1] is not only formally exact, but also computationally advantageous when dealing with many-electron dynamics in time-dependent external fields [2, 3]. Extensive numerical simulations based on TDDFT have been performed to study high harmonic generation and ultrafast spectroscopy in attosecond science [4], electronic excited states in optical materials and in photochemistry [5], and excited-state electron-ion dynamics in biological systems [6]. Furthermore, the real-time TDDFT in the context of quantum optimal control theory also opens up the possibility of manipulating interacting quantum systems [7]. Recently, TDDFT has been extended to explore, for instance, the Kondo effect [8], many-electron systems interacting with cavity photons [9], thermoelectric phenomena [10], electrical currents induced by ultrafast laser excitation [11], ion-material collisions [12], and laser-induced interlayer in layered materials [13].

In spite of a plethora of successful applications of TDDFT, the exact form of the exchange-correlation (xc) potential has defied efforts seeking its discovery, and time-dependent xc potentials obtained directly from the adiabatic extension of approximate density-dependent functionals, such as LDA [14] and GGA [15], suffer from several significant drawbacks including (1) the existence of an undesirable Hartree self-interaction, (2) the absence of the intrinsic derivative discontinuity, and (3) the lack of a proper memory effect [16]. A promising approach to overcome these drawbacks is through the use of functionals that utilize Kohn-Sham (KS) orbitals $\varphi_{j\sigma}(\mathbf{r},t)$ instead of the density $\rho(\mathbf{r},t)$ [17–19]. For example, the exact-exchange functional is free of the Hartree self-interaction error and leads to the correct $-1/r$ asymptotic behavior for finite systems [20]. In addition, orbital-dependent functionals naturally incorporate the derivative discontinuity [21, 22]. Furthermore, orbital-dependent functionals make possible systematic construction of the exchange-correlation potential via either the Keldysh perturbation expansion [23] or the time-dependent generalization of the Görling-Levy perturbation expansion [24]. It will be shown in this letter that the memory effect is inherent in the orbital-dependent functional approach.

To incorporate orbital-dependent functionals in time-dependent Kohn-Sham framework, a time-dependent optimized-effective potential (TDOEP) integral equation needs to be solved efficiently and accurately for orbital-independent multiplicative potentials [25, 26]. Although construction of TDOEP is an important undertaking in TDDFT [27–29], the full TDOEP integral equation thus far has been only implemented in exact-exchange for a quasi-one-dimensional quantum well [30] because the equation is highly nonlocal both temporally and spatially [3, 31]. Many DFT and TDDFT calculations have adopted the Krieger-Li-Iafrate (KLI) approximation due

to its simplicity [25, 32], despite the KLI approximation overestimating the polarizability and hyperpolarizability even in static cases [33, 34]. A straightforward application of the time-dependent KLI approximation to molecules also produced inadequate short bond lengths and unexpected high dissociation energies [35]. Moreover, Mundt and Kümmel showed that the time-dependent KLI approximation in the exact-exchange functional violates both the zero-force theorem and energy conservation [36]. Recently, it was shown that an exact solution of the TDOEP equation for a quasi-one-dimensional model quantum well problem has much richer temporal charge-density oscillation features in the time-dependent dipole moment than do solutions of the time-dependent KLI and the adiabatic approximation [30]. These findings clearly indicate the need for a full, yet efficient solution beyond the KLI approximation.

An efficient and stable method for solving the exact TDOEP has remained elusive [25, 30, 37]. The step-by-step approach proposed by Mundt and Kümmel was numerically unstable [30, 31, 37]. The global self-consistency scheme proposed by Wijewardane and Ullrich [30], in which the nonlinear TDOEP integral was solved iteratively, is computationally too expensive for two- and three-dimensional problems. In order to circumvent these difficulties, this letter derives an equivalent Sturm-Liouville-type time-local TDOEP equation that is amenable to a direct solution in real time.

Much effort has gone into the construction of the xc potential containing the memory effect, including time-dependent current density functional theory (TDCDFT) approach, which utilizes both the time-dependent current density and time-dependent density [38–44], and time-dependent deformation functional theory (TDDefFT) approach, which reformulates TDDFT in a co-moving Lagrangian reference frame [44–46]. In these approaches, stress-like tensors in the hydrodynamic context were formulated to incorporate the xc scalar potential as well as the xc vector potential in the most general case. In this letter, it is shown that the time-local TDOEP equation can be cast in terms of a stress-like tensor, which incorporates the non-adiabatic effect in time-dependent effective memory orbitals (orbital shifts in Ref. [37]) and the orbital-dependent current density.

The time-dependent xc potential, $v_{xc\sigma}(\mathbf{r}, t)$, associated with orbital-dependent functionals satisfies a self-consistent nonlinear integral equation [25, 26]

$$-i\sum_{j=1}^{N_\sigma}\int_{-\infty}^{t}dt'\int d^3r'\varphi^*_{j\sigma}(\mathbf{r},t)\sum_{k=1}^{\infty}\varphi_{k\sigma}(\mathbf{r},t)\varphi^*_{k\sigma}(\mathbf{r}',t') \times\left[v_{xc\sigma}(\mathbf{r}',t')-u^*_{xc\,j\sigma}(\mathbf{r}',t')\right]\varphi_{j\sigma}(\mathbf{r}',t')+c.c.=0\,, \tag{1}$$

where the subscript σ denotes electron spin, $\varphi_{j\sigma}(\mathbf{r}, t)$ is the time-dependent KS orbital satisfying

the time-dependent KS equation,

$$\left[i\frac{\partial}{\partial t} - \hat{H}_\sigma\right]\varphi_{j\sigma}(\mathbf{r},t) = 0, \tag{2}$$

with $\hat{H}_\sigma = -\frac{\nabla^2}{2} + v(\mathbf{r},t) + v_{\rm H}(\mathbf{r},t) + v_{xc\sigma}(\mathbf{r},t)$ being the time-dependent KS Hamiltonian consisting of the external potential $v(\mathbf{r},t)$, Hartree potential $v_{\rm H}(\mathbf{r},t)$, and exchange-correlation potential $v_{xc\sigma}(\mathbf{r},t)$, and $u_{xcj\sigma}(\mathbf{r},t)$ is defined as

$$u_{xcj\sigma}(\mathbf{r},t) = \frac{1}{\varphi^*_{j\sigma}(\mathbf{r},t)}\frac{\delta A_{xc}[\{\varphi_{i\sigma}\}]}{\delta\varphi_{j\sigma}(\mathbf{r},t)}\,, \tag{3}$$

which involves the functional derivative of the exchange-correlation action functional A_{xc} with respect to $\varphi_{j\sigma}(\mathbf{r},t)$. We remark that there have been discussions recently regarding whether the action-integral functional can be used to establish the equation of motion for time-dependent quantum systems at the density-functional level [47, 48]. Nonetheless, we emphasize that the TDOEP method is an exact procedure to construct an optimized effective time-dependent xc potential from an orbital-dependent action functional taking into account the proper non-adiabatic (memory) effect in the time-dependent KS equation, Eq. (2).

Following Ref. [37], Eq. (1) is rewritten in a compact form as

$$\sum_{j=1}^{N_\sigma}\varphi^*_{j\sigma}(\mathbf{r},t)\chi_{j\sigma}(\mathbf{r},t) + c.c. = g_\sigma(\mathbf{r},t)\,, \tag{4}$$

in terms of the time-dependent KS orbitals $\varphi_{j\sigma}(\mathbf{r},t)$ and the time-dependent *effective memory* (EM) orbitals $\chi_{j\sigma}(\mathbf{r},t)$ defined as

$$\begin{aligned}\chi_{j\sigma}(\mathbf{r},t) \equiv -i\int_{-\infty}^{t}dt'\int d^3r'\sum_{k=1}^{\infty}\varphi_{k\sigma}(\mathbf{r},t)\varphi^*_{k\sigma}(\mathbf{r}',t')\Big\{v_{xc\sigma}(\mathbf{r}',t') \\ -u^*_{xcj\sigma}(\mathbf{r}',t') - \Big[\bar{v}_{xcj\sigma}(t') - \bar{u}^*_{xcj\sigma}(t')\Big]\Big\}\varphi_{j\sigma}(\mathbf{r}',t')\,,\end{aligned} \tag{5}$$

where

$$\bar{v}_{xcj\sigma}(t) = \int\varphi^*_{j\sigma}(\mathbf{r},t)v_{xc\sigma}(\mathbf{r},t)\varphi_{j\sigma}(\mathbf{r},t)d^3r\,, \tag{6}$$

$$\bar{u}^*_{xcj\sigma}(t) = \int\varphi^*_{j\sigma}(\mathbf{r},t)u^*_{xcj\sigma}(\mathbf{r},t)\varphi_{j\sigma}(\mathbf{r},t)\,d^3r\,, \tag{7}$$

$$g_\sigma(\mathbf{r},t) = i\sum_{j=1}^{N_\sigma}|\varphi_{j\sigma}(\mathbf{r},t)|^2\int_{-\infty}^{t}\Big[\bar{u}_{xcj\sigma}(t') - \bar{u}^*_{xcj\sigma}(t')\Big]dt'\,. \tag{8}$$

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

$$\left[i\frac{\partial}{\partial t}-\hat{H}_\sigma\right]\chi_{j\sigma}(\mathbf{r},t)=\Big\{v_{xc\sigma}(\mathbf{r},t)-u^*_{xcj\sigma}(\mathbf{r},t) - \left[\bar{v}_{xcj\sigma}(t)-\bar{u}^*_{xcj\sigma}(t)\right]\Big\}\varphi_{j\sigma}(\mathbf{r},t). \tag{9}$$

The time-dependent EM orbital $\chi_{j\sigma}(\mathbf{r},t)$ defined by Eq. (5) is formally identical to the orbital shift coined by Mundt and Kümmel [37]; however, in this work, it is specifically designated to manifest the memory effect in the time-local TDOEP equation, see Eqs. (18) and (20) below and the corresponding discussion. In the static limit, $\chi_{j\sigma}(\mathbf{r},t)$ can be written as $\chi_{j\sigma}(\mathbf{r},t)=\chi_{j\sigma}(\mathbf{r},0)\exp[-i\epsilon_j t]$, and Eq. (4) reduces to the static OEP integral equation [37, 49]. For a system prepared in a ground state at $t=0$, the initial KS orbitals $\varphi_{j\sigma}(\mathbf{r},0)$, EM orbitals $\chi_{j\sigma}(\mathbf{r},0)$, and xc potential $v_{xc\sigma}(\mathbf{r},0)$ are obtained by solving the corresponding static OEP [50]. The time-dependent EM orbitals $\chi_{i\sigma}(\mathbf{r},t)$ are endowed with the memory effect of the TDOEP as shown in Eq. (5) and (9). It will be further shown that the KS orbitals together with the EM orbitals are sufficient to determine the TDOEP directly at each instant t using a Sturm-Liouville-type equation.

A large class of the orbital-dependent xc actions A_{xc}, see Ref. [3, 19], can be written in the form of either $A_{xc}=\sum_i\sum_k\int\int\int F[\{\varphi_{i\sigma}(\mathbf{r},t')\,\varphi^*_{k\sigma}(\mathbf{r},t')\,\varphi^*_{i\sigma}(\mathbf{r}',t')\,\varphi_{k\sigma}(\mathbf{r}',t')\}]\,d^3r'd^3r\,dt'$ or $A_{xc}[\{|\varphi_{i\sigma}(\mathbf{r},t)|^2\}]$, including the widely used exact-exchange functional [30, 37]

$$A_x^{exact}[\{\varphi_{i\sigma}\}]=-\frac{1}{2}\sum_\sigma\sum_{j,k=1}^{N_\sigma}\int_{-\infty}^{t}dt'\int d^3r\int d^3r'\,\frac{\varphi^*_{j\sigma}(\mathbf{r}',t')\varphi_{k\sigma}(\mathbf{r}',t')\varphi_{j\sigma}(\mathbf{r},t')\varphi^*_{k\sigma}(\mathbf{r},t')}{|\mathbf{r}-\mathbf{r}'|}, \tag{10}$$

resulting in the following relations:

$$\int\frac{\delta A_{xc}}{\delta\varphi_{j\sigma}(\mathbf{r},t)}\,\varphi_{j\sigma}(\mathbf{r},t)\,d^3r-c.c.=0, \tag{11}$$

and

$$\sum_j\frac{\delta A_{xc}}{\delta\varphi_j(\mathbf{r},t)}\,\varphi_j(\mathbf{r},t)-c.c.=0. \tag{12}$$

Eq. (11) leads to a real function $\bar{u}_{xcj\sigma}(t)$, which in turn yields the equality $g_\sigma(\mathbf{r},t)=0$ [27], and Eq. (12) results in the equality $\sum_j i\,u_{xcj\sigma}(\mathbf{r},t)\,|\varphi_{j\sigma}(\mathbf{r},t)|^2+c.c.=0$. Without loss of generality, we only consider the TDOEP in exchange-correlation functionals satisfying Eq. (11) and Eq. (12) in the following analysis. Moreover, to facilitate the presentation, we adopt 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 $u_{xcj\sigma}=u_{xcj\sigma}(\mathbf{r},t)$ whenever it is unambiguous.

It has been pointed out that the Volterra-like integral TDOEP equation, Eq. (1), does not possess a nonzero upper limit at $t' = t$, making it difficult to solve for $v_{xc\sigma}(\mathbf{r}, t)$, step by step, while the time-dependent KS orbitals propagate in time domain [30]. This predicament can be overcome by further differentiating Eq. (1), or equivalently Eq. (4), with respect to time until reaching an equation that can explicitly reveal the intended $v_{xc\sigma}(\mathbf{r}, t)$. To this end, by differentiating Eq. (4) with respect to time,

$$\frac{\partial}{\partial t}\left[\sum_{j=1}^{N_\sigma} \varphi^*_{j\sigma}(\mathbf{r}, t)\chi_{j\sigma}(\mathbf{r}, t)\right] + c.c. = 0\,, \tag{13}$$

and using the time-dependent KS equation and the time-dependent EM orbital equation, we derive the equation

$$\sum_{j=1}^{N_\sigma}\left[i\left(\hat{H}_\sigma\varphi^*_{j\sigma}\right)\chi_{j\sigma} - i\varphi^*_{j\sigma}\left(\hat{H}_\sigma\chi_{j\sigma}\right)\right] + c.c. = 0\,, \tag{14}$$

which can be written succinctly as

$$\nabla\cdot\vec{\mathbb{J}}_\sigma = 0\,, \tag{15}$$

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

$$\vec{\mathbb{J}}_\sigma = \sum_{j=1}^{N_\sigma}\frac{i}{2}\left[\left(\nabla\varphi^*_{j\sigma}\right)\chi_{j\sigma} - \varphi^*_{j\sigma}\left(\nabla\chi_{j\sigma}\right)\right] + c.c. \tag{16}$$

Introducing Eq. (5) and Eq. (16) into Eq. (15) leads to a non-linear integro-differential equation for the function $v_{xc\sigma}(\mathbf{r}, t)$. Numerically solving $\varphi_{j\sigma}$ and $v_{xc\sigma}$, which are required to satisfy the time-dependent KS equation Eq. (2) and the non-linear integro-differential equation Eq. (15) concurrently, poses a computationally daunting task for two- and three- dimensional problems. To circumvent this difficulty, we first differentiate Eq. (15) with respect to time to obtain the relation,

$$\begin{aligned}\nabla\cdot\sum_{j=1}^{N_\sigma}\frac{i}{2}\Big\{&\left[\left(\nabla\partial_t\varphi^*_{j\sigma}\right)\chi_{j\sigma} + \left(\nabla\varphi^*_{j\sigma}\right)\left(\partial_t\chi_{j\sigma}\right)\right.\\ &\left.-\left(\partial_t\varphi^*_{j\sigma}\right)\left(\nabla\chi_{j\sigma}\right) - \varphi^*_{j\sigma}\left(\nabla\partial_t\chi_{j\sigma}\right)\right]\Big\} + c.c. = 0\,.\end{aligned} \tag{17}$$

By invoking Eq. (2), Eq. (4), Eq. (9), and the equality $g_\sigma(\mathbf{r}, t) = 0$, Eq. (17) can be cast into a real-time TDOEP equation,

$$\nabla\cdot(\rho_\sigma\nabla v_{xc\sigma}) = \zeta_\sigma\,, \tag{18}$$

for $v_{xc\sigma}(\mathbf{r},t)$, where

$$\zeta_\sigma = \sum_{j=1}^{N_\sigma}\Big\{\Big(\triangle\triangle\varphi^*_{j\sigma}\Big)\chi_{j\sigma} - 2\Big(\triangle\varphi^*_{j\sigma}\Big)\Big(\triangle\chi_{j\sigma}\Big) + \varphi^*_{j\sigma}\Big(\triangle\triangle\chi_{j\sigma}\Big) + \Big(\triangle\varphi^*_{j\sigma}\Big)\Big(u^*_{xcj\sigma}\varphi_{j\sigma}\Big) - \varphi^*_{j\sigma}\Big[\triangle\Big(u^*_{xcj\sigma}\varphi_{j\sigma}\Big)\Big]\Big\} + c.c.\,. \tag{19}$$

and $\triangle = -\frac{\nabla^2}{2}$. Eq. (18) is a Sturm-Liouville-type equation that possesses a unique solution when subject to appropriate physical boundary conditions [51, 52]. Furthermore, we differentiate Eq. (4) with respect to $\mathbf{r}$ to yield the relation $\nabla^2\left(\sum_{j=1}^{N\sigma}\varphi^*_{j\sigma}\chi_{j\sigma} + c.c.\right) = 0$. With the aid of this relation, Eq. (18) can also be written in a compact tensor form,

$$\nabla\cdot(\rho_\sigma\nabla v_{xc\sigma}) = -\nabla\cdot(\mathbf{F}^{(t)}_\sigma + \mathbf{F}^{(w)}_\sigma)\,, \tag{20}$$

which contains two xc force terms

$$\mathbf{F}^{(t)}_{\sigma\mu} = \sum_{\nu=1,2,3}\partial_\nu\tau_{\sigma\mu\nu} \tag{21}$$

and

$$\mathbf{F}^{(w)}_{\sigma\mu} = \sum_{j=1}^{N_\sigma}\left[i\,\mathbf{j}_{j\sigma\mu}\Big(u_{xcj\sigma} - c.c.\Big) - \frac{|\varphi_{j\sigma}|^2}{2}\partial_\mu\Big(u_{xcj\sigma} + c.c.\Big)\right], \tag{22}$$

where the time-dependent kinetic-like stress tensor

$$\tau_{\sigma\mu\nu} = \sum_{j=1}^{N_\sigma}\frac{1}{2}\left[(\partial_\mu\varphi^*_{j\sigma})(\partial_\nu\chi_{j\sigma}) + (\partial_\nu\varphi^*_{j\sigma})(\partial_\mu\chi_{j\sigma}) + c.c.\right] \tag{23}$$

and the orbital-dependent current density

$$\mathbf{j}_{j\sigma\mu} = \frac{i}{2}\left[(\partial_\mu\varphi^*_{j\sigma})\varphi_{j\sigma} - \varphi^*_{j\sigma}(\partial_\mu\varphi_{j\sigma})\right], \tag{24}$$

with $\mu,\nu = 1,2,3$ labeling the Cartesian coordinate $\mathbf{x} = (x_1, x_2, x_3)$, and ∂_μ denotes $\partial/\partial x_\mu$. Finally, we remark that it is in principle possible to introduce a new orthogonal coordinate system $\mathbf{x}' = \mathbf{x}'(\mathbf{x})$ corresponding to the Jacobian matrix $\mathrm{J_{ij}} = \partial\mathrm{x}'_\mathrm{i}/\partial\mathrm{x_j} = [\rho_\sigma(\mathbf{x},\mathrm{t})]^{-1}\delta_{\mathrm{ij}}$, as well as subject to the condition $\mathbf{x}'(\mathbf{x}=0) = 0$, such that Eq. (18) can be rewritten as a Poisson-like equation

$$\nabla'^2 v_{xc\sigma}(\mathbf{x}',t) = \zeta'_\sigma(\mathbf{x}',t)\,, \tag{25}$$

where $\zeta'_\sigma(\mathbf{x}',t) = \rho_\sigma(\mathbf{x}',t)\zeta_\sigma(\mathbf{x}',t)$ and ∇' denotes the differential operator with respect to the new coordinate $\mathbf{x}'$.

It is instructive that the TDOEP equation, Eq. (20), can be cast in a hydrodynamic context as in the other non-adiabatic approaches [39–46], showing that the nonadiabatic dynamics is manifested in the time-dependent kinetic-like stress tensor τ_σ and orbital-dependent current density $\mathbf{j}_{j\sigma}$. In addition, Eq. (22) shows two different aspects of the non-locality of the exchange-correction potential, one to do with the orbital-dependent current density $\mathbf{j}_{j\sigma}$ and the other with the orbital-dependent density $|\varphi_{j\sigma}|^2$. These observations suggest that Eq. (20) may be amenable to further development in non-adiabatic xc potentials as well as orbital-dependent current density functionals. Moreover, we remark that Ruggenthaler and Bauer have found an local Hatree-exchange only (LHXO) approximation for the effective potential corresponding to the exact Hartree-exchange forces, while the correlation part of the interacting wave function is ignored [53]. Interestingly, our time-local TDOEP equation reduces to the LHXO approximation when omitting the EM orbitals, resulting in $\mathbf{F}_\sigma^{(t)} = 0$ in Eq. (20).

Finally, it is important to point out that the time-local equation, Eq. (20), can be solved in parallel to Eqs. (2) and (9), respectively, for the KS orbitals $\varphi_{j\sigma}(\mathbf{r}, t)$ and the EM orbitals $\chi_{j\sigma}(\mathbf{r}, t)$. In contrast, solving the non-linear, nonlocal integral equation, Eq. (1) would require all past dynamical information about the KS orbitals. In this regard, the instantaneous EM orbital $\chi_{j\sigma}(\mathbf{r}, t)$ effectively carries all memory of the evolving system. Within the framework of time-dependent EM orbitals, the time-dependent xc potential is considered as a functional of the instantaneous KS and EM orbitals, analogous to the Hartree potential as a functional of the occupied KS orbitals. From a numerical perspective, solving the time-local TDOEP equation also benefits from avoiding the storage of the entire history of time-dependent KS orbitals $\varphi_{j\sigma}(\mathbf{r}, t')$ and $v_{xc\sigma}(\mathbf{r}, t')$ for all $t' < t$. It is remarked that the exact-exchange only TDOEP equation does not contain the memory loss associated with the unaccounted for correlation component, which is an essential feature in post-ALDA TDDFT [54]. In addition, solving the highly nonlinear Eqs. (9) and (20) concomitantly would require extremely accurate time-dependent EM orbitals $\chi_{j\sigma}(\mathbf{r}, t)$ at each time step, since a small numerical error incurred at t' will be quickly amplified at $t > t'$, resulting in large errors in the xc force term, $\mathrm{F}_\sigma^{(\mathrm{t})}$ in Eq. (9), which involves second-order derivatives of EM orbitals. To this end, an efficient modified exponential time-differencing (ETD) integration scheme [55, 56], in conjunction with the Chebychev expansion [57] for propagation of the KS orbitals , is adopted to simulate the memory loss when solving the exact-exchange only TDOEP equation and to control unwanted error accumulation when solving Eq. (9) for the time-dependent EM orbitals (see Supplemental Material for the details [58]).

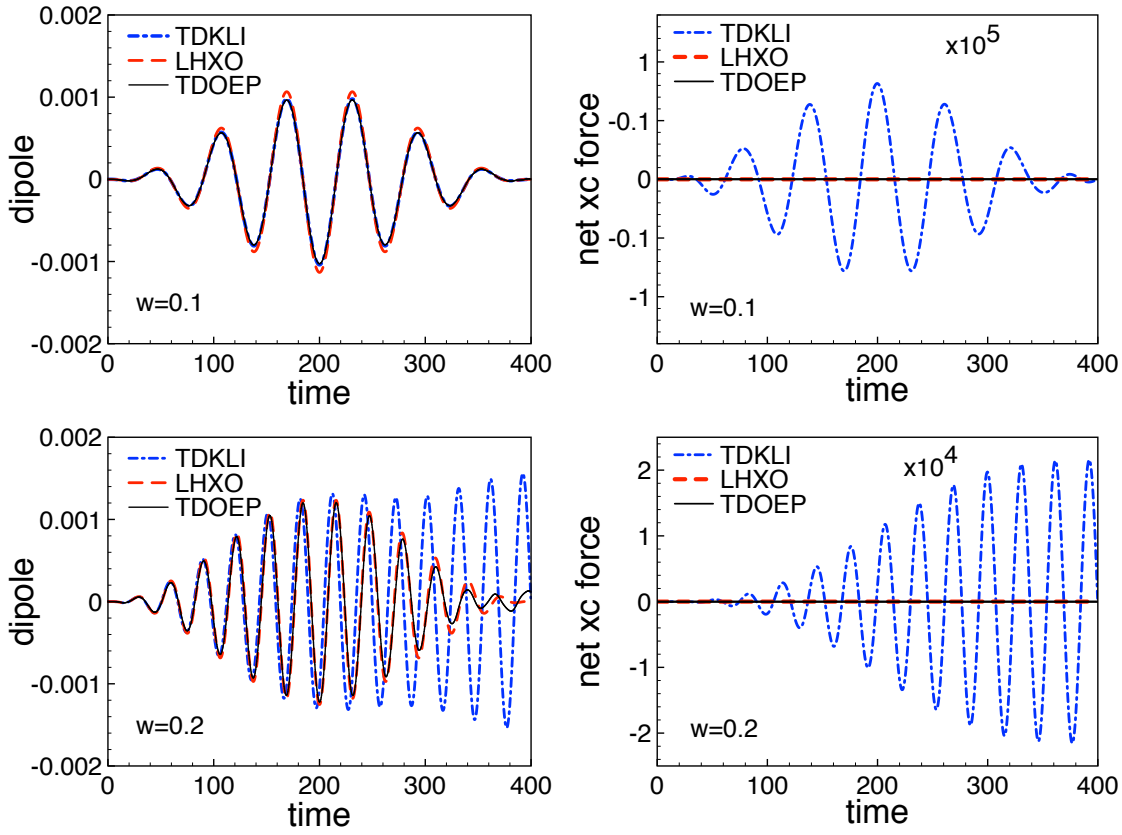

FIG. 1. Comparison between the TDOEP, TDKLI and LHXO approximations. In TDOEP simulations, we choose $\Delta t = 0.001$ for the time step and $\tau = 2$ for the memory loss in the modified ETD integration scheme. The external field is a sine square pulse with frequency $\omega = 0.1, 0.2$ (upper, lower panels) and length T = 400. The left-hand side is the resulting the time-dependent dipole, and the right-hand side shows the net xc force.

As an illustration, we consider a one-dimensional chain of hydrogen atoms in the presence of an external sine-square pulse, using a model Hamiltonian with the exact-exchange functional [37]. Figure (1) shows that time-dependent dipole and the net xc force, defined as $\int \rho(x,t)\nabla v_{xc}(x,t)\,dx$, corresponding to various approximated $v_{xc\sigma}$. For the external field with a low frequency, the calculated dipole moments (upper-left panel) for TDOEP and TDKLI are seen to be very similar, justifying the adiabatic approximation. However, by doubling the frequency of the external field ($\omega = 0.1 \rightarrow 0.2$), the discrepancy in the calculated dipole moments (lower-left panel) is found to be quite large at later times (i.e., $t > 200$ a.u.). For both frequencies, the dipole moments for the LHXO approximation, which is a non-adiabatic approach, are seen to be close to those for the TDOEP. It is also found that in general the TDOEP results in smaller and slower dipole oscillation

than the TDKLI and the LHXO do. In a previous TDCDFT study of electron liquid in extended systems, it was shown that the post-ALDA correction makes deformation of the electron density less likely [44]. This non-adiabatic feature is also observed in our TDOEP simulations. The right panels of Fig. (1) show that the zero-force theorem is satisfied in both the TDOEP and LHXO schemes, whereas the violation of the zero-force theorem in TDKLI causes unphysical dipole oscillation in the end of the laser pulse.

In summary, we have formulated an exact, Sturm-Liouville-type, time-local TDOEP equation for orbital-dependent xc functionals in terms of time-dependent Kohn-Sham and effective memory orbitals. The many-electron dynamics of a hydrogen chain has been successfully solved to show the applicability of the time-local TDOEP equation. The numerical simulations show that the time-local TDOEP rigorously obeys the zero-force theorem . This new reformulation is intended to expedite the construction of the TDOEP in real-time and to facilitate studies on various orbital-dependent functionals beyond the adiabatic approximation. Finally, the time-local TDOEP equation in the hydrodynamic context can be readily extended to include both scalar and vector potentials.

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[1] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).

[2] M. A. L. Marques, N. T. Maitra, F. M. S. Nogueira, E. K. U. Gross, and A. Rubio, eds., *Fundamentals of Time-Dependent Density Functional Theory* (Springer Berlin Heidelberg, 2012).

[3] C. A. Ullrich, *Time-dependent Density functional theory* (Oxford University Press, 2012).

[4] M. Chini, X. Wang, Y. Cheng, H. Wang, Y. Wu, E. Cunningham, P.-C. Li, J. Heslar, D. A. Telnov, S.-I. Chu, and Z. Chang, Nature Photonics **8**, 437 (2014).

[5] M. E. Casida, Journal of Molecular Structure: THEOCHEM **914**, 3 (2009).

[6] M. A. L. Marques, X. López, D. Varsano, A. Castro, and A. Rubio, Phys. Rev. Lett. **90**, 258101 (2003).

[7] A. Castro, J. Werschnik, and E. K. U. Gross, Phys. Rev. Lett. **109**, 153603 (2012).

[8] G. Stefanucci and S. Kurth, Phys. Rev. Lett. **107**, 216401 (2011).

[9] I. V. Tokatly, Phys. Rev. Lett. **110**, 233001 (2013).

[10] F. G. Eich, M. Di Ventra, and G. Vignale, Phys. Rev. Lett. **112**, 196401 (2014).

[11] G. Wachter, C. Lemell, J. Burgdörfer, S. A. Sato, X.-M. Tong, and K. Yabana, Phys. Rev. Lett. **113**, 87401 (2014).

[12] Z. Wang, S.-S. Li, and L.-W. Wang, Phys. Rev. Lett. **114**, 63004 (2015).

[13] Y. Miyamoto, H. Zhang, T. Miyazaki, and A. Rubio, Phys. Rev. Lett. **114**, 116102 (2015).

[14] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[15] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[16] N. T. Maitra, K. Burke, and C. Woodward, Phys. Rev. Lett. **89**, 23002 (2002).

[17] T. Grabo, T. Kreibich, S. Kurth, and E. K. U. Gross, in *Strong Coulomb Correlations in Electronic Structure Calculations*, Advances in Condensed Matter Science, edited by V. I. Anisimov (Taylor & Francis, 2000).

[18] E. Engel, in *A Primer in Density Functional Theory*, Lecture Notes in Physics, Vol. 620, edited by C. Fiolhais, F. Nogueira, and M. Marques (Springer Berlin Heidelberg, 2003) pp. 56–122.

[19] S. Kümmel and L. Kronik, Reviews of Modern Physics **80**, 3 (2008).

[20] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).

[21] J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Rev. A **45**, 101 (1992).

[22] M. Mundt and S. Kümmel, Phys. Rev. Lett. **95**, 203004 (2005).

[23] R. van Leeuwen, Phys. Rev. Lett. **76**, 3610 (1996).

[24] A. Görling, Phys. Rev. A **55**, 2630 (1997).

[25] C. A. Ullrich, U. J. Gossmann, and E. K. U. Gross, Phys. Rev. Lett. **74**, 872 (1995).

[26] R. van Leeuwen, Phys. Rev. Lett. **80**, 1280 (1998).

[27] E. K. U. Gross, J. F. Dobson, and M. Petersilka, in *Density Functional Theory II*, Topics in Current Chemistry, Vol. 181, edited by R. F. Nalewajski (Springer Berlin Heidelberg, 1996) pp. 81–172.

[28] P. Elliott, F. Furche, and K. Burke, in *Reviews in Computational Chemistry* (John Wiley & Sons, Inc., 2009) pp. 91–165.

[29] M. E. Casida and M. Huix-Rotllant, Annual Review of Physical Chemistry **63**, 287 (2012).

[30] H. O. Wijewardane and C. A. Ullrich, Phys. Rev. Lett. **100**, 056404 (2008).

[31] S. Kümmel, in *Fundamentals of Time-Dependent Density Functional Theory*, Lecture Notes in Physics, Vol. 837, edited by M. A. L. Marques, N. T. Maitra, F. M. S. Nogueira, E. K. U. Gross, and A. Rubio (Springer Berlin Heidelberg, 2012) Chap. 6, pp. 125–138.

[32] J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Rev. A **46**, 5453 (1992).

[33] O. V. Gritsenko, S. J. A. van Gisbergen, P. R. T. Schipper, and E. J. Baerends, Phys. Rev. A **62**, 12507 (2000).

[34] S. Kümmel, L. Kronik, and J. P. Perdew, Phys. Rev. Lett. **93**, 213002 (2004).

[35] T. Körzdörfer, S. Kümmel, and M. Mundt, J. Chem. Phys. **129**, 014110 (2008).

[36] M. Mundt, S. Kümmel, R. van Leeuwen, and P.-G. Reinhard, Phys. Rev. A **75**, 50501 (2007).

[37] M. Mundt and S. Kümmel, Phys. Rev. A **74**, 022511 (2006).

[38] S. K. Ghosh and A. K. Dhara, Phys. Rev. A **38**, 1149 (1988).

[39] G. Vignale and W. Kohn, Phys. Rev. Lett. **77**, 2037 (1996).

[40] J. F. Dobson, M. J. Bünner, and E. K. U. Gross, Phys. Rev. Lett. **79**, 1905 (1997).

[41] G. Vignale, C. A. Ullrich, and S. Conti, Phys. Rev. Lett. **79**, 4878 (1997).

[42] G. Vignale, Phys. Rev. B **70**, 201102 (2004).

[43] Y. Kurzweil and R. Baer, Phys. Rev. B **72**, 35106 (2005).

[44] C. A. Ullrich and I. V. Tokatly, Phys. Rev. B **73**, 235102 (2006).

[45] I. V. Tokatly and O. Pankratov, Phys. Rev. B **67**, 201103 (2003).

[46] I. V. Tokatly, Phys. Rev. B **71**, 165105 (2005).

[47] J. Schirmer, Phys. Rev. A **86**, 12514 (2012).

[48] G. Vignale, Phys. Rev. A **83**, 46501 (2011).

[49] E. K. U. Gross, C. A. Ullrich, and U. J. Gossmann, in *Density Functional Theory*, edited by E. K. U. Gross and R. M. Dreizler (Springer US, 1995) pp. 149–171.

[50] S. Kümmel and J. P. Perdew, Phys. Rev. Lett. **90**, 043004 (2003).

[51] E. K. U. Gross and W. Kohn, Advances in Quantum Chemistry **21**, 255 (1990).

[52] R. van Leeuwen, Phys. Rev. Lett. **82**, 3863 (1999).

[53] M. Ruggenthaler and D. Bauer, Phys. Rev. A **80**, 52502 (2009).

[54] H. O. Wijewardane and C. A. Ullrich, Phys. Rev. Lett. **95**, 86401 (2005).

[55] G. Beylkin, J. M. Keiser, and L. Vozovoi, J. Comput. Phys. **147**, 362 (1998).

[56] A. Y. Suhov, J. Sci. Comput. **60**, 684 (2014).

[57] H. Tal-Ezer and R. Kosloff, J. Chem. Phys. **81**, 3967 (1984).

[58] See Supplemental Material at http://link.aps.org/supplemental/xx.xxxx/PhysRevLett.xxx.xxxxxx, which includes Refs. [37, 55–57], for numerical implementation details.