

Harnessing dressed time-dependent density functional theory for the nonperturbative regime: Electron dynamics with double excitations

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Recent progress has been made in capturing spectral features of electronic states of double-excitation character in time-dependent density functional theory (TDDFT) through a frequency-dependent kernel. While it might appear that this development is limited to the perturbative regime, we show that when used within response-reformulated TDDFT (RR-TDDFT), it accurately captures strong-field dynamics involving states of double-excitation character. More generally, this demonstrates how RR-TDDFT enables exchange-correlation functional developments in the response regime, which have so far been more successful than those in the nonlinear regime, to be exploited for nonperturbative dynamics, thus significantly broadening their range of applications.

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While time-dependent density functional theory (TDDFT) [1–3] has emerged as a method of choice for calculating electronic spectra and nonperturbative dynamics, it is well recognized that the approximate functionals used today suffer from well-known failures. These are particularly severe in the nonperturbative regime, as demonstrated by, e.g., resonantly driven dynamics [4–7], long-range charge transfer [8–11], and unphysical spurious peak shifting [12–14]. One key reason is that the exchange-correlation (xc) potential, $v_{\text{xc}}[n; \Psi_0, \Phi_0](\mathbf{r}, t)$, that appears in the time-dependent Kohn-Sham (TDKS) equations of TDDFT, depends on the history of the density, the initial many-body state, and the initial Kohn-Sham (KS) state, but this memory dependence is neglected in the calculations: The commonly used adiabatic approximations depend only on the instantaneous density, $v_{\text{xc}}^{\text{A}}[n; \Psi_0, \Phi_0](\mathbf{r}, t) = v_{\text{xc}}^{\text{g.s.}}[n(t)](\mathbf{r})$, where $v_{\text{xc}}^{\text{g.s.}}[n](\mathbf{r})$ is a ground-state functional. Practical memory-dependent functionals in the nonperturbative regime remain elusive, despite intense and varied efforts [15]. Orbital-dependent functionals contain some degree of memory since instantaneous functionals of the orbitals contain some history dependence of the density, but these have been limited to exact exchange in hybrid functionals and miss important memory effects in the correlation potential, such as step and peak features [15,16].

So far, there has been more success for memory-dependent functional development in the linear-response regime, notably for double excitations [17–24] and dissipation/relaxation in metallic systems [25,26]. In this regime, memory dependence manifests as frequency dependence in the xc kernel, which is the Fourier transform of $f_{\text{xc}}[n^{\text{g.s.}}](\mathbf{r}, \mathbf{r}', t - t') = \frac{\delta v_{\text{xc}}[n](\mathbf{r}, t)}{\delta n(\mathbf{r}', t')}|_{n=n^{\text{g.s.}}}$, generating shifts and creating new excitation energies with corrected transition densities.

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Recently, a reformulation of TDDFT was proposed, which offers the possibility to use these successes for fully nonperturbative dynamics [27]. This response-reformulated TDDFT (RR-TDDFT) bypasses the xc potential of TDKS, solving instead for coefficients of the many-body wavefunction, without needing the wavefunction itself, and requires xc functionals only in the ground-state, linear, and quadratic response regimes. Since the xc functionals are thus evaluated only near a ground state, adiabatic approximations perform far better than they do for the xc potential appearing in the TDKS equation, redeeming, for example, Rabi oscillations for which the traditional TDKS with adiabatic functionals fails [27]. However, RR-TDDFT is limited by the accuracy of the xc functional in the response regime, and a well-known failure of the adiabatic approximation is the inability to capture excitations that have some double-excitation character (double excitations, *tout court*) [18]. On the other hand, nonperturbative TDKS with adiabatic functionals can access double excitations, but the description is unreliable, unphysically dependent on the field parameters driving the system [28]. Recently, a nonadiabatic “dressed” xc kernel was derived that captures both excitation energies and oscillator strengths of double excitations [23,24]. While shown to successfully predict the $2^1\text{Ag}-1^1\text{Bu}$ curve crossing and double character in butadiene, a challenge even for high-level wavefunction methods [29], and excited-state densities in model one-dimensional (1D) systems [30], the prospect of using the kernel for fully nonlinear processes beyond the response regime had not been exploited, let alone envisioned.

In this work, we extend dressed TDDFT beyond its linear-response application by employing RR-TDDFT. This extension enables real-time simulations of nonperturbative dynamics involving double excitations with a reliability comparable to that of dressed TDDFT in describing their excitation energies and response properties. More generally, this work shows how the RR-TDDFT formalism enables any functional developed in the response regime to now be useful for fully nonequilibrium dynamics.

RR-TDDFT operates by solving a system of ordinary differential equations (ODEs) for coefficients of the many-body time-dependent state expanded in unperturbed many-body states Ψ_m , in the flavor of time-dependent configuration interaction (TDCI), but with the important difference that no many-body states are actually needed or calculated. We note that RR-TDDFT could be viewed as an exactification of the approach to strong-field molecular dynamics in Refs. [31–33] where linear-response TDDFT quantities and auxiliary wavefunctions were used in a TDCI-like framework. Under the Runge-Gross theorem [1], with the applied potential being a one-body multiplicative operator, all the input ingredients to the ODEs, as well as all observables, can be obtained from ground-state DFT or response TDDFT: energies E_m (from ground state ($m = 0$) and linear response [34–37]), transition densities out of the ground state, $\rho_{0m}(\mathbf{r}) = \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_m \rangle$ (from linear response [34–37]), transition densities between excited states, $\rho_{mn}(\mathbf{r}) = \langle \Psi_m | \hat{n}(\mathbf{r}) | \Psi_n \rangle$ (from quadratic response [38,39]), and state densities $\rho_{mm}(\mathbf{r}) = \langle \Psi_m | \hat{n}(\mathbf{r}) | \Psi_m \rangle$ (from ground-state DFT ($m = 0$) or linear response [30,40,41]). The equations are

$$i \dot{C}_m(t) = E_m C_m(t) + \sum_n V_{mn}^{\text{app}}(t) C_n(t), \quad (1)$$

with the driving matrix elements defined as

$$V_{mn}^{\text{app}}(t) = \langle \Psi_m | V^{\text{app}}(t) | \Psi_n \rangle = \int d^3r v^{\text{app}}(\mathbf{r}, t) \rho_{mn}(\mathbf{r}), \quad (2)$$

and observables extracted (in principle [1]) from the density

$$n(\mathbf{r}, t) = \sum_{n,m} C_n^*(t) C_m(t) \rho_{nm}(\mathbf{r}). \quad (3)$$

We will consider here uniform applied electric fields, $\mathcal{E}(t)$, such that $V_{mn}^{\text{app}}(t) = \mathcal{E}(t) \cdot \mathbf{d}_{mn}$, and the dipole moment as our observable, $\mathbf{d}(t) = \sum_n \sum_m C_n^*(t) C_m(t) \mathbf{d}_{nm}$, where $\mathbf{d}_{nm} = \langle \Psi_n | \hat{\mathbf{r}} | \Psi_m \rangle = \int d^3r \mathbf{r} \rho_{nm}(\mathbf{r})$. The xc functional (ground state and response, as detailed above) enters in the

calculation of the energies E_m , the transition densities ρ_{mn} , and the densities ρ_{mm} ; the latter two weigh the integral in the matrix element of the applied potential $V_{mn}^{\text{app}}(t)$.

The advantage of RR-TDDFT over traditional TDKS calculations becomes salient when considering the nature of the xc functionals that are needed in each approach: The TDKS equations, $i\partial_t\phi_i(\mathbf{r}) = \{-\frac{1}{2}\nabla^2 + v_S(\mathbf{r})\}\phi_i(\mathbf{r})$, where $v_S(\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) + v_H[n](\mathbf{r}, t) + v_{\text{XC}}[n, \Psi_0, \Phi_0](\mathbf{r}, t)$, require the xc potential evaluated in the fully nonequilibrium domain, but adiabatic approximations simply take a ground-state functional, $v_{\text{XC}}^A[n, \Psi_0, \Phi_0](\mathbf{r}, t) = v_{\text{XC}}^{\text{g.s.}}[n(t)](\mathbf{r}, t)$, approximating the xc effects of the fully nonequilibrium system by ground-state xc. On the other hand, as is evident in Eqs. (1)–(3), the xc functional is required only near the ground state for RR-TDDFT, that is, near the domain for which the adiabatic functionals were derived. Reference [27] showed how Eqs. (1)–(3) were able to capture Rabi oscillations and charge-transfer dynamics using adiabatic approximations, even when those same adiabatic approximations dramatically failed when used within the traditional TDKS scheme. However, when the dynamics accesses states whose response properties are not well predicted by adiabatic approximations, then RR-TDDFT with these functionals will also not perform well. This is the case for double excitations. Instead, the frequency-dependent kernel of dressed TDDFT (DTDDFT) [23] predicts their excitation energies, transition densities out of the ground state, and densities [30] well. We now use the DTDDFT xc kernel in RR-TDDFT to predict fully nonperturbative dynamics that access double excitations.

Excitation energies in response TDDFT are obtained as eigenvalues of the matrix

$$\Omega_{qq'}(\omega) = v_q^2 \delta_{qq'} + 4 \sqrt{v_q v_{q'}} f_{\text{HXC}, qq'}(\omega), \quad (4)$$

with $f_{\text{HXC}, qq'}(\omega) = \iint d\mathbf{r} d\mathbf{r}' \Phi_q(\mathbf{r}) f_{\text{HXC}}(\mathbf{r}, \mathbf{r}', \omega) \Phi_{q'}(\mathbf{r}')$ and $f_{\text{HXC}}(\mathbf{r}, \mathbf{r}', \omega) = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{XC}}(\mathbf{r}, \mathbf{r}', \omega)$. Here, the KS transition density $\Phi_q(\mathbf{r}) = \phi_i^*(\mathbf{r})\phi_a(\mathbf{r})$ is the product of occupied (i) and unoccupied (a) KS orbitals, and $v_q = \epsilon_a - \epsilon_i$ are their orbital energy differences. The oscillator strengths and transition densities are obtained from eigenvectors $\mathbf{G}_I$ of the matrix [Eq. (4)] when normalized according to [35]

$$\mathbf{G}_I^\dagger \left(1 - \frac{d\Omega}{d(\omega^2)} \bigg|_{\omega=\omega_I} \right) \mathbf{G}_I = 1. \quad (5)$$

Adiabatic approximations yield no frequency dependence in the matrix of Eq. (4), but frequency dependence is at the heart of DTDDFT in capturing double excitations. Here, we will consider DTDDFT in a case where the KS single excitations are well separated, such that a small-matrix approximation (SMA) may be applied that keeps only the diagonal elements of Eq. (4). When one single excitation $q = i \rightarrow a$ mixes with one double excitation, DTDDFT reduces to dressed SMA (DSMA), where the xc kernel has the diagonal element [23,30,42]:

$$f_{\text{XC}, qq}^{\text{DSMAA0}}(\omega) = f_{\text{XC}, qq}^A + \frac{|H_{qd}|^2}{4 v_q} \left(1 + \frac{(\Omega_q^A + (H_{dd} - H_{00}))^2}{\omega^2 - [(H_{dd} - H_{00})^2 + H_{qd}^2]} \right). \quad (6)$$

Here, f_{XC}^A is a chosen adiabatic xc kernel approximation, upon which DSMA is built, H_{ij} are the matrix elements of the true Hamiltonian involving the KS ground state (0), single excitation (q), and double excitation (d), and Ω_q^A denotes the adiabatic TDDFT prediction for the single excitation. There are different possible variants for the dressing [42,43] but all have the general form in Eq. (6).

Due to its frequency dependence, Eq. (6) folds in the double excitation to the single excitation q , shifting the adiabatic prediction for the latter and generating an additional excitation, and Eq. (5) redistributes the KS transition density into that for the resulting states of mixed single- and double-excitation character. The densities of these states are obtained from the functional derivative of their energies with respect to the external potential, following the procedure in Ref. [30]. Thus, we obtain $E_n, \rho_{n0}, \rho_{nn}$ for these two states. The remaining ingredient for RR-TDDFT is ρ_{nm} , the transition density between these states and between other excited states. For this, a dressed quadratic

TABLE I. Permanent dipole moments, d_{mm} (a.u.) from AEEX and DSMA_{A0} based on AEEX (DSMA/AEEX), compared to the exact.

	d_{00}	d_{11}	d_{22}	d_{33}
Exact	-0.1601	-0.3240	-0.5038	-0.4948
AEEX	-0.1599	-0.3245	-0.5084	-
DSMA/AEEX	-0.1599	-0.3159	-0.5037	-0.4938

response would need to be developed. Instead, here we simply approximate ρ_{nm} along the lines of the auxiliary wavefunction approach of Ref. [43], using the eigenvectors G_I to weight the KS determinants. For the simple model system we study here, the excitations appear in relatively separated multiplet structures, and this approximation is reasonable, as manifest when comparing the resulting couplings to the exact ones. In general, relaxation terms from a proper quadratic response formalism may be more important. Finally, we note that the dressed xc kernel is a correction only to this single excitation, while the other excitations of the system are predicted with adiabatic TDDFT within the usual TDDFT matrix framework.

We now demonstrate the capability of RR-TDDFT for dynamics involving double excitations on a simple model system of two soft-Coulomb interacting electrons in a 1D anharmonic oscillator:

$$\hat{H}(x_1, x_2) = \sum_{i=1,2} \left(-\frac{1}{2} \partial_{x_i}^2 + \hat{v}_{\text{ext}}(x_i) \right) + \hat{w}(x_1, x_2), \quad (7)$$

where $\hat{w}(x_1, x_2) = \frac{1}{\sqrt{(x_1 - x_2)^2 + \lambda^2}}$, with $\lambda = 2$ being the softening parameter, and $\hat{v}_{\text{ext}}(x) = \frac{1}{2}x^2 + \gamma x^3$ with the parameter $\gamma = 0.05$ that tunes the cubic anharmonicity. The anharmonicity is needed to avoid parity preventing access to excited states by an applied laser field of $v^{\text{app}}(x, t) = \mathcal{E}(t)x$. With these parameters, the unperturbed system is weakly interacting enough that the predominant correlation effect is through mixing of a single excitation with a double excitation; this allows us to highlight the ability of RR-TDDFT to describe dynamics accessing these states. The lowest four exact excitation energies are (in a.u.) 0.9787, 1.8462, 1.9478, and 2.7750, where the second and third excitations have mixed single and double character, with $G_2^2 = 0.775$ and $G_3^2 = 0.316$ indicating their single-excitation components, respectively [23]. Adiabatic TDDFT yields only one excitation in the second multiplet, and for our choice of functional, adiabatic exact exchange (AEEX), the three energies in this range are (in a.u.) 0.9788, 1.8848, and 2.7900. DSMA_{A0} built on AEEX (DSMA/AEEX) retrieves the mixing with the KS double excitation, yielding four energies in reasonable agreement with the exact (in a.u.): 0.9788, 1.8456, 1.9490, and 2.7327, with the single-excitation components of the second and third states predicted as $G_2^2 = 0.6215$ and $G_3^2 = 0.3784$. The remaining ingredients for RR-TDDFT are the permanent and transition dipoles; these are given in Tables I and II, respectively. Note that the missing elements for AEEX are those involving the missing state in the second multiplet.

The exact results in the tables were obtained by solving the two-electron Schrödinger equation in the Octopus [44,45] code, which was also used for the EXX ground state, KS states, AEEX excitation energies, AEEX ground-to-excited transition dipoles, and the TDKS and exact (denoted

TABLE II. As for Table I, but for the magnitude of the transition dipole moments, d_{mn} (a.u.).

	d_{01}	d_{02}	d_{03}	d_{12}	d_{13}	d_{23}
Exact	1.0072	0.0518	0.0325	0.1860	1.4180	0.0090
AEEX	1.0073	0.0604	-	1.029	-	-
DSMA/AEEX	1.0073	0.0458	0.0348	0.1813	1.4411	0.0051

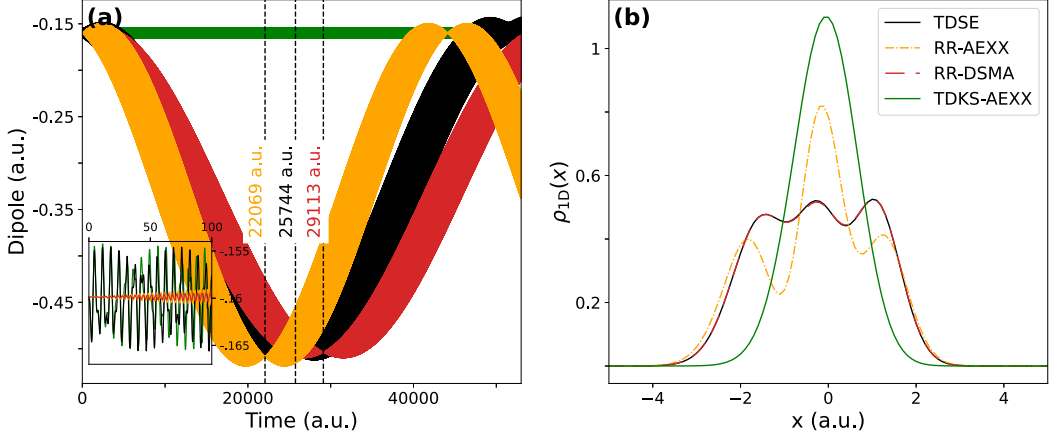


FIG. 1. Rabi oscillations to the second excited state. (a) Dipole predicted by the TDKS propagation with AEEXX (green), AEEXX used within RR-TDDFT (RR-AEEXX, orange), DSMA/AEEXX within RR-TDDFT (RR-DSMA, red), and exact (TDSE, black), each driven at their respective resonant frequency. The vertical lines indicate the half-Rabi period for the respective method, and the inset zooms into short times. (b) The densities for each of the calculations in panel (a), plotted at the respective $T_R/2$.

as TDSE) dynamics (see shortly). A grid spacing of 1 a.u. and hard-wall box size of 10 a.u. were used. The excited-state densities based on Ref. [30], transition densities based on weighted KS determinants, and the RR-TDDFT dynamics were calculated using an in-house code. A time step of 0.03 au was used for both the TDSE and TDKS runs in Octopus using the enforced time-reversal symmetry method, and the RR-TDDFT coefficient dynamics using RK45.

Turning now to dynamics, we drive the system at the frequency of the second excitation, ω_2 , to induce a Rabi oscillation, with applied field $\mathcal{E}(t) = \mathcal{E}_0 \sin(\omega_2 t) \hat{x}$, where $\mathcal{E}_0 = 1/(300\sqrt{2}) = 0.002357$ a.u. After half a Rabi period, $\frac{T_R}{2} = \frac{\pi}{\omega_2 \mathcal{E}_0}$, we expect the population to fully transfer to the excited state. Figure 1 shows the results of TDKS propagation with AEEXX, RR-TDDFT with AEEXX, and RR-TDDFT with DSMA built on AEEXX, all compared to the exact TDSE solution, each driven at their respective resonant ω_2 . The TDKS-AEEXX dipole strikingly fails to capture the Rabi oscillation, because ground-state xc is inadequate to describe systems far from a ground state. On the other hand, when used within RR-TDDFT, AEEXX does yield a Rabi oscillation, and the density does correspond to the density of the AEEXX excited state; however, because the description of this state lacks the double-excitation component, the density is badly reproduced as evident in Fig. 1(b). RR-TDDFT used with DSMA/AEEXX captures the dipole Rabi oscillation and also accurately reproduces the exact density at $T_R/2$. The inset in Fig. 1(a), showing very short times, indicates that the error in RR-TDDFT here arises because it was calculated with only two states; however, this error is very small on the scale of the overall density change over time.

Next, we give an example where more than two states are involved in the dynamics and apply a pulse of the form $\mathcal{E}(t) = \mathcal{E}_0 \sin^2(\frac{\pi t}{2\sigma}) \sin(\omega_c t)$, which turns off at $t = 2\sigma$. The driving frequency ω_c , amplitude $\mathcal{E}_0$, and pulse width σ are tuned to achieve a coherent evolving superposition of the four lowest states. To isolate errors of the DSMA/AEEXX functional approximation from that of truncating our Hilbert space in RR-TDDFT to four states, we further compute the ingredients for the latter using exact wavefunctions, denoting this truncated TDCI, or TDCI for short.

Figure 2 shows dynamics resulting from a nonresonant driving frequency in between the second and third excited states of $\omega_c = 1.9$ a.u., strength $\mathcal{E}_0 = 0.3$ a.u., and width parameter $\sigma = 50$ a.u., denoted as Pulse 1. In the exact evolution, the pulse causes about 4% of the population (not shown) to leave the ground state, almost equally populating the second and third excited states; during the pulse, there is also a small transient population in the lowest excited state. Both TDKS-AEEXX

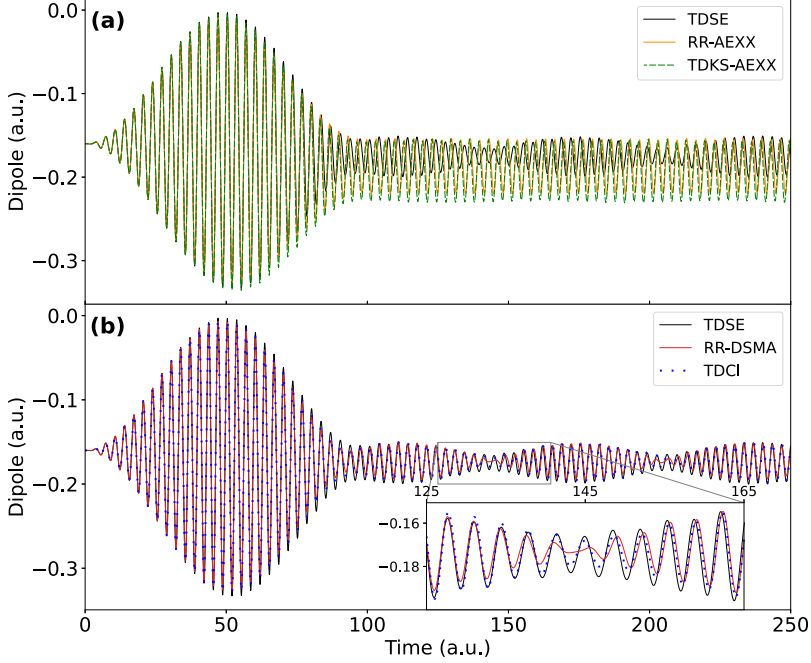


FIG. 2. The dipole moment driven with Pulse 1, predicted by (a) TDKS propagation with AEEX (green, dashed), AEEX used within RR-TDDFT (RR-AEEX, orange), and exact (black); and (b) DSMA built on AEEX within RR-TDDFT (RR-DSMA, red), truncated TDCI (blue, dotted), and exact (black).

and RR-AEEX give a qualitatively different prediction of the dipole oscillations after about $t = 75$ a.u., missing the beating and overestimating the average dipole magnitude. Unlike the previous case, TDKS-AEEX and RR-AEEX predict similar dynamics; this is likely because during much of the pulse the external potential dominates over xc, and because relatively small population leaves the ground state. RR-AEEX yields about twice as much population in its second excited state as the exact, and the purely single-excitation character of the AEEX state results in a wrong density and dipole moment. In contrast, RR-DSMA/AEEX accurately captures both the magnitude and the beating pattern. The accuracy of the TDCI confirms that the four-state truncation is adequate here. The small discrepancy between RR-DSMA/AEEX and exact highlighted in the inset is caused by the small errors in the DSMA predictions of the energies and (transition) densities.

Finally, we drive the system at a frequency near the first excited state, with a strength that induces significant population in all three lowest excitations. Choosing $\mathcal{E}_0 = 0.04$ a.u., $\omega_c = 0.98$ a.u., and $\sigma = 50$ a.u., Pulse 2 is obtained. Figure 3 shows that after the increase of the dipole during the pulse, TDKS-AEEX fails to capture the decrease in magnitude of the exact dipole oscillations over the time period shown. The decrease manifests the beginning of free evolution of a superposition of predominantly four states [see Fig. 3(c)], giving modulations to the dominant frequency oscillations ω_1 . It is qualitatively captured by RR-AEEX, but the incorrect frequency and dipole moment of the second excited state caused by the lack of double-excitation character give an incorrect beat frequency. RR-TDDFT with DSMA/AEEX ingredients accurately captures the dynamics. The truncated TDCI and the exact dipoles suggest that the small discrepancy in the RR-DSMA/AEEX dipole is both from small populations transferred to higher excited states and from the small differences in the energies and (transition) density predictions. The RR-DSMA populations shown in Fig. 3(c) track the exact closely, while RR-AEEX only significantly transfers to the first excited state. Movies of the corresponding densities under Pulse 1 and Pulse 2 are provided in the Supplemental Material [46].

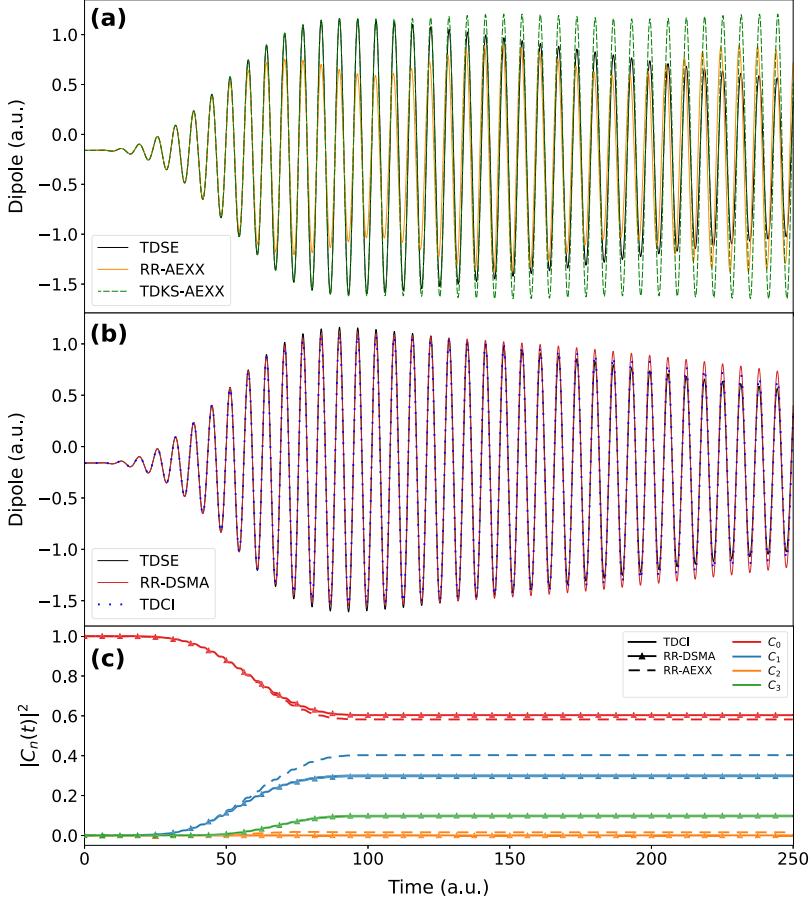


FIG. 3. The dipole moment driven by Pulse 2: (a) predicted by TDKS propagation with AEXX (green, dashed), AEXX used within RR-TDDFT (RR-AEXX, orange), and exact (black); and (b) predicted by DSMA built on AEXX within RR-TDDFT (RR-DSMA, red), truncated TDCI (blue, dotted), and exact (black). (c) Populations of the first four states under Pulse 2.

In summary, we have shown how nonperturbative dynamics accessing double excitations can be reliably reproduced in TDDFT by using DTDDFT approximations developed in the response regime within the RR-TDDFT formalism. The idea generalizes: Any functional developments made in the response regime, which has proved to be a more fruitful playground for nonadiabatic functionals than the real-time domain, can be exploited for nonequilibrium dynamics via RR-TDDFT. The ingredients are excitation energies and transition densities out of the ground state, obtained from poles and residues of the linear density response function (equally, eigenvalues and eigenvectors of the matrix equation), excited-state densities from the potential functional derivative of the energies, and transition densities between excited states from quadratic response, or approximated by auxiliary wavefunctions as done in the present work. As discussed in Ref. [27], RR-TDDFT requires calculating $M(M - 1)$ couplings, where M is the number of states anticipated to be involved in the dynamics. However, the response quantities need to be computed once and for all, and then can be used for any applied fields [47]. We emphasize that RR-TDDFT will only be as good as the TDDFT description of the response spectra. For example, if the dynamics accesses continuum states, then an appropriate and large enough basis would be needed to compute the energies and response quantities; the accuracy of the dynamics from RR-TDDFT will directly relate to their accuracy, and

further, unphysical reflections from reaching any boundary need to be sensibly treated. We note that analogous basis set and boundary concerns arise in the traditional TDKS approach.

Concerning the observables, as in the traditional TDKS approach, observables directly related to the density can be extracted without further approximation, but other observables such as kinetic energy spectra, double ionization yields, and momentum densities need in principle to be expressed through an additional functional of the density. In the traditional TDKS approach, often the TDKS time-dependent determinant is treated as an approximation of the true wavefunction for this particular purpose, a somewhat uncontrolled approximation. A similar approximation could be made in RR-TDDFT, treating the configuration-state functions constructed from the ground-state KS determinant and its excitations as approximations to the static many-body wavefunctions.

Future work will apply RR-TDDFT with DTDDFT to dynamics involving double excitations in a range of real molecules (e.g., Refs. [28,48]), establish quadratic response within the DTDDFT approach for excited-excited state couplings, and explore other nonadiabatic functionals developed in the response regime (e.g., Refs. [25,26]) that can now be used for nonequilibrium dynamics via RR-TDDFT.

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Data availability. The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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