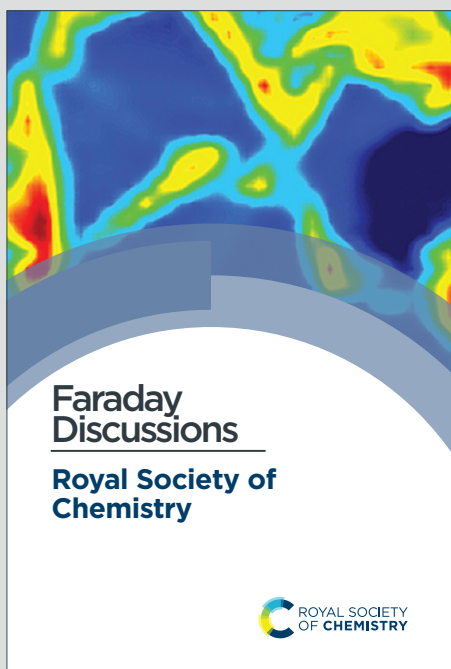


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Cite this: DOI: 00.0000/xxxxxxxxxx

Developing new and understanding old approximations in TDDFT

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Received Date
Accepted Date

DOI: 00.0000/xxxxxxxxxx

When a system has evolved far from a ground-state, the adiabatic approximations commonly used in time-dependent density functional theory calculations completely fail in some applications, while giving qualitatively good predictions in others, sometimes even quantitatively so. It is not clearly understood why this is so, and developing practical approximations going beyond the adiabatic approximation remains a challenge. This paper explores three different lines of investigation. First, an expression for the exact time-dependent exchange-correlation potential suggests that the accuracy of an adiabatic approximation is intimately related to the deviation between the natural orbital occupation numbers of the physical system and those of the Kohn-Sham system, and we explore this on some exactly-solvable model systems. The exact expression further suggests a path to go beyond the adiabatic approximations, and in the second part we discuss a newly proposed class of memory-dependent approximations developed in this way. Finally, we derive a new expression for the exact exchange-correlation potential from a coupling-constant path integration.

Time-dependent density functional theory (TDDFT) continues to be a method of choice for the calculation of electronic spectra and dynamics of molecules and solids, where its favorable system-size scaling enables computations on large systems that could not be done otherwise¹⁻⁴. An area of application that particularly demonstrates this is non-adiabatic electron-ion dynamics, which requires efficient and accurate electronic structure methods to be used on the fly with nuclear trajectories evolving in a high-dimensional space. For example, an illustrative recent example is the photo-induced dynamics of the rotary molecular machines and 1- and 3-pore covalent organic frameworks of Ref.⁵ which involved up to 600 atoms; a feat which would be a challenge for any alternative electronic structure method of similar accuracy, even with the GPU acceleration that was used. The real-time TDDFT equations are highly scalable and parallelizable, as demonstrated, in another example, by the first-principles calculations of electronic stopping power and conductivity in a system of 5400 disordered Al atoms (59,400 electrons)⁶.

There are in fact very few practical alternatives to TDDFT for dynamics when the electronic system is driven far from any ground-state, such as when driven by a strong external field, or when prepared in a superposition state. In this regime, recent work on model systems shows that the exact exchange-correlation (xc) potential typically exhibits large dynamical features that the approximations commonly used in calculations can-

not capture e.g. Refs.⁷⁻¹⁴. These approximations are "adiabatic", meaning that they input the instantaneous density into a chosen ground-state approximation, while it is known that the exact xc potential depends on the history of the density, as well as the initial interacting and Kohn-Sham states. Due its lack of this memory, the adiabatic approximation completely fails in some applications, e.g. Refs.¹⁵⁻²¹. Yet, in other cases, the adiabatic approximation is found to give good predictions. The adiabatic approximation is derived under the condition of an initial ground-state subject to a slowly-varying perturbation, which is hardly the situation in most of the applications considered. For example, quite often TDDFT simulates dynamics after a photo-excitation in a molecule (e.g. in photovoltaic applications) where the initial state is an excited, e.g. Refs.^{5,22,23}. In other applications, the system starts in a ground-state but is driven by a strong laser field, e.g. Refs.²⁴⁻²⁶. These are hardly in an adiabatic regime. Why and when does adiabatic TDDFT give even qualitatively correct predictions, let alone quantitatively useful results? It is true that its complete neglect of memory results in its satisfaction of a number of exact conditions that are important in the time-dependent case^{27,28}, but a complete characterization of when it is expected to work well is lacking. How can we derive approximations that include memory while also satisfying exact conditions that are important for the time-dependent case?

In this paper we take walks along three paths to investigate these questions, guided by exact expressions for the xc potential. First, decomposing the xc potential into a part depending on the

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kinetic term and one depending on the interaction term, hints to us that when the natural orbital occupation numbers of the physical system begin relatively close to those of the Kohn-Sham system and do not change significantly during the dynamics, the adiabatic approximations could give reasonable results provided the dynamics does not critically rely on resonant frequencies of the system. Such a situation can encompass dynamics far from any ground-state, and we show (Sec. 2), using model systems, that then even ALDA can predict the dynamics well. This is especially true when only spatially-averaged observables such as the dipole moment are of interest. The choice of initial KS state is critical: if this is chosen to have a configuration similar to that of the physical system, non-adiabatic features such as steps and peaks can be minimized. However, when the true dynamics is such that its natural orbital occupation numbers do change significantly in time, or when the dynamics does depend critically on the resonant frequencies, approximations going beyond the adiabatic ones are required, and this leads us to the second path: developing approximations based on the exact decomposition (Sec. 3). Facing some numerical up-hills along this path, we take a different path in Sec. 4, exploring the use of a coupling-constant integration to transform away the challenging kinetic term.

1 The exact xc potential

TDDFT calculations proceed by solving for non-interacting electrons, beginning in an initial state $\Phi(\mathbf{r}_1 \dots \mathbf{r}_N, 0)$, and evolving in a one-body potential, $v_{\text{ext}}(\mathbf{r}, t) + v_{\text{H}}(\mathbf{r}, t) + v_{\text{xc}}(\mathbf{r}, t)$ where v_{ext} is the potential from the nuclei plus any externally applied fields, $v_{\text{H}}(\mathbf{r}, t) = \int d\mathbf{r}' w(|\mathbf{r} - \mathbf{r}'|) n(\mathbf{r}', t)$ is the Hartree potential for two-body electron interaction w , and $v_{\text{xc}}(\mathbf{r}, t) = v_{\text{xc}}[n; \Psi_0, \Phi_0](\mathbf{r}, t)$ is the xc potential, a functional of the density, including its history, the physical initial state of the system $\Psi(0)$ and the KS initial state $\Phi(0)$. This state $\Phi(0)$ can be chosen quite freely, but subject to the condition that its initial one-body-density $n(\mathbf{r}, 0)$ and the first time-derivative $\dot{n}(\mathbf{r}, 0)$ coincide with that of the initial interacting state. The xc potential $v_{\text{xc}}(\mathbf{r}, t)$ depends heavily on this choice.

An exact expression for the xc potential arises from equating $\ddot{n}(\mathbf{r}, t)$ in the Kohn-Sham (KS) system to that of the true system. This yields a "force-balance" equation^{29–31} for the exact xc potential:

$$\nabla \cdot (n \nabla v_{\text{xc}}) = \nabla \cdot \left(n(\mathbf{r}, t) \nabla v_{\text{xc}}^{\text{W}}(\mathbf{r}, t) \right) + \nabla \cdot \left(n(\mathbf{r}, t) \nabla v_{\text{c}}^{\text{T}}(\mathbf{r}, t) \right) \quad (1)$$

where the interaction component v_{xc}^{W} satisfies

$$\nabla \cdot (n \nabla v_{\text{xc}}^{\text{W}}) = \nabla \cdot \left[n(\mathbf{r}, t) \int n_{\text{xc}}(\mathbf{r}', \mathbf{r}, t) \nabla w(|\mathbf{r}' - \mathbf{r}|) d^3 r' \right], \quad (2)$$

and the kinetic component v_{c}^{T} satisfies:

$$\nabla \cdot (n \nabla v_{\text{c}}^{\text{T}}) = \nabla \cdot \left[\mathcal{D}(\rho_1(\mathbf{r}', \mathbf{r}, t) - \rho_{1,s}(\mathbf{r}', \mathbf{r}, t))|_{\mathbf{r}=\mathbf{r}} \right], \quad (3)$$

with $\mathcal{D} = \frac{1}{4}(\nabla' - \nabla)(\nabla'^2 - \nabla^2)$. Above, n_{xc} is the time-dependent xc hole defined as

$$n_{\text{xc}}(\mathbf{r}, \mathbf{r}', t) = \rho_2(\mathbf{r}, \mathbf{r}'; \mathbf{r}, \mathbf{r}', t) / n(\mathbf{r}', t) - n(\mathbf{r}, t) \quad , \quad (4)$$

with the two-body reduced density-

matrix (2RDM) $\rho_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}'_1, \mathbf{r}'_2, t) = \frac{1}{N(N-1)} \int d\mathbf{r}_3 \dots d\mathbf{r}_N \Psi^*(\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}_3, \dots, \mathbf{r}_N, t) \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N, t)$, the one-body reduced density matrix (1RDM) $\rho_1(\mathbf{r}, \mathbf{r}', t) = N \int d\mathbf{r}_2 \dots d\mathbf{r}_N \Psi^*(\mathbf{r}', \mathbf{r}_2, \dots, \mathbf{r}_N, t) \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N, t)$, and $\rho_{1,s}$ is the 1RDM of the KS system.

From the form of Eqs (2), (3) above, one expects that v_{xc}^{W} has a relatively smooth form where the integral could be relatively forgiving to approximations of the integrand. On the other hand, the multiple gradients in the expression for v_{c}^{T} may create relatively rapidly varying structures, enhanced at minima of the density, and v_{c}^{T} appears far more sensitive to approximations to the 1RDM than v_{xc}^{W} would be to the xc hole. These expectations are borne out in numerical examples on model systems for which the exact xc potential and its decomposition can be calculated, as in Refs.^{27,30,32}. Typically, while v_{xc}^{W} mostly cradles the density in a well that tends to fall off to zero as $-1/r$ asymptotically, v_{c}^{T} displays peak and step structures that often dominate the form of v_{xc} .

In Figure 1 we give one example to illustrate this; it is a snapshot taken during a key part of the process of scattering of one electron from a hydrogen atom, a problem studied in Refs.^{10,33,34} using a one-dimensional (1D) model. Specifically, the electrons interact via soft-Coulomb $w = 1/\sqrt{(x_1 - x_2)^2 + 1}$, and $v_{\text{ext}}(x) = -1/\sqrt{(x + 10)^2 + 1}$ is used to represent a hydrogen atom at $x = -10$ a.u. with one electron initially in its ground-state, $\phi_{\text{H}}(x)$, and the other as a Gaussian wavepacket incoming from the right, $\phi_{\text{in}}(x) = (0.2/\pi)^{1/4} e^{-0.2(x-10)^2 - i1.5(x-10)}$. While in the exact dynamics, there is about a 20% probability of electron reflection, Refs.^{10,33} found that adiabatic approximations were simply unable to capture any noticeable reflection, as the ground-state approximations underlying these do not capture the peak and step/valley structures, shown at one time-snapshot in Fig. 1 that are essential to split off part of the electron density. It is clear that the structure in v_{c}^{T} is crucial for the scattering process: The small peak and step down just to the right of $x = -10$ a.u. persists in time and contains the effective correlation needed for reflection of part of the density of the two non-interacting electrons. The adiabatically-exact (AE) approximation, defined by $v_{\text{xc}}^{\text{AE}} = v_{\text{xc}}^{\text{g.s.}}[n(t)](\mathbf{r})$, where g.s. denotes the exact ground-state functional, is the "best" adiabatic approximation in the sense that the only error in it arises from making the adiabatic approximation, rather than from additional approximations from the choice of ground-state approximation. The $v_{\text{xc}}^{\text{AE}}$ can be analogously decomposed into kinetic and interaction components, and it is clear from the figure that the AE approximation to v_{c}^{T} is far poorer than that to v_{xc}^{W} .

The figure also plots a non-adiabatic approximation introduced in several recent works^{10,27,35}, denoted v_{xc}^{S} , which replaces the exact xc hole with the KS hole in v_{xc}^{W} . This yields quite a reasonable and practical approximation to that term. In general, v_{xc}^{S} is not an adiabatic approximation, since the orbital-dependence of the KS hole makes it implicitly depend on the history of the density. This is true even for two electrons, except when the initial KS state is a spin-singlet chosen to be a single doubly-occupied orbital, in which case v_{xc}^{S} reduces to exact exchange, v_{x} .

The choice of the KS initial state directly affects the struc-

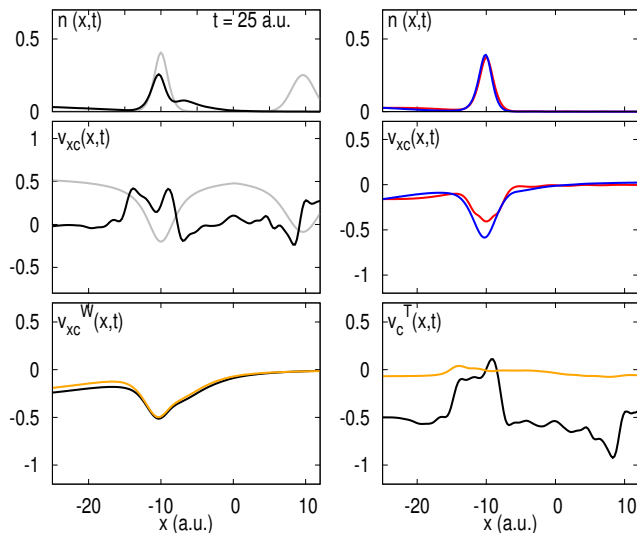


Fig. 1 1D e-H scattering problem. A snapshot in time is shown of the exact density (black) in the top left panel, at a time where the electron is beginning to reflect from the H atom target, and partially transmit on the right. In grey is the initial density, for reference. The middle left panel shows the exact xc potential at this time, and in grey the initial time. Notably, the peak and step down to the right at $x = -10$ a.u. is a crucial and persistent structure that is responsible for the scattering, and is completely missing in the adiabatic approximations. The top and middle right show the density and xc potential from LDA (red) and v_{xc}^S (blue) approximations, neither of which yield significant electron reflection. In the lower left panel, the exact v_{xc}^W component (black) is well-approximated by the best adiabatic approximation to this term, the AE (orange), while on the right, the AE approximation to v_{xc}^T does a poor job of capturing the structure of the exact v_{xc}^T , in particular missing the essential feature that induces the reflection.

ture of both v_{xc}^W and v_{xc}^T . In particular, v_{xc}^T can be reduced, at least at short times, by choosing an initial KS state “close” to the true initial state^{10,35,36}. In the plots above we have chosen the initial KS state identical to the true initial state, which is a natural choice for the scattering of one electron from a one-electron atom, for which the spatial part of the wavefunction is $\Phi(0) = \Psi(0) = (\phi_H(x_1)\phi_{in}(x_2) + \phi_{in}(x_1)\phi_H(x_2))/\sqrt{2}$. The results for another natural choice, a Slater determinant, were shown in Ref.¹⁰, which would be the relevant choice if the system had begun with two electrons in the atom, subject to a laser field that had caused an ionization of one electron, that is now returning to re-scatter off the parent ion when the field cycle reverses sign. With this choice even from the beginning, large step structures in v_{xc} appear that are missing in approximations, with grave consequences for the dynamics even at early times yielding incorrectly oscillating densities. Again it is the kinetic component, v_{xc}^T in which these structures appear.

2 Role of Time-Dependent Natural Orbital Occupation Numbers in Accuracy of ALDA

The observations in Sec. 1 suggest that an adiabatic approximation would have the most chance of predicting reasonably accurate dynamics in cases where the near-diagonal elements of the KS 1RDM remain close to the true 1RDM throughout the dynamics, so that the peak and step structures of the exact potential, appearing in the v_{xc}^T component, do not get large. The xc effects contained in v_{xc}^W would still play an important part in the dynamics, but as this term is less sensitive to approximations made for the xc hole, the idea is that such approximations could at least qualitatively work well. To investigate this further, consider now the natural orbital expansion,

$$\rho_1(\mathbf{r}, \mathbf{r}', t) = \sum_i \eta_i(t) \psi_i^*(\mathbf{r}', t) \psi_i(\mathbf{r}, t), \quad \text{with } \sum_i \eta_i(t) = N, \quad (5)$$

for the physical 1RDM, where both the natural orbitals $\psi_i(\mathbf{r}, t)$ and their occupation numbers $\eta_i(t)$ are generally time-dependent. In contrast, in the expansion for the KS 1RDM, $\rho_{1S}(\mathbf{r}, \mathbf{r}', t) = \sum_i \eta_{Si} \phi_i^*(\mathbf{r}', t) \phi_i(\mathbf{r}, t)$, the KS natural orbitals are equal to the KS orbitals, and their occupation numbers η_{Si} are constant in time, fixed at the initial time when the KS initial state is chosen, due to the one-body nature of the KS evolution. In terms of the natural orbital expansion then, we can write

$$\begin{aligned} \nabla \cdot (n(\mathbf{r}, t) v_{xc}^T(\mathbf{r}, t)) &= \sum_i \eta_i(t) \frac{\nabla^2}{4} (4|\nabla \psi_i|^2 - \nabla^2 |\psi_i|^2) \\ &\quad - \sum_i \eta_{Si} \frac{\nabla^2}{4} (4|\nabla \phi_i|^2 - \nabla^2 |\phi_i|^2) \end{aligned} \quad (6)$$

What is common in the two 1RDM's is their diagonal value, equal to the one-body density; the difference in their deviations away from the diagonal are what contribute to v_{xc}^T . Clearly, if the occupation numbers $\eta_i(t)$ and η_{Si} are very different, then the exact v_{xc}^T , along with its non-adiabatic features, could be relatively large. But if $\eta_i(t)$ and η_{Si} are close enough, then it is possible that the

natural orbitals $\psi_i(\mathbf{r}, t)$ and KS orbitals could be close enough such that the exact v_C^T is relatively small. Given that the KS occupation numbers are fixed in time, we are then led to test the following question: *If the KS initial state is chosen with occupation numbers close to the true initial state, can the adiabatic approximation qualitatively capture the true dynamics when the time-dependent natural orbitals of the physical system do not evolve significantly in time?* This could cover situations where the system is driven far from any ground state, since the natural orbitals and KS orbitals could vary significantly in time, while the natural orbital occupation numbers do not change much. We must make an exception for when the dynamics depends critically on resonant frequencies of the system because generally adiabatic approximations violate the “resonance condition”, which is the condition that the resonant frequencies of a system should not change after the system is driven away from its ground-state³⁷. Transition amplitudes between states should change but the frequencies themselves should be invariant to whatever the non-equilibrium state the system is left in. This is violated by adiabatic approximations, so that caution must be applied when using TDDFT to examine pump-probe spectra, dynamics that directly depends on resonant frequencies such as for resonantly-driven Rabi oscillations, or dynamics of superposition states evolving freely.

The relation between TD occupation numbers and the exact xc potential was studied earlier in Ref.³⁰ however in a limited sense: the size of the non-adiabatic step features in a range of two-electron model systems, with the KS state taken as a Slater determinant, was shown to correlate with local minima in oscillations of the largest occupation number, regardless of how close the occupation number was to the KS value of 2. In some of these cases, the steps were relatively sharp structures that appeared in regions of low density, so their “force-density”, $n(\mathbf{r}, t)\nabla v_{xc}(\mathbf{r}, t)$, appears less imposing, and further, in some cases they oscillated in time rapidly enough, that their influence on the dynamics was relatively small. Non-adiabatic structures beyond global step structures are also important.

We consider four examples to examine the question above, focusing on propagation with the simplest approximation, ALDA. In seeking examples we have tried to pick a range of different cases (beginning in the ground-state versus excited states, field-driven versus field-free) where occupation numbers change relatively little for some time but while there is significant dynamics. Our first example returns to the model scattering problem.

2.1 Scattering

The scattering example in Fig. 1 does not depend critically on the satisfaction of the resonant condition, and since the initial KS state chosen $\Phi(0) = \Psi(0)$, the initial KS and true occupation numbers are identical. The fact that the dynamics from the adiabatic approximations does not qualitatively reproduce the true dynamics suggests that the true occupation numbers change significantly over time. This expectation is borne out, as evident in Fig. 2 where one sees large deviations of the occupation numbers at times where the incoming electron density approaches the target. Before this time, the deviation is relatively small, and dynam-

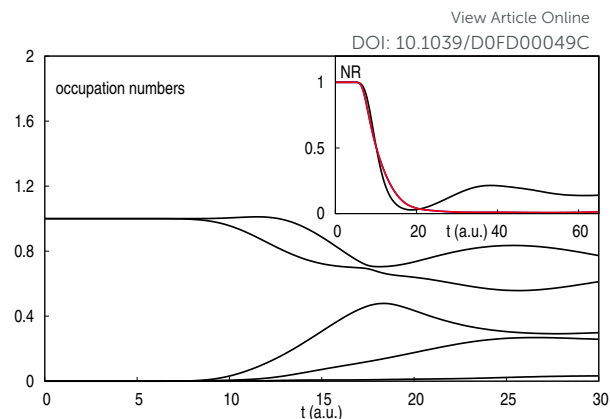


Fig. 2 Time-dependent occupation numbers for the scattering problem. The inset shows the exact (black) and ALDA (red) reflected probability density $N_R(t)$.

ics from the adiabatic approximations were qualitatively reasonable (snapshots in Refs.^{10,33}); for example, in ALDA, there is an over-spreading of the density, but it does roughly capture the exact dynamics, and ALDA does very well when averaged quantities are considered such as the reflection probability $N_R = \int_{-5}^{\infty} n(x, t) dx$, shown in the inset, until the occupation numbers of the physical system begin to significantly change.

We note that in this example, the two occupation numbers beginning with a value of 1 correspond to the incoming electron’s orbital and the target electron’s orbital. The state is a double Slater determinant, and could be called strongly correlated, if correlation is measured by how far the occupation numbers are from the Slater determinant values of 0 and 2.

2.2 Superposition states

In this example we consider a field-free evolution of a superposition state of a 1D He atom ($\psi_{\text{ext}}^{\text{1DHe}}(x) = -1/\sqrt{x^2 + 1}$). We consider a 20:80 superposition of its ground and first excited state, $\Psi(0) = (\Psi^{\text{g.s.}} + 2\Psi^{\text{e}})/\sqrt{5}$, and the freely-evolving density has a periodic dynamics of period $T = 2\pi/(E_e - E_{\text{g.s.}}) = 11.788\text{a.u.}$ There are two dominant initial occupation numbers as shown in Fig. 3, around 1.55 and 0.44, neither of which evolve further than about 0.049 from their initial values, while the density sloshes back and forth in the well. If we begin in a KS excited state of the same configuration, we find that ALDA propagation of its dipole oscillates with a similar period but there is also a very slow period beating, which is only just visible over the duration shown. The ALDA densities in Fig. 4 also follow closely the exact, especially so if local details are averaged over. This is an example where the system is far from the ground-state, there is significant dynamics while the occupation numbers do not deviate significantly from their initial values, and (locally-averaged) ALDA predicts the dynamics accurately from a KS initial state chosen with a similar configuration to the exact, consistent with the suggestion from the exact expression.

Generally however, with freely-evolving superposition states the violation of the resonance-condition³⁷ mentioned earlier adversely affects the dynamics even when the occupation numbers

do not deviate far from their initial values. Dynamics in free evolution is purely dependent on the resonant frequencies of the system; the oscillation periods in the dipole are a direct measure of these frequencies. With adiabatic TDDFT, the xc potential leads to these frequencies being generally different when the system is left in different superposition states³⁷: essentially, the time-evolving density gives time-dependence to the instantaneous KS potential and its bare KS frequencies, which is not compensated for correctly in the generalized xc kernel defined for non-equilibrium states. On the other hand, the exact frequencies are invariant to which state the system is in. In the particular case above, and some other linear combinations of the ground and first excited state, there is a relatively small violation of the resonance condition, provided the initial KS state is chosen with a similar configuration to the exact. The ALDA frequency of the lowest excitation as computed by linear response from the ground-state is 0.480 a.u., while that computed from the period of oscillation in Fig. 3 is 0.553 a.u. (interestingly, closer to the exact value of 0.533 a.u.). Thus the violation of the resonance condition is evident, since the approximation should give the same value whatever the initial state is, but not so severe, and in this case, because the violation brings the ALDA value closer to the exact value as compared to that computed from the ground-state, the density dynamics is quite well-reproduced. We found that when we tried to make more general superposition states, especially with two excited states, ALDA dynamics was very poor due to the violation of the resonance condition, with several frequencies appearing in the ALDA dynamics instead of one, even when the occupation numbers did not change much in time and the initial KS state is chosen to have a similar configuration, or be identical with, the true initial state.

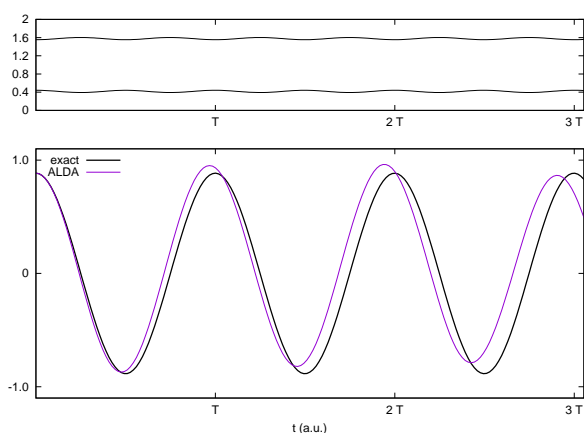


Fig. 3 Time-dependent occupation numbers (upper panel) and exact (black) and ALDA (purple) dipole moments (lower panel) for superposition state example.

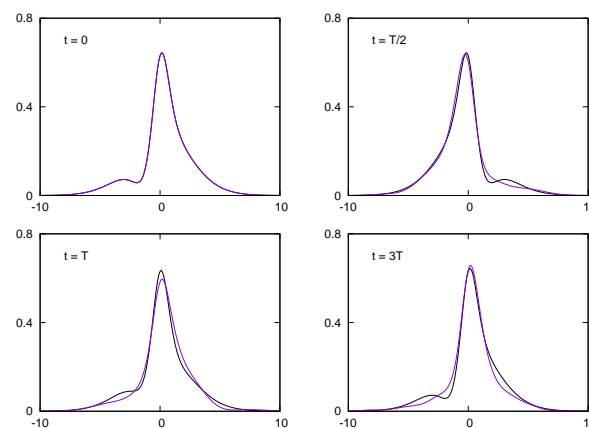


Fig. 4 Snapshots of the exact (black) and ALDA (purple) densities for the superposition state example.

2.3 Laser-driven ground-state

Here we consider an example where we begin in the ground-state of our 1D He atom and drive it with a non-perturbative non-resonant electric field. The system begins weakly-correlated, in contrast to the previous examples, as indicated by the largest occupation number beginning at 1.98, with the others all below 0.02. Unless otherwise stated, we choose the initial KS state as identical to the physical state, which gives practically the same dynamics as starting in a Slater determinant with the exact initial density as the true state.

In Fig. 5, a field $\mathcal{E}(t) = 0.5 \sin(t)$ is linearly ramped on over the first 20 a.u. and then held constant. After some time there is a significant change in the occupation numbers and large amplitude dipole oscillations, yet the ALDA dipole plotted in this figure appears to match the exact very closely. That the dipole paints a much rosier picture than the truth is evident in the densities plotted in Fig. 6. ALDA is very good at first, capturing the density-oscillations and the details of the lobes evolving outwards accurately. The system evolves very far from a ground-state during the first 30 a.u. or so, and still ALDA is working well provided the initial KS state is a good one, meaning it captures the initial density well. At later times, for example from 35 a.u. shown in the figure onwards, the ALDA propagation becomes significantly worse, concomitant with the larger deviation of the dominant occupation number $\Delta\eta$ indicated in the figure. Note that the density becomes increasingly oscillatory in the tails of both the exact and ALDA densities as time evolves due to reflections from the hard-wall boundaries at ± 40 a.u. This example also seems to answer our question affirmatively: ALDA predicted a good density-dynamics while the deviation of the occupation numbers remained within about 0.5 of their initial value. The importance of having a good initial state is clear, since when instead the LDA ground-state is propagated, the density is considerably worse even at very short times, as evident from the red curve in Fig. 6.

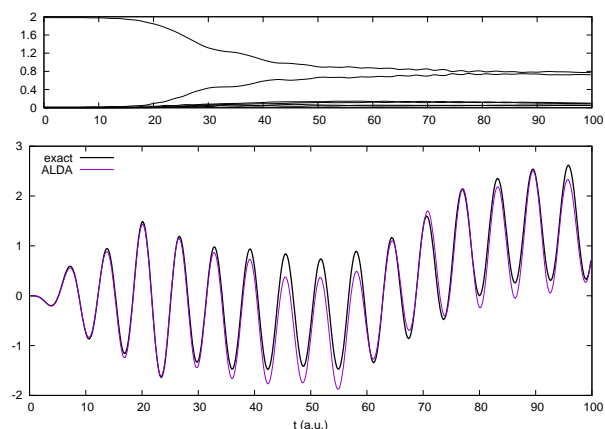


Fig. 5 Time-dependent occupation numbers (top panel) and exact (black) and ALDA (purple) dipole moments (lower panel) for 1D He ground-state driven with $\mathcal{E}(t) = 0.5 \sin(t)$ ramped on over 20 a.u.

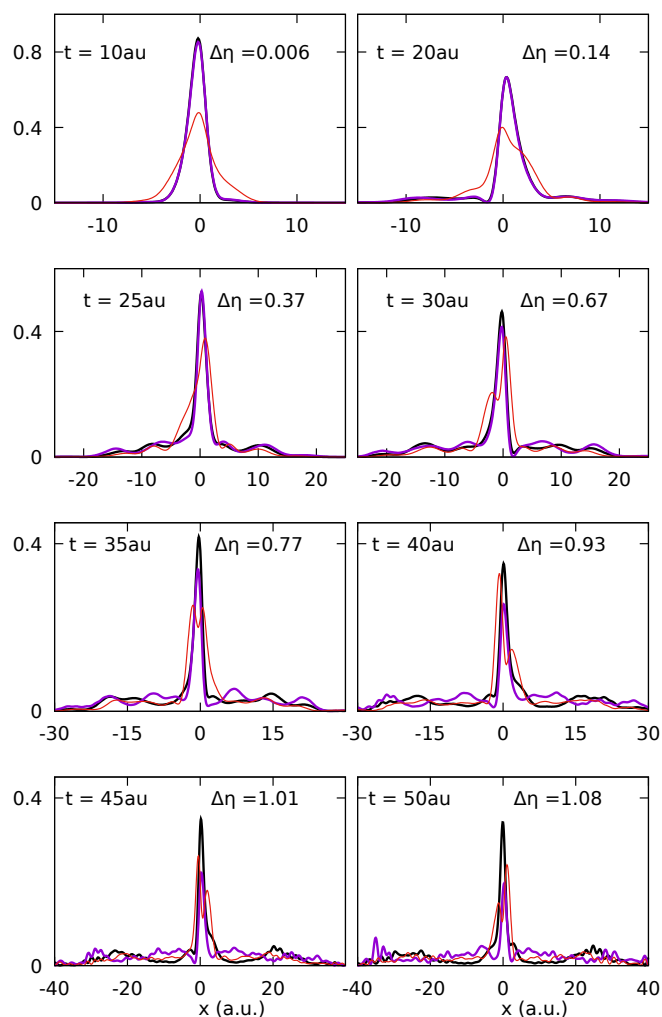


Fig. 6 Snapshots of the exact (black) and ALDA (purple) densities from evolving the 1D He ground-state with $\mathcal{E}(t) = 0.5 \sin(t)$ ramped on over 20 a.u. The density evolving from the LDA ground state propagated using ALDA is shown as the thin red line.

2.4 Laser-driven excited-state

In our last example, we begin already far from a ground-state. The same electric field as in the previous example drives the 1D He atom now initially in its first excited state. In this case there are two initial natural orbital occupations both within 0.003 of 1, so we start with a KS initial state that is in an excited state configuration of a non-interacting system with the property that the initial density reproduces that of the physical initial state. In fact, taking $\Phi(0) = \Psi(0)$ gave us identical density-evolution. Similar examples in the past^{10,35,36} have shown that propagations with an adiabatic approximation on an initial Slater determinant choice for the KS system gives much poorer dynamics than when the KS initial state is chosen with a similar configuration to that of the true system, as discussed also for the scattering example here earlier.

The resulting dipole dynamics is accurately captured by ALDA however a look at the densities in Fig. 8 shows us that again, globally averaging over the density gives an overly positive picture of the performance of ALDA. The densities show that although the average behavior and density oscillations are well-captured in ALDA before the occupation numbers deviate too far, the ALDA density is missing details of the structure, such as the shoulders in the exact densities seen in the top panels of Fig. 8. At the initial time, since the KS initial state is chosen to reproduce the true density, these shoulders are there but ALDA rapidly broadens them and washes them out, even by 5 a.u. Still, if we consider *locally* averaging over this type of structure in the density, ALDA does quite well even as far as about 25 a.u., after which the largest deviation in the occupation numbers reaches about 0.3, and locally-averaged ALDA develops a more significant error.

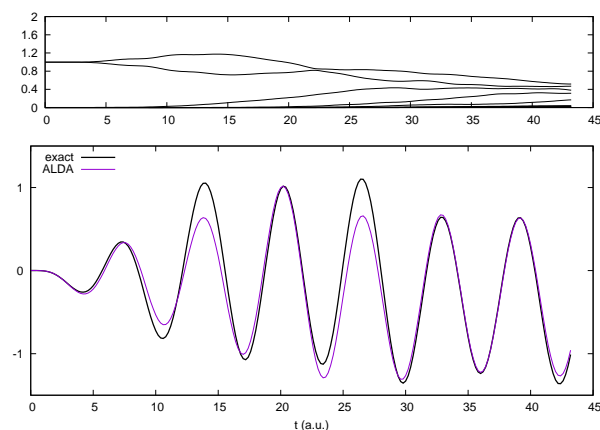


Fig. 7 Time-dependent occupation numbers (upper panel) and exact (black) and ALDA (purple) dipole moments (lower panel) for laser-driven excited-state example.

In summary, the four examples here illustrate that when the natural occupation numbers remain close to their initial values, ALDA evolution can yield a reasonably accurate density, while errors grow in cases where the occupation numbers deviate significantly from their initial values. It is important to note that

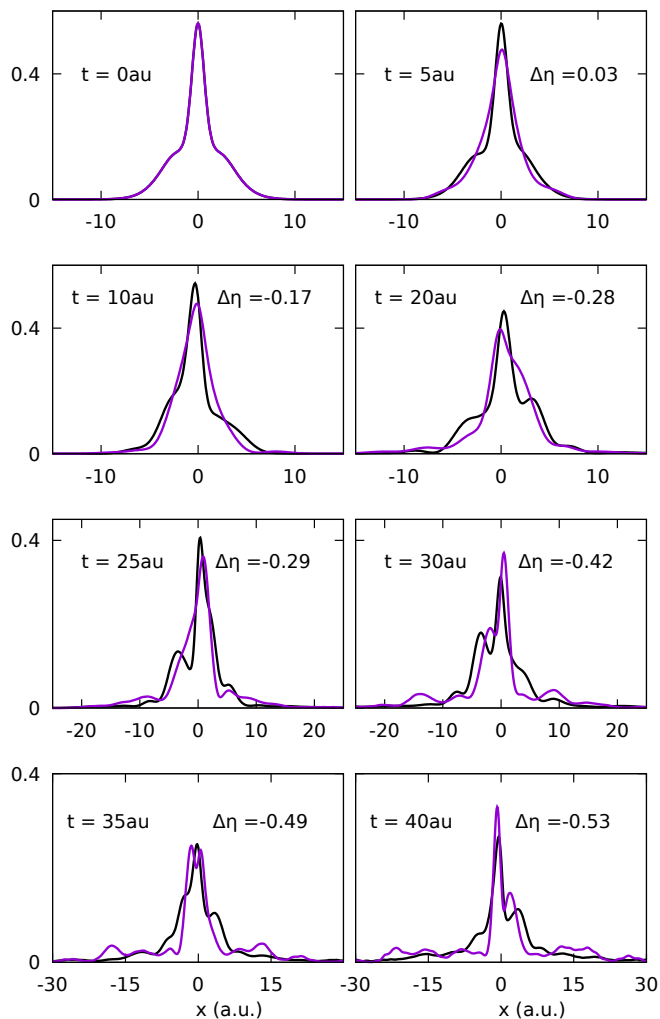


Fig. 8 Snapshots of the exact (black) and ALDA (purple) densities for the laser-driven excited state example. The largest deviation of the occupation number at each is indicated in each panel as $\Delta\eta$.

the adiabatic approximation performed well even when the system was far from any ground-state and key to this is the choice of the KS initial state. We chose the KS initial state to have a configuration very close to that of the true initial state in each case, as earlier work had shown that if this is not the case, adiabatic approximations work much less well; this is clear also from the exact expression for v_{xc} . In some cases globally averaged observables such as the dipole were accurate even when the occupation numbers had great deviation. Beyond resorting to a justification in terms of ALDA satisfying a number of exact conditions, this cannot easily be explained from the exact expressions.

3 Density-Matrix Coupled xc Approximations

To go beyond the adiabatic approximation, Ref.³² introduced a class of approximations based on the exact decomposition, Eqs. (1)–(3). The idea is to use an auxiliary 2RDM $\tilde{\rho}_2$ to approximate the two parts in the expression that are inaccessible from a KS evolution, ρ_1 and n_{xc} . As shown there, the KS equation is considered to be coupled to the first equation of the BBGKY hierarchy that gives an equation for the 1RDM: the 2RDM that appears in this equation is approximated by the auxiliary $\tilde{\rho}_2$ as a functional of the KS wavefunction $\Phi(t)$ and the 1RDM resulting from the BBGKY equation, $\tilde{\rho}_1(t)$. At each time-step, the propagation of the BBGKY equation produces an output $\tilde{\rho}_1$, which, when inserted into Eq. (3) and put together with Eq. (2) using the xc hole constructed from $\tilde{\rho}_2$, gives a non-adiabatic approximation to v_{xc} that satisfies exact conditions such as the zero-force theorem and the harmonic potential theorem, and captures non-adiabatic step features in the xc potential. The first BBGKY equation and the KS equation should be solved self-consistently, exchanging inputs at each time-step, and it can be shown that such a scheme ensures that propagation yields the same density in each.

For example, one can choose $\tilde{\rho}_2 = \rho_{2,s}$, an approximation we denoted in Ref.³² as $v_{xc}^{\tilde{\rho}_2}$, which results in the interaction component v_{xc}^W coinciding with v_{xc}^S and a non-zero kinetic component. Unfortunately, although this first DMxc approximation captured the elusive non-adiabatic structures in model systems, after too short a time the dynamics developed sharp structures that rapidly self-amplified and killed the calculation. It was observed in that work that if instead a Hartree-Fock (HF) driven calculation was performed, where $\tilde{\rho}_2$ is taken to be the HF functional of $\tilde{\rho}_1$, step and peak structures appeared in the correlation potential in general, and the dynamics remained stable. However as such a calculation simply reproduces the HF density, it is not of practical use. (In the special case of two electrons in KS state which is a doubly-occupied spatial orbital, HF propagation would reduce to exact-exchange, which is adiabatic and has no step structures if the initial $\tilde{\rho}_1(0)$ is chosen to coincide with the KS 1RDM. Choosing it to be the true $\rho_1(0)$ of the interacting system however does generate step structure).

Still, the observation raises the possibility of using a “hybrid” $\tilde{\rho}_2$, which is a linear combination of $\rho_{2,s}$ and $\rho_2^{\text{HF}}[\tilde{\rho}_1]$ with the hope that the HF component tames the instability. Here we test this for the scattering problem discussed in Secs. 1 and 2. We

now denote the approximation where $\tilde{\rho}_2 = \rho_{2,s}$ as $v_{xc}^{\rho_{2,s}}$, while we define the hybrid approximation through

$$v_{xc}^{a\rho_{2,s}} : \tilde{\rho}_2 = (1-a)\rho_2^{\text{HF}}[\tilde{\rho}_1] + a\rho_{2,s} \quad (7)$$

with $0 \leq a \leq 1$. For the scattering problem, Ref.³² had shown that $v_{xc}^{\rho_{2,s}}$ captures a peak/step-like increase behind the target that develops when the incoming electron begins to meet the target which plays an important role of delaying the transit of the incoming electron through the target so allowing more correlation with the target. The ALDA, v_{xc}^S , and other adiabatic approximations studied in Ref.¹⁰ did not have this structure, with resulting densities with larger tails on the other side of the target. But $v_{xc}^{\rho_{2,s}}$ continued only a short time beyond this, failing after about 12 a.u. before there is appreciable reflection.

In Fig. 9 we see that numerical stability is improved the more the amount of $\rho_2^{\text{HF}}[\tilde{\rho}_1]$ is included in the approximation; $v_{xc}^{0.8\rho_{2,s}}$ that mixed 0.2 of HF propagated for 12.2 a.u. before the instability killed it, $v_{xc}^{0.5\rho_{2,s}}$ for 13.8 a.u., and $v_{xc}^{0.2\rho_{2,s}}$ propagated until the end of the simulation. At early times (first panel in the figure), before there is much overlap between the incoming electron and the target, the approximations with a larger a , i.e. larger fraction of $\rho_{2,s}$ and less of $\rho_2^{\text{HF}}[\tilde{\rho}_1]$, do the best, with their xc potentials also giving a better approximation to the exact for larger a . Actually at these early times, Ref.^{10,33} showed that v_{xc}^S , which completely neglects v_c^T and approximates v_{xc}^W by using the KS hole in place of the true hole, also does almost perfectly, in contrast to ALDA (and adiabatic exact exchange) which give densities that are too spread. As the incoming electron's density begins to overlap more with the target (second panel), the densities in the target region and also just behind it, are better approximated the larger the fraction of $\rho_{2,s}$ is included. At these times a crucial role is played by the peak structure that develops early behind the target, as mentioned above. When HF dilutes the approximation, this peak is subdued as evident in the plot of the potentials, and the effect of the increased interaction time is diminished. However, the approximations that manage to survive for times long enough to witness reflection, do not contain enough of $\rho_{2,s}$: their dominantly HF nature is unable to capture the important persistent step structure down to the right of the center of the target ($x = -10$ a.u.) that develops soon after 20 a.u. that is crucial to reflect the electron back to the right and as a result, the reflection result is not improved. Even though these approximations contain a lot of structure, they rapidly vary in space and time such that there is not a significant impact on the resulting dynamics (in contrast to the persistent step down structure in the exact potential, see movie Supplementary information of Ref.¹⁰).

Thus, although the "hybrid" non-adiabatic approximation is able to stabilize the calculation for longer times, and, if the fraction of HF is not too large then non-adiabatic structures are captured, the fraction of HF needed to stabilize for long enough times to witness reflection is too large compared to the $\rho_{2,s}$ component such that non-adiabatic features get lost. Indeed, as we see on the Fig. 9 at time $t = 22$ a.u. the density remaining at the target is almost the same for $v_{xc}^{0.2\rho_{2,s}}$, ALDA, and HF, whereas the exact calculation shows a smaller and more spread density, resulting from

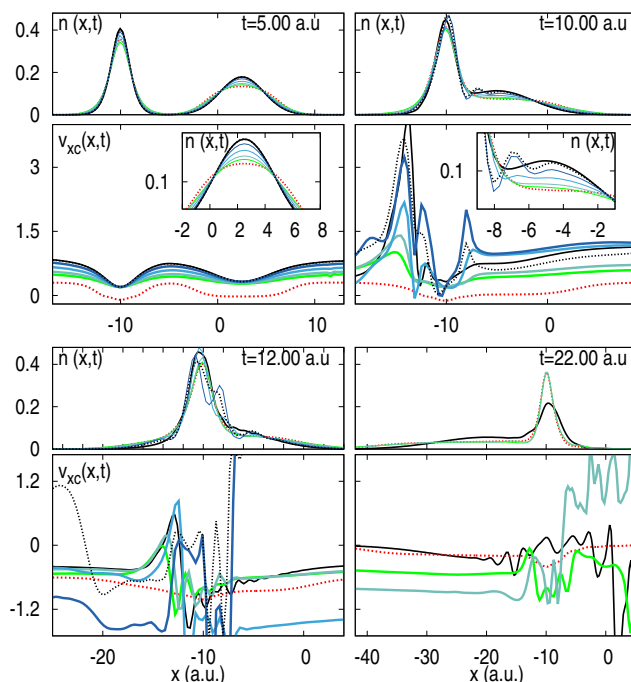


Fig. 9 Snapshots of the density and xc potential for exact (black solid), ALDA (red dotted) and computed with the density-matrix coupled approximations with different ratio of $\rho_{2,s}$ and $\rho_2[\tilde{\rho}_1]$ from green to black: $v_{xc}^{0.2\rho_{2,s}}$ (light green), $v_{xc}^{0.5\rho_{2,s}}$ (dark green), $v_{xc}^{0.8\rho_{2,s}}$ (light blue), $v_{xc}^{\rho_{2,s}}$ (dark blue) and $v_{xc}^{\rho_{2,s}}$ (black dotted). Insets at time $t = 5.00$ a.u. and $t = 10.00$ a.u. are a zoom on the density in the regions with the largest differences.

reflection and an energy transfer between the target and the incoming wavepacket.

4 Coupling Constant Integrations

Finding an adequate approximation for v_c^T is challenging, as evident from the above sections. Here we consider whether there is a way to "hide" this kinetic contribution to correlation in a coupling-constant integral, analogously to the adiabatic connection expression for the xc energy^{38,39} in ground-state DFT.

The notion of coupling-constant connection was introduced in TDDFT in Ref.⁴⁰ where it was used to develop a perturbation theory for v_{xc} . Here instead we search for a coupling-constant integral expression which usurps v_c^T . We consider then the Hamiltonian

$$H^\lambda = T + \lambda W + V^\lambda(t) \quad (8)$$

where the coupling-constant λ is a parameter taking us from the KS system at $\lambda = 0$ to the true system at $\lambda = 1$, while the density $n^\lambda(\mathbf{r}, t) = n(\mathbf{r}, t)$ for all values of λ . We have

$$H^\lambda \Psi^\lambda(t) = i\partial_t \Psi^\lambda(t), \quad n_{\Psi^\lambda}(\mathbf{r}, t) = n(\mathbf{r}, t) \quad (9)$$

with the initial state for each λ , $\Psi^\lambda(0)$, being freely chosen with the only restriction that its initial density and initial first-time derivative of its density is equal to that of the true wavefunction, $\Psi^{\lambda=1}(0) = \Psi(0)$. Unlike in the ground-state case, due to

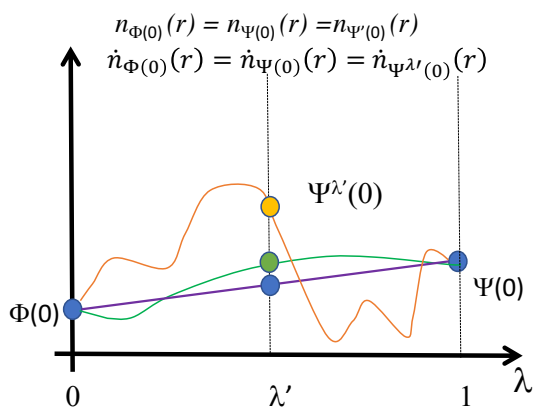


Fig. 10 Sketch of three different possible coupling-constant paths for the time-dependent case. (See text)

the initial-state freedom there are an infinite number of possible coupling-constant paths for a given choice of KS initial state, $\Psi^{\lambda=0}(0) = \Phi(0)$, as illustrated in the cartoon in Fig. 10. The hope is then to express

$$v_{xc}[n; \Psi(0), \Phi(0)](\mathbf{r}, t) = \int_0^1 f(\lambda) d\lambda \quad (10)$$

where the kinetic term no longer appears, but instead is usurped by the coupling-constant integral. Different components of $f(\lambda)$ will look completely for different coupling-constant paths, yet the total integral will be the same. Here we do not discuss the question of the existence of a given path in λ , and simply assume that the initial λ -path can be propagated, remaining v -representable and differentiable with respect to λ at every time. We note this freedom of the path in λ is distinct from the freedom of choice of the initial KS state, that is, for a given physical initial state $\Psi(0)$, there are infinitely many possible initial KS states $\Phi(0)$, each of which gives a different $v_{xc}(\mathbf{r}, t)$.

In the ground-state case, the adiabatic connection expression for the xc energy eliminates the kinetic contribution by taking the λ -derivative of the expectation value of the energy, making use of the Hellmann-Feynmann theorem, and then integrating $\lambda = 0$ to 1. Here in the time-dependent case, we consider instead the integral that follows from evaluating the Dirac action at λ on the solution to Eq. (9):

$$A^\lambda = \int_0^T dt' \langle \Psi^\lambda(t') | i\partial_{t'} - \hat{H}^\lambda | \Psi^\lambda(t') \rangle = 0. \quad (11)$$

Computing the integrand of the left-hand-side of

$$\int_0^1 d\lambda \frac{\partial}{\partial \lambda} A^\lambda = A^{\lambda=1} - A^{\lambda=0} = 0, \quad (12)$$

eliminates the kinetic term in the Hamiltonian, and after some

manipulations, we arrive at

$$\int_0^T dt' \int dr' v_{xc}(r', t') n(r', t') = \frac{1}{2} \int_0^T dt' \int \int dr_1 dr_2 w(r_1, r_2) \overline{n_{xc}^\lambda(r_1, r_2; t')} n(r_1, t') - \int_0^T U[n(t')] dt' + \left(\overline{\langle \Psi^\lambda(T) | -i \frac{\partial}{\partial \lambda} \Psi^\lambda(T) \rangle} - \overline{\langle \Psi^\lambda(0) | -i \frac{\partial}{\partial \lambda} \Psi^\lambda(0) \rangle} \right) \quad (13)$$

where $U[n]$ is the Hartree energy and the overline notation denotes the coupling-constant integral $\bar{f} = \int_0^1 f(\lambda) d\lambda$. Applying now the functional derivative, $\frac{\delta}{\delta n(\mathbf{r}, t)}$ where $0 < t < T$, to Eq. (13), yields

$$v_{xc}(r, t) = - \int_0^T dt' \int dr' f_{xc}(r', t'; r, t) n(r', t') - v_H(r, t) + \frac{\delta}{\delta n(\mathbf{r}, t)} \left(\overline{\langle \Psi^\lambda(T) | -i \frac{\partial}{\partial \lambda} \Psi^\lambda(T) \rangle} - \overline{\langle \Psi^\lambda(0) | -i \frac{\partial}{\partial \lambda} \Psi^\lambda(0) \rangle} \right) + \frac{1}{2} \int_0^T dt' \int \int dr_1 dr_2 w(r_1, r_2) \left[\frac{\delta}{\delta n(\mathbf{r}, t)} \overline{n_{xc}^\lambda(r_1, r_2; t')} \right] n(r_1, t') + \frac{1}{2} \int dr_2 w(r, r_2) \overline{n_{xc}^\lambda(r, r_2; t)} \quad (14)$$

where $f_{xc}(r', t'; r, t) = \frac{\delta v_{xc}(r', t')}{\delta n(\mathbf{r}, t)}$ is a generalized linear response kernel, measuring the response of the xc potential at time t' to a density perturbation at time t . Given that $0 < t < T$ and that v_{xc} is a causal function, there is a significant amount of cancellation between the terms. Making use of causality and taking $T = t^+$, we write

$$v_{xc}(r, t) = - \int_t^{t^+} dt' \int dr' f_{xc}(r', t'; r, t) n(r', t') - v_H(r, t) + \frac{1}{2} \int dr_2 w(r, r_2) \overline{n_{xc}^\lambda(r, r_2; t)} + \frac{\delta}{\delta n(\mathbf{r}, t)} \overline{\langle \Psi^\lambda(t) | -i \frac{\partial}{\partial \lambda} \Psi^\lambda(t) \rangle} + \frac{1}{2} \int_t^{t^+} dt' \int \int dr_1 dr_2 w(r_1, r_2) \left[\frac{\delta}{\delta n(\mathbf{r}, t)} \overline{n_{xc}^\lambda(r_1, r_2; t')} \right] n(r_1, t'). \quad (15)$$

It may appear that by trying to avoid computing and approximating the challenging term v_C^T , we have jumped from the frying pan into the fire, with perhaps the hottest flames coming from the terms involving the density-functional derivative of the coupling-constant integral of the Berry-like wavefunction projection of the λ -derivative of the wavefunction.

In fact, considering the ground-state limit of this expression sheds some light on this term. Returning momentarily to Eq. (13), and taking $\Psi^\lambda(t) = e^{-iE_0^\lambda t} \Psi_0^\lambda$ with the eigenstate satisfying $(T + V^\lambda + \lambda W) \Psi_0^\lambda = E_0^\lambda \Psi_0^\lambda$, it is straightforward to compute

$$\frac{1}{T} \left(\overline{\langle \Psi^\lambda(T) | -i \frac{\partial}{\partial \lambda} \Psi^\lambda(T) \rangle} - \overline{\langle \Psi^\lambda(0) | -i \frac{\partial}{\partial \lambda} \Psi^\lambda(0) \rangle} \right) = E_0^{\lambda=0} - E_0^{\lambda=1} = \int dr' v_{xc}(r', t') n(r', t') + U[n] - E_{xc}[n]$$

which resolves the rather unusual appearance of the Hartree energy in Eq. (13), and Hartree potential in Eq. (15). Using the fact that $E_0^{\lambda=1} = T_s[n] + U[n] + E_{xc}[n] + \int dr' v_{\text{ext}}(r', t') n(r', t')$ is the true physical energy, and that $E_0^{\lambda=0} = T_s[n] + \int dr' v_{\text{ext}}(r', t') n(r', t') + \int dr' v_{\text{H}}(r', t') n(r', t') + \int dr' v_{xc}(r', t') n(r', t')$ is the sum of the KS eigenvalues, this retrieves the ground-state adiabatic connection formula, $E_{xc}[n] = \frac{1}{2} \int \int dr_1 dr_2 w(r_1, r_2) n_{xc}^{\lambda}(r_1, r_2) n(r_1)$.

It can also be shown that in the general time-dependent case, there is some cancellation between the Berry-like term and the other terms in Eq. (15) including the Hartree potential. The question then is how to approximate this term and the others in order to get a good practical approximation for v_{xc} . What would be most desirable is to somehow extract out adiabatic terms, and approximate the rest. This term should not be considered in isolation from the last two terms in Eq. (15), since different coupling-constant integration paths (see Fig. 10) weigh the terms differently, yet their sum is the same.

This is but one possible coupling-constant formula. There are other paths one could follow, for example considering the Dirac action for a fixed potential as a functional of the density⁴¹, or making a coupling-constant path between the exact adiabatic approximation and the exact one, which would give a formula directly for the memory-dependent part of v_{xc} as a correction to the adiabatic through coupling-constant integration. Future work will also consider whether the scaling relations derived in Ref.⁴² could be used to approximately evaluate some of these terms.

5 Conclusions and Outlook

This paper has explored three different lines of functional development in TDDFT: whether one can characterize the accuracy of adiabatic TDDFT by considering how strongly the natural orbital occupation numbers evolve in time, how one can use a decomposition of the exact xc potential to develop density-matrix coupled xc approximations, and an introduction of the idea of memory-dependent functionals based on coupling-constant integration.

The first part paints a partially reassuring picture on the use of adiabatic approximation, in that the range of validity of ALDA appears wider than weak perturbations of the ground-state. On the other hand this seems to be limited to the cases where occupation numbers do not change significantly during the dynamics which can be hard to predict in practice. It should also be noted that in some applications the external field dominates over xc effects in driving the dynamics, and it could well be that in many applications on realistic systems where the occupation numbers vary significantly and yet the adiabatic approximation works well, the essential role of xc is to counter self-interaction in the Hartree potential, sometimes even just at the ground-state level.

From our density-matrix coupled approximation we learned that the structure of the force balance equations for the exact potential, especially for v_C^T , seem to naturally generate the non-adiabatic features even when the exact 1RDM is replaced by a relatively simple approximation. This gives us hope on the possible development of approximations based on this expression. Also, even if the particular choices for the 1RDM explored here led to a numerically unstable approach, the derivation of a linear-response exchange-correlation kernel is still possible, and could

provide useful insights. Moreover, linear-response calculations should limit the possibility of numerical instabilities.

Of course, the perfect solution to the difficulty of modeling v_C^T would be to get rid of this term altogether, using a coupling-constant integration, as in the final part of this paper. While it is not clear what and how approximations could be obtained from the expression presented here, it opens up a new avenue for future derivations of non-adiabatic functionals for TDDFT.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial support from the US National Science Foundation CHE-1940333 (N.T.M) and the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences under Award DE-SC0020044 (L.L) are gratefully acknowledged.

Notes and references

- 1 E. Runge and E. K. U. Gross, *Phys. Rev. Lett.*, 1984, **52**, 997–1000.
- 2 N. T. Maitra, *J. Chem. Phys.*, 2016, **144**, 220901.
- 3 *Fundamentals of time-dependent density functional theory*, ed. M. A. Marques, N. T. Maitra, F. M. Nogueira, E. K. Gross and A. Rubio, Springer, 2012, vol. 837.
- 4 C. A. Ullrich, *Time-dependent density-functional theory: concepts and applications*, Oxford University Press, 2011.
- 5 L. D. M. Peters, J. Kussmann and C. Ochsenfeld, *Journal of Chemical Theory and Computation*, 2019, **15**, 6647–6659.
- 6 E. W. Draeger, X. Andrade, J. A. Gunnels, A. Bhatele, A. Schleife and A. A. Correa, *Journal of Parallel and Distributed Computing*, 2017, **106**, 205 – 214.
- 7 P. Elliott, J. I. Fuks, A. Rubio and N. T. Maitra, *Phys. Rev. Lett.*, 2012, **109**, 266404.
- 8 J. Ramsden and R. Godby, *Phys. Rev. Lett.*, 2012, **109**, 036402.
- 9 J. I. Fuks, P. Elliott, A. Rubio and N. T. Maitra, *J. Phys. Chem. Lett.*, 2013, **4**, 735–739.
- 10 Y. Suzuki, L. Lacombe, K. Watanabe and N. T. Maitra, *Phys. Rev. Lett.*, 2017, **119**, 263401.
- 11 F. Covito, E. Perfetto, A. Rubio and G. Stefanucci, *Phys. Rev. A*, 2018, **97**, 061401.
- 12 N. Dittmann, J. Splettstoesser and N. Helbig, *Phys. Rev. Lett.*, 2018, **120**, 157701.
- 13 C. Verdozzi, *Phys. Rev. Lett.*, 2008, **101**, 166401.
- 14 V. Kapoor, *Phys. Rev. A*, 2016, **93**, 063408.
- 15 S. Raghunathan and M. Nest, *J. Chem. Theory and Comput.*, 2011, **7**, 2492–2497.
- 16 S. Raghunathan and M. Nest, *J. Chem. Phys.*, 2012, **136**, –.
- 17 S. Raghunathan and M. Nest, *J. Chem. Theory and Comput.*, 2012, **8**, 806–809.
- 18 B. F. Habenicht, N. P. Tani, M. R. Provorse and C. M. Isborn, *J. Chem. Phys.*, 2014, **141**, 184112.

- 19 H. O. Wijewardane and C. A. Ullrich, *Phys. Rev. Lett.*, 2008, **100**, 056404.
- 20 C.-Z. Gao, P. M. Dinh, P.-G. Reinhard and E. Suraud, *Phys. Chem. Chem. Phys.*, 2017, **19**, 19784–19793.
- 21 C. A. Ullrich, *The Journal of Chemical Physics*, 2006, **125**, 234108.
- 22 C. A. e. a. Rozzi, *Nat. Comm.*, 2013, **4**, 1602.
- 23 A. Bruner, S. Hernandez, F. Mauger, P. M. Abanador, D. J. LaMaster, M. B. Gaarde, K. J. Schafer and K. Lopata, *The Journal of Physical Chemistry Letters*, 2017, **8**, 3991–3996.
- 24 P. Elliott, T. Müller, J. K. Dewhurst, S. Sharma and E. Gross, *Sci. Rep.*, 2016, **6**, 38911.
- 25 S. Yamada, M. Noda, K. Nobusada and K. Yabana, *Phys. Rev. B*, 2018, **98**, 245147.
- 26 T. T. Gorman, T. D. Scarborough, P. M. Abanador, F. Mauger, D. Kiesewetter, P. SÅandor, S. Khatri, K. Lopata, K. J. Schafer, P. Agostini, M. B. Gaarde and L. F. DiMauro, *The Journal of Chemical Physics*, 2019, **150**, 184308.
- 27 J. I. Fuks, L. Lacombe, S. E. B. Nielsen and N. T. Maitra, *Phys. Chem. Chem. Phys.*, 2018, **20**, 26145–26160.
- 28 L. O. Wagner, Z.-h. Yang and K. Burke, in *Exact Conditions and Their Relevance in TDDFT*, ed. M. A. Marques, N. T. Maitra, F. M. Nogueira, E. Gross and A. Rubio, Springer Berlin Heidelberg, Berlin, Heidelberg, 2012, pp. 101–123.
- 29 R. van Leeuwen, *Phys. Rev. Lett.*, 1999, **82**, 3863.
- 30 K. Luo, J. I. Fuks, E. D. Sandoval, P. Elliott and N. T. Maitra, *J. Chem. Phys.*, 2014, **140**, 18A515.
- 31 M.-L. M. Tchenkoue, M. Penz, I. Theophilou, M. Ruggenthaler and A. Rubio, *The Journal of Chemical Physics*, 2019, **151**, 154107.
- 32 L. Lacombe and N. T. Maitra, *Journal of Chemical Theory and Computation*, 2019, **15**, 1672–1678.
- 33 L. Lacombe, Y. Suzuki, K. Watanabe and N. T. Maitra, *The European Physical Journal B*, 2018, **91**, 96.
- 34 Y. Lee, X. Yao, M. V. Fischetti and K. Cho, *Phys. Chem. Chem. Phys.*, 2020, –.
- 35 J. I. Fuks, S. Nielsen, M. Ruggenthaler and N. T. Maitra, *Phys. Chem. Chem. Phys.*, 2016, **18**, 20976.
- 36 P. Elliott, J. I. Fuks, A. Rubio and N. T. Maitra, *Phys. Rev. Lett.*, 2012, **109**, 266404.
- 37 J. I. Fuks, K. Luo, E. D. Sandoval and N. T. Maitra, *Phys. Rev. Lett.*, 2015, **114**, 183002.
- 38 O. Gunnarsson and B. I. Lundqvist, *Phys. Rev. B*, 1976, **13**, 4274–4298.
- 39 J. P. Perdew and S. Kurth, in *Density Functionals for Non-relativistic Coulomb Systems in the New Century*, ed. C. Fiolhais, F. Nogueira and M. A. L. Marques, Springer Berlin Heidelberg, Berlin, Heidelberg, 2003, pp. 1–55.
- 40 A. Görling, *Phys. Rev. A*, 1997, **55**, 2630–2639.
- 41 G. Vignale, *Phys. Rev. A*, 2008, **77**, 062511.
- 42 P. Hessler, J. Park and K. Burke, *Phys. Rev. Lett.*, 1999, **82**, 378–381.