Reformulation of Time-Dependent Density Functional Theory for Non-Perturbative Dynamics: The Rabi Oscillation Problem Resolved

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Rabi oscillations have long been thought to be out of reach in simulations using time-dependent density functional theory (TDDFT), a prominent symptom of the failure of the adiabatic approximation for non-perturbative dynamics. We present a reformulation of TDDFT which requires response quantities only, thus enabling an adiabatic approximation to predict such dynamics accurately because the functional is evaluated on a domain much closer to the domain for which it was derived. Our reformulation applies to *any* real-time dynamics, redeeming TDDFT far from equilibrium. Examples of a resonantly-driven local excitation in a model He atom, and charge-transfer in the LiCN molecule are given.

While the balance between accuracy and efficiency makes time-dependent density functional theory (TDDFT) a very successful method for predictions of molecular spectra and response [1–5], the difficulty in obtaining functional approximations that perform reliably beyond the response regime has dogged its general use in applications where the system is driven far from equilibrium [6, 7]. Advances in experiments and in technologies involving non-perturbative electron dynamics, triggered for example by laser fields or collisions with ions, give urgency to solving this problem, especially given the dearth of alternative computationally feasible methods on complex systems. In some situations, the TDDFT simulations nevertheless give useful mechanistic information and sometimes give results that qualitatively match the experiment [8–11] but in others, such as scattering [12–14] and pump-probe spectroscopy [15–18], TDDFT can give large errors, and even completely fail, such as for Rabi oscillations [15, 19–23] or long-range charge-transfer dynamics [24–27].

In the non-perturbative regime, TDDFT operates via the time-dependent Kohn-Sham (TDKS) equations, in which the many-body effects are mapped to a one-body potential, the exchange-correlation (xc) potential. The root of the failures is the adiabatic approximation to the xc functional [7], which is unable to capture step and peak features that depend on local KS velocities and accelerations of the electron density [28], and that are a signature of memory-dependence of the exact xc functional. While the exact $v_{\rm XC}[n;\Psi(0),\Phi(0)](\mathbf{r},t)$ depends on the history of the density $n(\mathbf{r},t'<t)$, the initial interacting state $\Psi(0)$ and the choice of the initial KS state $\Phi(0)$, this dependence is neglected in adiabatic approximations that insert the instantaneous density $n(\mathbf{r},t)$ into a ground-state approximation $v_{\rm XC}^{\rm g.s.}[n(t)](\mathbf{r})$. The non-adiabatic features play a critical role in correcting spurious frequency-shifts in spectral peaks of systems driven out of a ground-state [15, 17, 18, 23] that occur in simulations using an adiabatic approximation. These shifts have an especially grave consequence for resonantly-driven systems, causing the adiabatic TDKS simulation to detune itself from the driving frequency. Even an adiabatically-exact approximation, meaning one where the exact ground-state functional is used in the TDKS propagation, fails [7, 29]. It is in fact surprising that there are situations where adiabatic TDKS predictions are qualitatively reasonable, given that the xc functional approximation is being evaluated on a fully non-equilibrium density where the underlying true and KS wavefunctions are typically far from any ground state, a domain far from which it was derived.

Although it is understood why Rabi oscillations, or driven dynamics generally, cannot be captured by adiabatic TDDFT approximations, finding a practical non-adiabatic approximation has proven elusive [7]. Developing improved functionals for excitations in the linear response regime has been more successful, e.g. those that incorporate exact-exchange can give improved Rydberg spectra and charge-transfer excitations [25, 30–33], double-excitation frequencies and oscillator strengths can be captured with frequency-dependent kernels in dressed TDDFT [34–36], excitonic spectra can be captured with long-ranged kernels [37–41], and relaxation and dissipation from electron viscosity can be captured with current-density functionals [42, 43]. However, the search for practical memory-dependent functionals that contain the requisite non-adiabatic features for non-perturbative dynamics has so far come up dry.

We present a reformulation of TDDFT that applies to non-perturbative electron dynamics while requiring xc functionals only in the linear and quadratic response regimes. This means that, instead of having to evaluate the xc functionals on the fully non-equilibrium system, they are evaluated always close to the ground-state, and thus are far more amenable to adiabatic approximations. In cases where the adiabatic approximation performs poorly in the response regime, improved non-adiabatic functionals are readily at hand. The same adiabatic functional performs far better in this response-reformulated TDDFT (RR-TDDFT) than it does in the traditional TDKS scheme. A special case of this ap-

proach was shown in earlier work on Ehrenfest dynamics [27], but here we show the approach can be extended to general non-perturbative problems, resolving the problem of missing Rabi oscillations and long-range charge-transfer dynamics in the TDKS approach.

The theorems of TDDFT [1] tell us that from the one-body density $n(\mathbf{r},t)$ one can extract all observables for a system evolving in the time-dependent many-body Schrödinger equation

$$i\hbar\partial_t|\Psi\rangle = (H^{(0)} + V^{\rm app}(t))|\Psi\rangle; \qquad (1)$$

where $H^{(0)} = T + W + V^{(0)}_{\rm ext}$ is the sum of the kinetic energy operator, electron-electron interaction, and static external potential due to the nuclei, respectively, and $V^{\rm app}(t) = \int d^3r v^{\rm app}(\mathbf{r},t)\hat{n}(\mathbf{r})$ is a one-body local potential operator representing an externally applied field, with $\hat{n}(\mathbf{r})$ the one-body density-operator. In standard TDDFT, the system is mapped to the non-interacting KS system that reproduces the exact interacting density $n(\mathbf{r},t)$ with a set of orbitals that evolve under the TDKS equations:

$$(-\nabla^2/2 + v_{\rm S}(\mathbf{r},t))\phi_i(\mathbf{r},t) = i\partial_t\phi_i(\mathbf{r},t), \qquad (2)$$

where $v_{\rm S}(\mathbf{r},t) = v^{(0)}_{\rm ext}(\mathbf{r},t) + v^{\rm app}(\mathbf{r},t) + v_{\rm H}(\mathbf{r},t) + v_{\rm XC}(\mathbf{r},t)$. Here $v_{\rm H}(\mathbf{r},t)$ is the Hartree potential, a functional of the instantaneous density, while $v_{\rm XC}(\mathbf{r},t) = v_{\rm XC}[n;\Psi(0),\Phi(0)](\mathbf{r},t)$ has the memory-dependence whose neglect in usual approximations leads to errors and failures.

Instead, RR-TDDFT bypasses the solution of the TDKS orbitals and solves for a set of TD expansion coefficients of the many-body state, but without needing to actually find the state. The idea may be seen as similar in spirit to time-dependent configuration interaction, but here linear and quadratic response TDDFT is used to obtain the static electronic structure quantities and we never find the wavefunction. We expand the time-dependent physical many-body wavefunction in terms of the (unknown) many-body eigenstates: $|\Psi(t)\rangle = \sum_n C_n(t)|\Psi_n\rangle$, where $|\Psi_n\rangle$ satisfies the static many-body equation: $H^{(0)}|\Psi_n\rangle = E_n|\Psi_n\rangle$. Inserting this into Eq. (1) gives

$$i\hbar\dot{C}_m(t) = E_m C_m(t) + \sum_n V^{\rm app}_{mn}(t)C_n(t) \qquad (3)$$

where the sum goes over all the eigenstates and

$$V^{\rm app}_{mn}(t) = \langle\Psi_m|V^{\rm app}(t)|\Psi_n\rangle = \int d^3r v^{\rm app}(\mathbf{r},t)\rho_{mn}(\mathbf{r}) \qquad (4)$$

with $\rho_{mn}(\mathbf{r}) = N\int d^3r_2..d^3r_N\Psi^*_m(\mathbf{r},\mathbf{r}_2..\mathbf{r}_N)\Psi_n(\mathbf{r},\mathbf{r}_2..\mathbf{r}_N)$ being the transition-density and N the number of electrons. The time-dependent one-body density can be extracted from

$$n(\mathbf{r},t) = \sum_{n,m} C^*_n(t)C_m(t)\rho_{nm}(\mathbf{r}) \qquad (5)$$

We now argue that Eqs. 3–5 provide a route to obtaining all observables of a non-perturbative real-time dynamics from just TDDFT response properties. First, invoking the Runge-Gross theorem, all observables can be obtained from the initial interacting state $|\Psi(0)\rangle$ and the time-evolving density $n(\mathbf{r},t)$. Eq. (5) provides $n(\mathbf{r},t)$, which requires solution of the coupled time-evolution equations, Eqs. (3) for the coefficients. To solve these, we need:
(i) energies E_m that can be obtained from adding frequencies from TDDFT linear response [44, 45] ω_m to the ground-state DFT energy E_0,
(ii) the transition-density $\rho_{mn}(\mathbf{r})$ which can be obtained from linear response TDDFT [44–46] for ground-excited transitions, and quadratic response for excited-excited transitions [47], and
(iii) the initial coefficients $C_m(0)$ which are obtained from expanding the initial many-body state $|\Psi(0)\rangle$ in terms of the many-body eigenstates of $H^{(0)}$. It is important to note that the interacting eigenstates themselves are not required, only knowledge of which states are occupied and with what amplitudes, which would be determined by the physics of the initial conditions of the problem. Often this is just the ground-state, in which case $C_0(0) = 1, C_{m\neq 0}(0) = 0$.

With the ingredients in (i)–(iii) all obtained from linear and quadratic response, the time-dependent density can be obtained, (note that $\rho_{mn}(\mathbf{r})$ also appear directly in the expression for the density in Eq. (5)), and hence all observables [1].

Comparing with the standard TDDFT procedure based on the TDKS equations, Eq. 2, the saliant advantage of RR-TDDFT is that the adiabatic xc functional approximations are evaluated far closer to the domain in which they were derived. That is, the xc functional in TDKS with an adiabatic approximation, $v^A_{\rm XC}[n;\Psi(0),\Phi(0)](\mathbf{r},t) = v^{\rm g.s.}_{\rm XC}[n(t)](\mathbf{r})$, applies a ground-state functional in a domain on the left which evolves far from any ground-state. Such an approximation is unlikely to be accurate. On the other hand, in RR-TDDFT, there are three xc objects: $v^{\rm g.s.}_{\rm XC}[n_{\rm g.s.}](\mathbf{r})$ (needed for E_0 and the KS orbitals and excitation energies that the linear response builds upon), $f_{\rm XC}[n_{\rm g.s.}](\mathbf{r},\mathbf{r}',\omega)$ (the central xc kernel in linear response TDDFT), and $g_{\rm XC}[n_{\rm g.s.}](\mathbf{r},\mathbf{r}',\mathbf{r}'',\omega,\omega')$ (the second-order response kernel). The latter two are related to functional derivatives of $v_{\rm XC}[n,\Psi(0),\Phi(0)](\mathbf{r})$ evaluated on a ground-state density, so the domain involves only small perturbations around a ground-state density.

Another fundamental difference is in the role of the initial state. Similar to TD wavefunction methods, the physical interacting initial state is a key input in RR-TDDFT, but it in the TDKS approach, it appears only through the functional dependence of $v_{\rm XC}[n;\Psi(0),\Phi(0)](\mathbf{r},t)$. In practise, this initial-state dependence is neglected in TDKS, since adiabatic func-

tionals depend only on the instantaneous density, but the exact xc functional varies significantly when the system starts in different initial states even if they all have the same one-body density [48, 49]. In a sense, the initial interacting state plays a more prominent, and conceptually easier, role in RR-TDDFT than in TDKS since it appears directly as an initial condition in the evolution equations, rather than in an unknown functional-dependence. In contrast, it is the KS initial state Φ_0 that appears directly in the equations to evolve in TDKS; Φ_0 is not unique, different choices give different xc potentials, and the adiabatic approximation gives significantly varying errors for different choices [14, 48, 50]. Adiabatic approximations perform particularly poorly when the rank of the true interacting density-matrix evolves significantly (e.g. $\Psi(t)$ going from close to a single Slater determinant to a singly-excited singlet state), because the TDKS state $\Phi(t)$ cannot change its rank. These challenging considerations are moot in RR-TDDFT.

We now give two examples to demonstrate how adiabatic functionals achieve Rabi oscillations when used within RR-TDDFT, while completely failing within TDKS. Atomic units ($e^2 = \hbar = m_e = 1$) are used unless otherwise stated.

Our first example is a one-dimensional Helium atom (1D He) with soft-Coulomb interactions, studied before in this context [19–22]: $v_{\rm ext}^{(0)} = -2/\sqrt{1+x^2}$, contained in a box of size -40 a.u. to 40 a.u. We apply a field $\mathcal{E}(t) = 0.00667\sin(\omega t)$ to the ground-state, where ω is resonant with the first singlet excitation, $\omega = \omega^{ex} = 0.5336$a.u. With the transition dipole moment of $\mu_{01} = 1.106$a.u., this gives a Rabi period of T_R where $T_R/2 = \frac{\pi}{0.00667\mu_{01}} = 425.9$a.u. The observable we are interested in is the dipole moment, $d(t) = \int xn(x,t)dx$ where $n(x,t) = \sum_{iocc}|\phi_i(x,t)|^2$ is obtained from the solution of Eq. (2) for TDKS and from Eq. (3)–(5) for RR-TDDFT. Owing to the spatial symmetry of the ground and first excited states resulting in a zero permanent dipole moment, the dipole moment from Eq. (5) simplifies to $d(t) = 2\Re\left[C_0^*(t)C_1(t)\right]\mu_{0,1}$.

The top panels of Fig. 1 depict the dipole moment dynamics obtained from real-time calculations. The left-most plot shows the exact solution from the TDSE, with the expected Rabi oscillation. The second and third plots in the top panels show the result of TDKS evolution with the exact exchange (EXX) approximation. While 1d He is driven by the same pulse as the exact in the second panel, in the third, it is driven instead at the frequency of the excited state predicted by EXX linear response, $\omega^{\rm EXX} = 0.5488$ a.u. As has been observed in earlier work [20], in both cases a significant deviation from the exact behavior is evident, underscoring the failure of TDKS to accurately replicate the observed dynamics. The dipole envelopes falsely suggest a Rabi-like oscillation albeit at wrong frequencies (the expected half-Rabi period calculated from $\mu_{01}^{\rm EXX} = -1.0924$ a.u. gives $T_R^{\rm EXX}/2 = 431.2$ a.u.): the density at the minimum of the dipole moment is not that of the EXX excited state (see the bottom right panel).

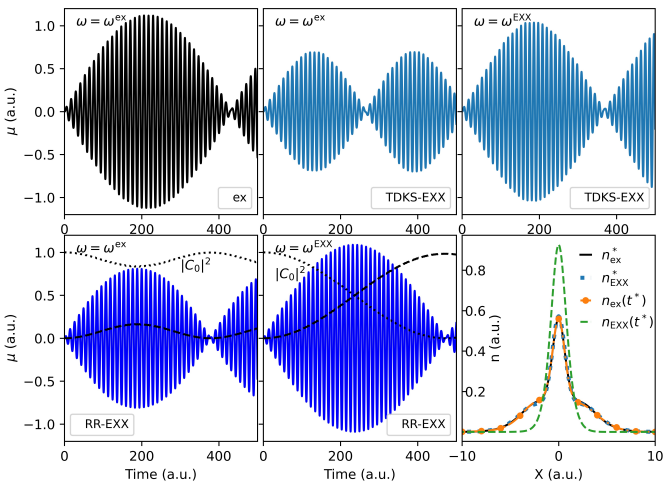

FIG. 1. Resonantly-driven dipole dynamics in 1D He. Top panels: (Left) Numerically exact result calculated using TDSE with a pulse, $\mathcal{E}(t) = 0.00667\sin(\omega t)$ and $\omega = \omega^{\rm ex} = 0.5336$a.u.; (Middle) TDKS with EXX functional; (Right) TDKS-EXX driven by $\omega^{\rm EXX} = 0.5488$a.u. Bottom panels: (Left and Middle) Dipole moments calculated from RR-TDDFT with EXX driven at $\omega^{\rm ex}$ and $\omega^{\rm EXX}$ respectively. Also shown in dotted and dashed lines are the populations of the ground and the first singlet excited states, $|C_0(t)|^2$ and $|C_1(t)|^2$ (unlabelled). (Right) The exact $n_{\rm ex}^*(x)$ (black solid) and EXX $n_{\rm EXX}(x)$ (blue dotted) excited-state densities calculated from static (response) calculations, compared with the exact time-evolved densities $n_{\rm ex}^*(x, t^* = 425.9$a.u.$)$ (orange with circle) and EXX, $n_{\rm EXX}(x, t^* = 364.35$a.u.$)$ (green dashed).

Turning now to our RR-TDDFT method, the first plot in the bottom panel shows the result of applying the pulse used in the exact case in Eqs. 3–5, with the energies and transition densities given by EXX. We observe the expected detuned Rabi oscillation, and only a partial population transfer, due to the mismatch of $\omega^{\rm EXX}$ with the driving ω. Applying the field instead at $\omega^{\rm EXX}$, displays at true Rabi oscillation as shown in the middle plot. There is a full population inversion at $T_R^{\rm EXX}/2$, and the right-most plot verifies this by showing the density at this time has the same shape as the excited state density, unlike that of the TDKS density at what looks like its half-Rabi time. This plot also shows the excited-state density $n_{\rm EXX}^*(x)$ computed from a response calculation with EXX [51–53], which is very close to the exact excited state density $n^*(x)$. Thus, while EXX failed to produce a Rabi oscillation when used within TDKS, this same functional approximation succeeded when used within RR-TDDFT.

We now turn to the case of the lithium cyanide (LiCN)

molecule, which has been studied in the past as a test system for light-driven dipole switching [26, 54]: the degenerate second (S_2) and third (S_3) excited states have a dipole moment along the bond-axis ($\hat{z}$) opposite to that in the ground-state. Applying a laser pulse resonant with the excitation frequency along the $\hat{x}$ ($\hat{y}$) direction, which coincides with the direction of the transition dipole to the S_2 (S_3) states respectively, drives the transition to the S_2 (S_3) state with a concomitant large change in the z-dipole moment. The known failure of the TDKS simulation to accurately describe this dipole switching is one of the prime examples of limitations of adiabatic approximation [6, 7, 17, 24, 26]. Here we show that the same adiabatic approximations perform well when applied instead within the RR-TDDFT approach. We use the NWChem [55] code to perform the real-time TDKS calculations, and its linear response module used to extract the ingredients in Eqs. 3–5 for the RR-TDDFT, truncated to two states: ground S_0 and excited S_2-state energies, dipole moments, and the transition dipole moment between these states.

We take a short enough pulse that the nuclei may be treated statically during the evolution, fixed at their equilibrium geometry, $R_{\mathrm{Li-C}} = 3.683$ a.u. and $R_{\mathrm{C-N}} = 2.168$ a.u [54]. The applied field is a resonant π-pulse [56] along the $\hat{x}$-direction,

$$v^{\mathrm{app}}(\mathbf{r}, t) = x f_0 \sin^2\left(\frac{\pi t}{2\sigma}\right)\sin(\omega t) \tag{6}$$

where ω is the excitation frequency of the S_2 state, σ is the half-width of the pulse envelope and the amplitude $f_0 = \frac{\pi}{\sigma|\mu_{0,2;x}|}$ with $\mu_{0,2;x}$, the x-transition dipole moment between states S_0 and S_2. (For a two-state problem, this pulse achieves population inversion by time $T = 50$fs). We will take the reference ("exact") calculation as the time-dependent CISD(10,15)/6-31G* simulation of Fig. 3 in Ref. [26], which applied this π-pulse at resonant frequency $\omega^{\mathrm{ex}} = 6.8$eV, close to the linear response CISD value of 6.77 eV, and $\sigma = 25$ fs, such that a full population inversion is achieved at around 38 fs.

The top panel of Fig. 2 shows the z-dipole moment μ_z when driven by the π-pulse of Eq. 6, as predicted from TDKS and our RR-TDDFT, using adiabatic PBE [57] and a tuned BNL (tBNL) [58, 59] functional, both using the same 6-31G* basis set as the reference CISD. The resonant frequencies predicted by linear response with these functionals are $\omega^{\mathrm{PBE}} = 4.31$eV, and $\omega^{\mathrm{tBNL}} = 6.80$eV where we tuned the range-separation parameter $\gamma_{BNL} = 0.8$ in order to align the excitation energy of S_2 state with the applied frequency. The complete failure of the TDKS simulations is evident in the figure, similar to what was observed in the earlier work [26] (the figures there used a different pulse for the TDKS calculations which led to more oscillatory behavior), and in model system analogs of the problem [24, 25, 29] (which used a flat envelope rather than a π-pulse). In particular, despite the excellent agreement of the tBNL linear response frequency with the reference, the real-time TDKS calculation of the dynamics is miserable. In contrast, RR-TDDFT with this functional (RR-tBNL in the figure) is extremely good.

The PBE functional does equally poorly as tBNL in the TDKS simulation, while when used in RR-TDDFT it also fails, giving even less of a response, as shown in the inset. This is because the PBE frequency is severely underestimated due to the charge-transfer nature of the excitation, and with such a weak field, off-resonant to any system frequency, the system is barely disturbed. Instead, however PBE achieves dipole switching for a pulse that is resonant with the PBE frequency. This is shown in the lower panel of Fig. 2 where we again show TDKS and RR-TDDFT with PBE and tBNL functionals, but with the frequency and transition dipole that enter into the resonant pulse Eq. 6 obtained from the corresponding underlying electronic structure. If we did not have a reference calculation, and were relying on the PBE (or tBNL) functional for our description of the system, these would be the π-pulse parameters we would use to achieve the resonant charge-transfer. Now we see that, due to the domain of the functionals being closer to the ground-state, RR-TDDFT with either the PBE or tBNL functional reproduce the dipole-switching well, while these same functionals used in the real-time TDKS scheme fail.

In summary, our reformulation of real-time TDDFT in terms of response quantities yields greatly improved electron dynamics far from the ground-state when used with standard functionals. While these same functionals fail to produce Rabi oscillations when used in the TDKS scheme, they succeed when used in the RR-TDDFT framework. This is because, in contrast to TDKS, the xc functionals in RR-TDDFT are required only in the response regime, where the xc potential is evaluated on densities close to the ground-state, a domain close that in which the functional approximations were derived.

Effectively, RR-TDDFT separates out the time and space-dependence of observables, and so reduces the complexity in the xc effects arising from the inherent entanglement of time- and spatial-non-locality [60, 61]. This leads to quite different numerical considerations in the two approaches: the RR-TDDFT trades a self-consistent solution of the set of N partial-differential TDKS equations in space and time for a self-consistent solution of a set of M ordinary differential equations in time, where M represents the anticipated number of many-body states that will likely be occupied during the dynamics. RR-TDDFT also needs to solve linear response equations for M energies, densities, and $M(M-1)$ couplings some of which require quadratic response. In scenarios where a very large number of states are likely to be involved, RR-TDDFT may become

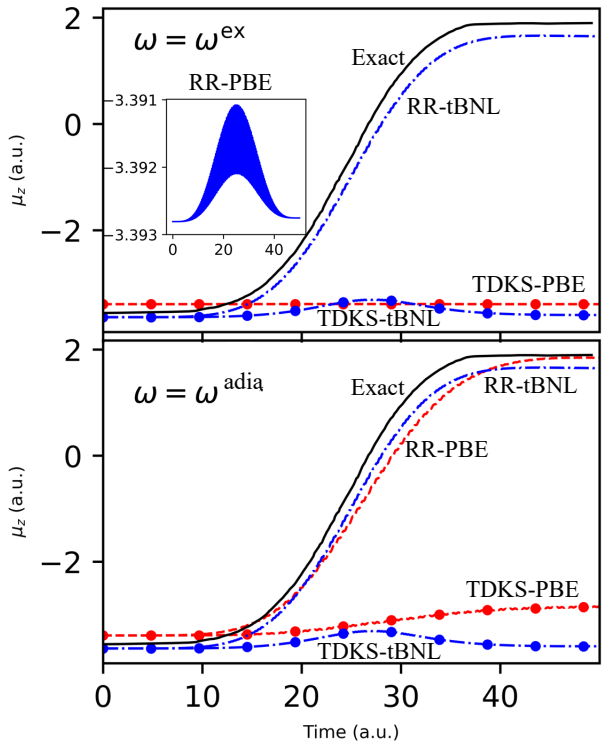

FIG. 2. Resonantly-driven charge-transfer in the LiCN molecule: Top panel: Dipole moment computed from TDKS, and RR-TDDFT, using PBE and tBNL functionals within the 6-31G* basis set. The applied $\pi-$ pulse has the parameters $\omega^{\text{app}} = \omega^{\text{ex}} = 6.8eV$, $\sigma = 25$ fs and $f_0 = 0.01019$ and the results are compared with the reference TD-CISD from Ref. [26]. Lower panel: Same quantities as above panel in which the pulse parameters are determined by the corresponding electronic structure.

unfeasible. But in many scenarios (like resonant driving), a smaller sector of the Hilbert space is involved, and RR-TDDFT, in addition to its much more reliable predictions, may also offer a computational advantage over TDKS due to its ordinary rather than partial differential equation nature. For computing excited-to-excited state couplings, we note that quadratic response may be circumvented by approximating these from linear response akin to the auxiliary wavefunction method employed to compute derivative couplings between excited states[46, 62].

Finally, we note that, like TDKS, RR-TDDFT is exact in principle, and need not be limited to using adiabatic approximations. RR-TDDFT with an adiabatic approximation will work poorly in cases where these approximations are known to fail in linear [34, 36] as well as quadratic [63, 64] response regimes, but given that it has so far proven to be clearer to identify such cases, and to develop improved non-adiabatic response functionals, RR-TDDFT promises to overcome the reliability challenges of TDDFT in the non-perturbative regime.

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