When Adiabatic TDDFT Breaks Down: New Routes to Nonperturbative Dynamics

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Oct 1, 2025

DFT & TDDFT

Interacting system: What do we want to get?

GS: **GS energies E_0, GS densities $n(\mathbf{r})$, geometries**

$$H\Psi_0(\mathbf{r}_1,\ldots,\mathbf{r}_N) = E_0\Psi_0(\mathbf{r}_1,\ldots,\mathbf{r}_N)$$

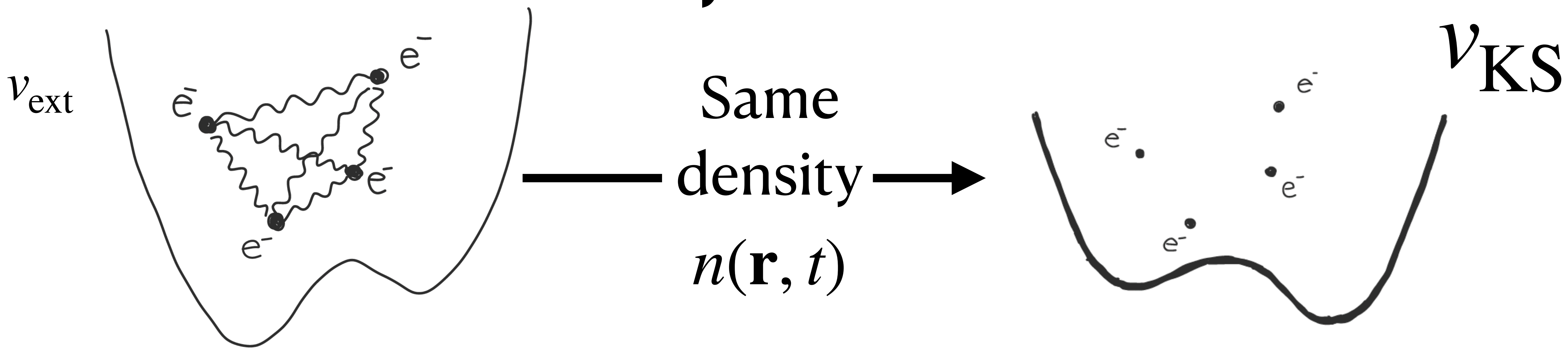
Excited states and response: **Spectral properties, excited-state densities**

$$H\Psi_m(\mathbf{r}_1,\ldots,\mathbf{r}_N) = E_m\Psi_m(\mathbf{r}_1,\ldots,\mathbf{r}_N)$$

Dynamics (e.g. driven by laser field): **TD properties (density, dipole moment, etc.)**

$$H(t)\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,t) = i\partial_t\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,t)$$

Non-Interacting Kohn-Sham (KS) system



Same density $n(\mathbf{r},t)$

Ground state Kohn-Sham eqns

GS: $$\left(-\frac{1}{2}\nabla_i^2 + v_{\text{KS}}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

Linear Response

Excited states and response: $$\delta n(\mathbf{r},t) = \int \chi(\mathbf{r},\mathbf{r}',t-t')\,V_{\text{ext}}(\mathbf{r}',t')\,d\mathbf{r}'dt'$$

Time-dependent Kohn-Sham eqns

Dynamics: $$\left(-\frac{1}{2}\nabla_i^2 + v_{\text{KS}}(\mathbf{r},t)\right)\phi_i(\mathbf{r},t) = i\partial_t\phi_i(\mathbf{r},t)$$

DFT/TDDFT enables study of large and complex many-body systems

Dynamics with TDDFT — Standard approach

Time-Dependent Kohn-Sham (TDKS)

Electron dynamics under an applied field v^{app} via

$$\left(-\frac{1}{2}\nabla_i^2 + v_{\text{KS}}(\mathbf{r},t)\right)\phi_i(\mathbf{r},t) = \mathrm{i}\partial_t\phi_i(\mathbf{r},t)$$

$$v_{\text{KS}}(\mathbf{r},t) = v_{\text{ext}}^{(0)}(\mathbf{r}) + v^{\text{app}}(\mathbf{r},t) + v_{\text{H}}[n](\mathbf{r},t) + v_{\text{XC}}\left[n;\Psi_0,\Phi_0\right](\mathbf{r},t)$$

$$n(\mathbf{r},t) = \sum_k \left|\phi_k(\mathbf{r},t)\right|^2$$

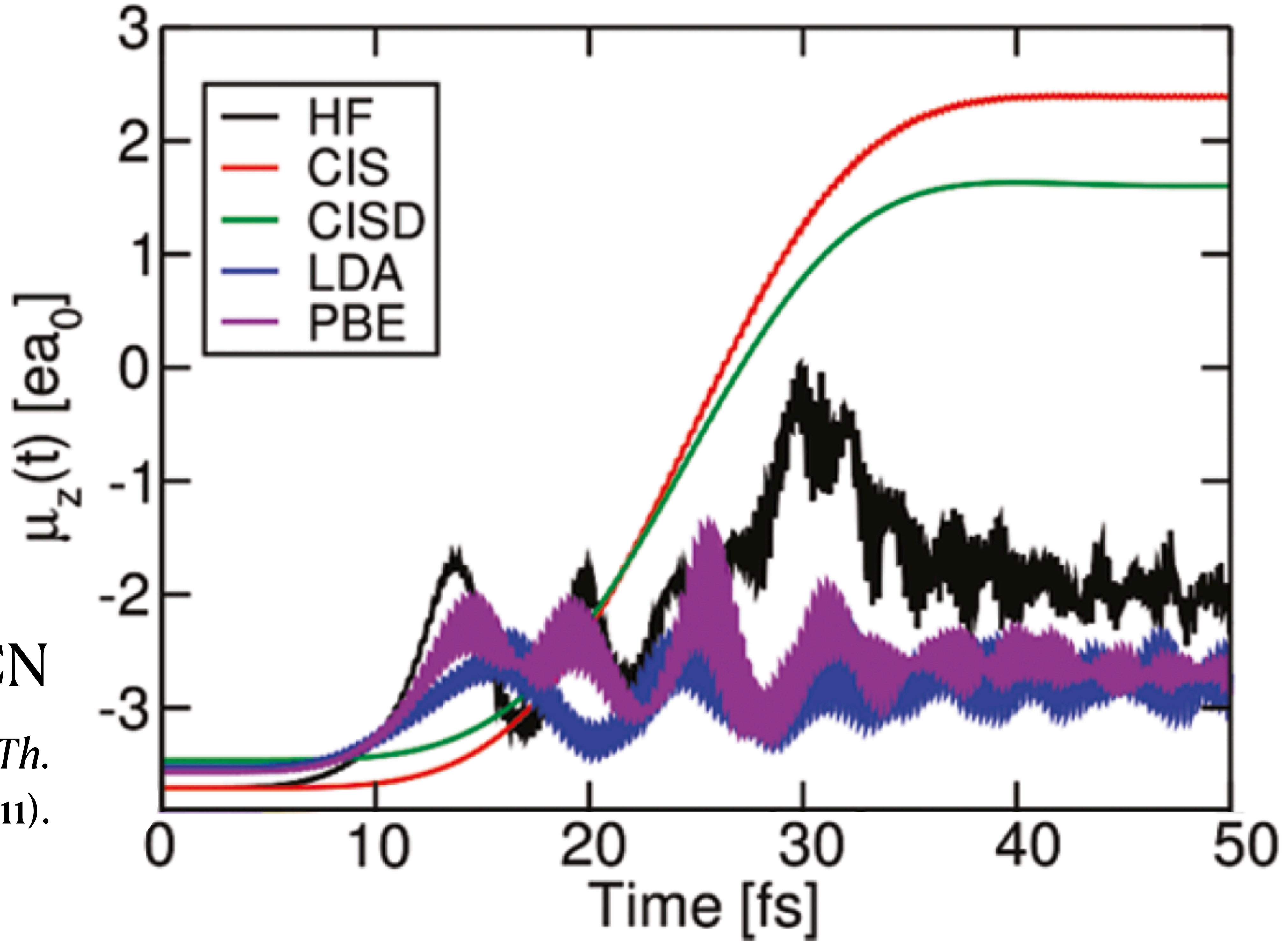
—> **any observable is accessible (by the Runge-Gross theorem)**

Adiabatic approximation:

$$v_{\text{XC}}[n;\Psi_0,\Phi_0](\mathbf{r},t) \approx v_{\text{XC}}^{\text{gs}}[n(t)](\mathbf{r})$$

- Uses xc from a ground-state for a non-ground-state system!
- No memory-dependence

Adiabatic approximation **fails** in certain kind of problems:



e.g. Charge-transfer dynamics in LiCN

S. Ragunathan, M. Nest, *J. Chem. Th. Comput.* **7**, 2492 (2011).

Dynamics with TDDFT — Response-Reformulated approach

TDKS

Electron dynamics under an applied field v^{app} via

$$\left(-\frac{1}{2}\nabla_i^2 + v_{\text{KS}}(\mathbf{r},t)\right)\phi_i(\mathbf{r},t) = \mathrm{i}\partial_t\phi_i(\mathbf{r},t)$$

$$v_{\text{KS}}(\mathbf{r},t) = v_{\text{ext}}^{(0)}(\mathbf{r}) + v^{\text{app}}(\mathbf{r},t) + v_{\text{H}}[n](\mathbf{r},t) + v_{\text{XC}}\left[n;\Psi_0,\Phi_0\right](\mathbf{r},t)$$

$$n(\mathbf{r},t) = \sum_k \left|\phi_k(\mathbf{r},t)\right|^2$$

Adiabatic approximation:

$$v_{\text{XC}}[n;\Psi_0,\Phi_0](\mathbf{r},t) \approx v_{\text{XC}}^{\text{gs}}[n(t)](\mathbf{r})$$

Requires xc functional on a fully non-equilibrium domain, but the adiabatic approx. uses xc of a ground-state!

RR-TDDFT

Instead, solve the problem in terms of *many-body* state expansion

$$|\Psi(t)\rangle = \sum_n C_n(t)\left|\Psi_n\right\rangle$$

Where

$$H^{(0)}\left|\Psi_n\right\rangle = E_n\left|\Psi_n\right\rangle$$

unperturbed Hamiltonian

$$\boxed{\dot{C}_k(t) = -\,iE_kC_k(t) - i\sum_j C_j(t)V_{kj}^{\text{app}}(t)}$$

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

$$\rho_{kj}(\mathbf{r}) = \left\langle\Psi_k\right|\hat{n}(\mathbf{r})\left|\Psi_j\right\rangle$$

The **time-dependent observables** are available with *just response quantities* — many-body wavefunctions need not to be calculated

$$n(\mathbf{r},t) = \sum_{jk} C_k^*(t)C_j(t)\rho_{kj}(\mathbf{r})$$

D. Dar, A. Baranova, N. T. Maitra, *Phys. Rev. Lett.* **133**, 096401 (2024)

RR-TDDFT : what ingredients do we need and why should we do this?

Solve ODE's

& extract observables

$$\dot{C}_k(t) = -iE_k C_k(t) - i\sum_j C_j(t) V^{\text{app}}_{kj}(t) \qquad V^{\text{app}}_{kj}(t) = \int d^3r\, v^{\text{app}}(\mathbf{r},t)\rho_{kj}(\mathbf{r}) \qquad n(\mathbf{r},t) = \sum_{jk} C^*_k(t) C_j(t)\rho_{kj}(\mathbf{r})$$

$$\rho_{kj}(\mathbf{r}) = \left\langle \Psi_k \middle| \hat{n}(\mathbf{r}) \middle| \Psi_j \right\rangle$$

•**Energies** E_k: from ground-state DFT (E_0) and LR-TDDFT ($E_{k\neq 0}$)

•**Transition densities** $\rho_{k\neq j}$: from LR-TDDFT (ρ_{k0}) and QR-TDDFT ($\rho_{k\neq j\neq 0}$))

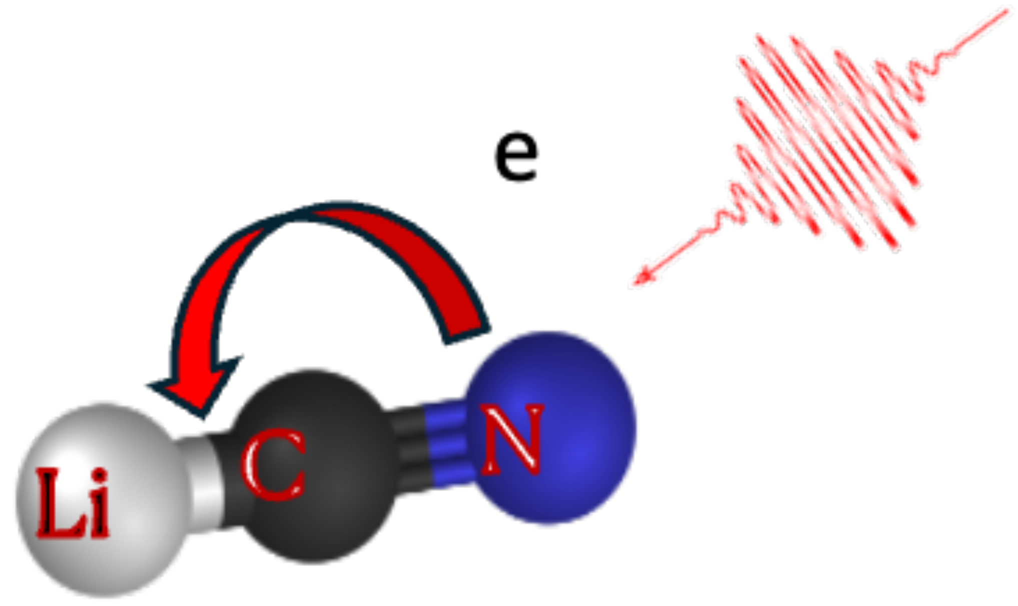
•**Densities** $\rho_{k=j}$: ground-state DFT (ρ_{00}) and LR-TDDFT ($\rho_{k=j\neq 0}$)

All ingredients involve xc evaluated only near a ground-state, $v_{\text{XC}}[n_0](\mathbf{r}), f_{\text{XC}}[n_0](\mathbf{r},\mathbf{r}',\omega), g_{\text{XC}}[n_0](\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\omega_1,\omega_2)$

→ adiabatic should work better than in TDKS where the fully non-equilibrium xc $v_{\text{XC}}[n;\Psi_0,\Phi_0](\mathbf{r},t)$ is needed

RR-TDDFT: LiCN Dipole Switching Revisited

Resonant Charge Transfer in LiCN under π-pulse



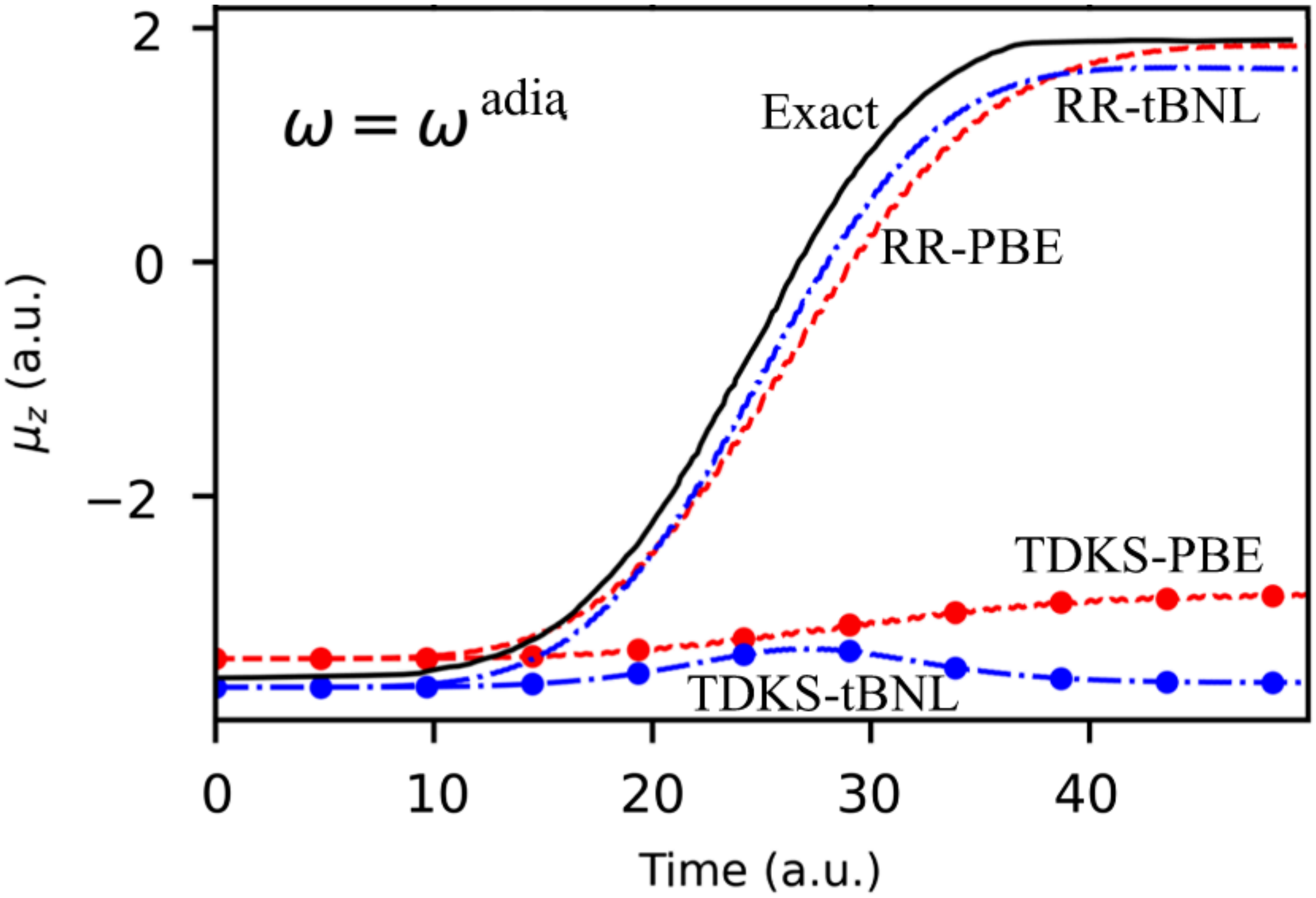
RR-TDDFT works where TDKS fails under the *same adiabatic functional*

D. Dar, A. Baranova, N. T. Maitra, *Phys. Rev. Lett.* **133**, 096401 (2024)

System driven by the pulse at the **TDDFT-predicted** resonant frequency:

$$\omega^{\text{PBE}} = 4.31\,\text{eV}$$
$$\omega^{\text{tBNL}} = 6.80\,\text{eV} \approx \omega^{\text{exact}}$$

"Exact" — TD-CISD reference
S. Ragunathan, M. Nest, *J. Chem. Th. Comput.* **7**, 2492 (2011).



RR-TDDFT can be used for non-perturbative dynamics with as much confidence as TDDFT in the response regime

But sometimes TDDFT with adiabatic functionals fails even in the response regime!

What to do when the adiabatic functionals fail even in the response regime?

Fortunately, when this happens is much better characterized than for non-equilibrium dynamics

And solutions exist!

→ Double excitations

✓Frequency-dependent kernel derived from first-principles — **Dressed TDDFT**

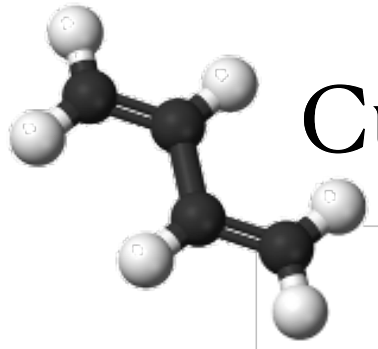
$$\Omega(\omega_k)\mathbf{G}_k = \omega_k^2\mathbf{G}_k$$

$$\Omega_{qq'}(\omega) = \nu_q\delta_{qq'} + 4\sqrt{\nu_q\nu_{q'}}f^{\mathrm{DTDDFT}}_{\mathrm{HXC}\,qq'}(\omega)$$

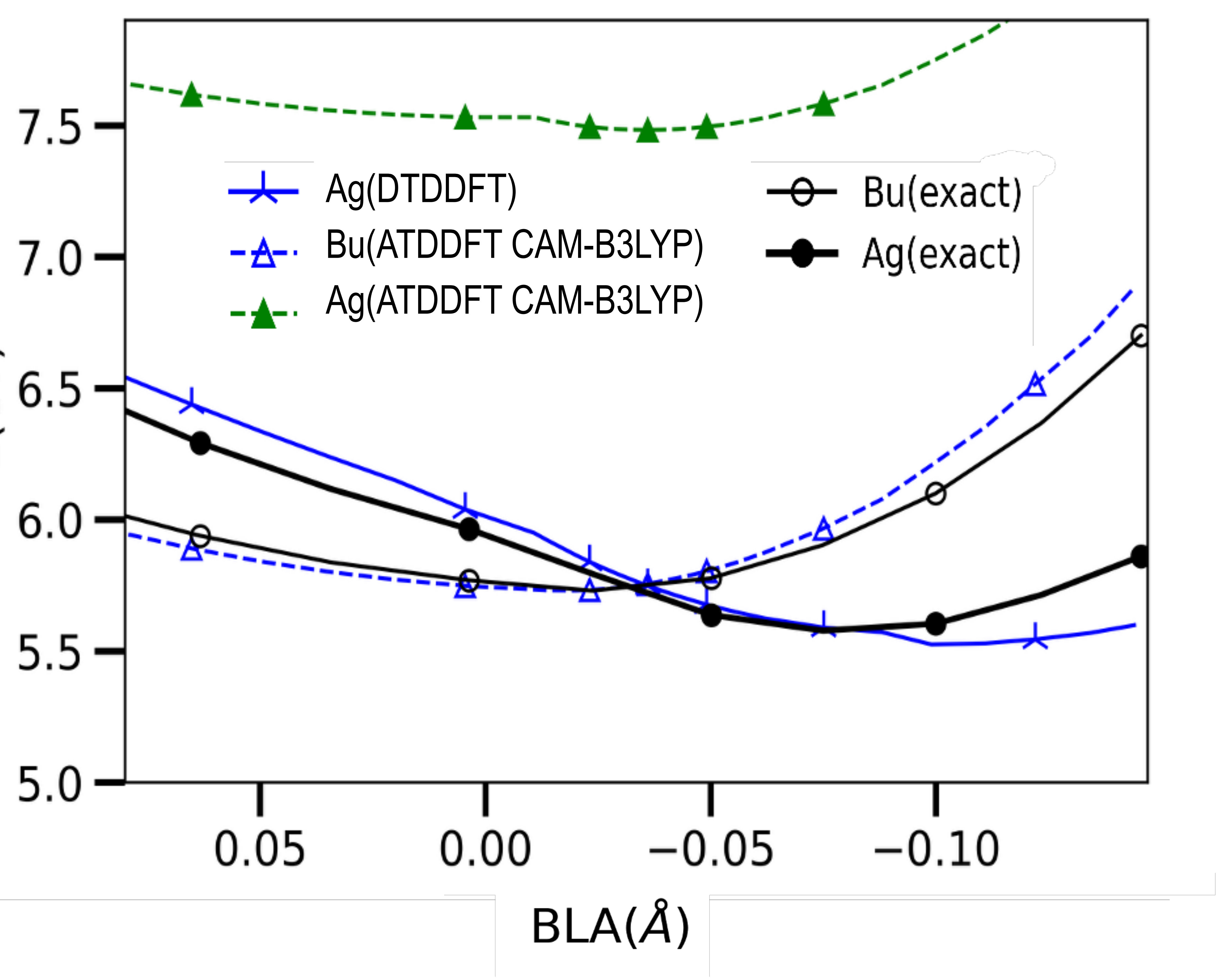
$$\mathbf{G}_k^\dagger\left(1 - \left.\frac{d\Omega}{d\left(\omega^2\right)}\right|_{\omega=\omega_k}\right)\mathbf{G}_k = 1$$

Gives good energies and oscillator strengths!

DTDDFT xc kernel: excitation energies and transition densities
D. B. Dar & N. T. Maitra, *J. Phys. Chem. Lett.* **16**, 703 (2025)



Curve-crossing between 1^1 Bu and 2^1 Ag states of butadiene



"Exact" — δ-CR-EOMCC(2,3) reference
W. Park, et al., *J. Phys. Chem. Lett.* **12**, 9720 (2021).

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Solve ODE's

$$\dot{C}_k(t) = -iE_k C_k(t) - i\sum_j C_j(t) V^{\rm app}_{kj}(t)$$

& extract observables

$$n(\mathbf{r},t) = \sum_{jk} C^*_k(t) C_j(t) \rho_{kj}(\mathbf{r}) \qquad V^{\rm app}_{kj}(t) = \int d^3r\, v^{\rm app}(\mathbf{r},t)\rho_{kj}(\mathbf{r})$$

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→ adiabatic should work better than in TDKS where the fully non-equilibrium xc $v_{\rm XC}[n;\Psi_0,\Phi_0](\mathbf{r},t)$ is needed

For double excitations:

- ω-dep xc kernel from Dressed TDDFT for both E_k and ρ_{k0}
  D. B. Dar & N. T. Maitra, *J. Phys. Chem. Lett.* **16**, 703 (2025)
- can we get excited state densities $n_k(\mathbf{r})$ from Dressed TDDFT? — Yes! A. Baranova & N. T. Maitra, *J. Chem. Theory Comput.*, to appear, 2025

Double excitations via linear response — excited state densities

The excited state densities are available through linear response in adiabatic approximation.

F. Furche, The Journal of Chemical Physics 114, 5982 (2001).
F. Furche and R. Ahlrichs, The Journal of Chemical Physics 117, 7433 (2002).

$$\delta E_k = \int d^3r\, n_k(\mathbf{r})\delta v_{\text{ext}}(\mathbf{r})$$

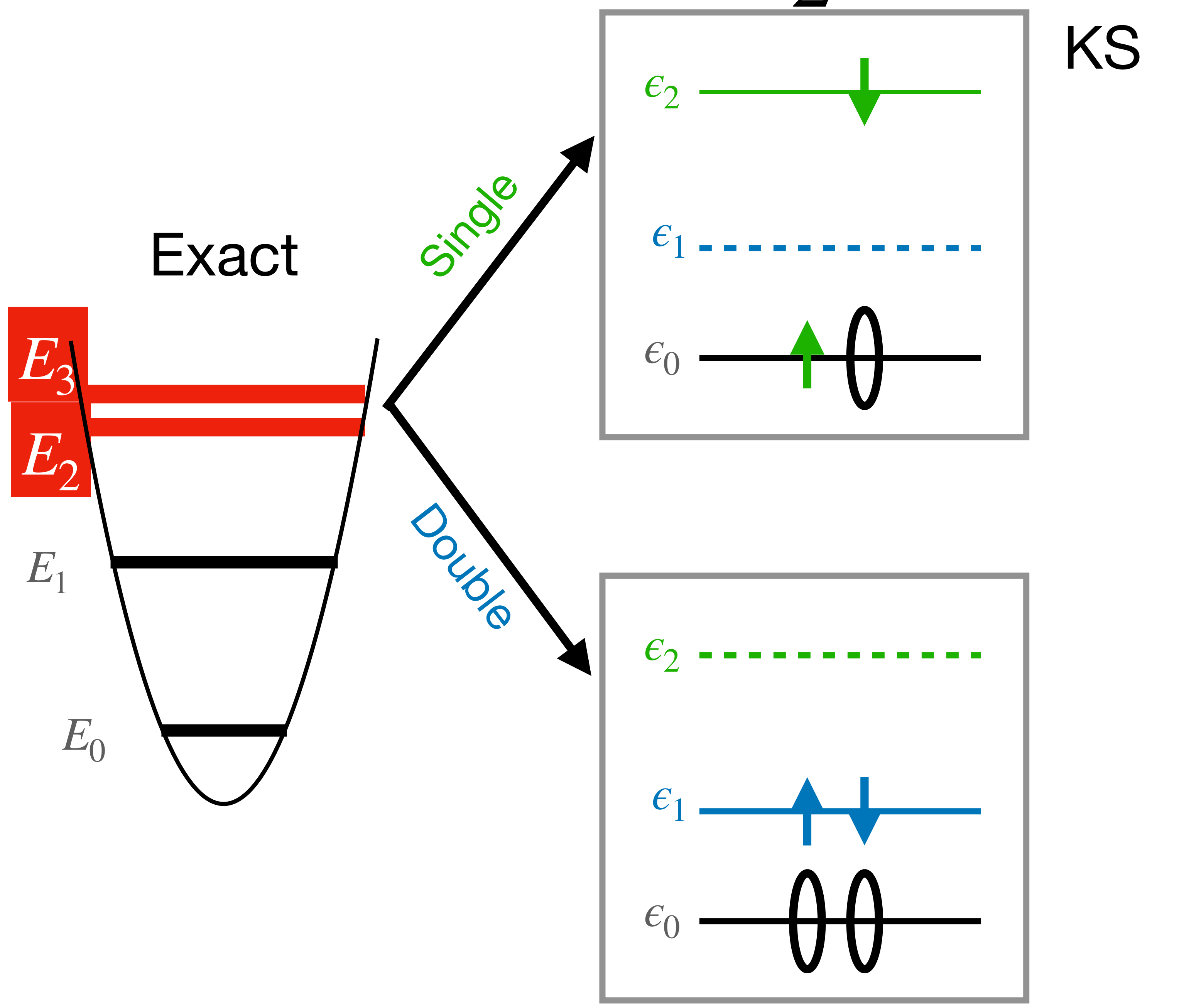
$$n_k(\mathbf{r}) = \frac{\delta E_k}{\delta v_{\text{ext}}(\mathbf{r})} = n_0(\mathbf{r}) + \frac{\delta \omega_k}{\delta v_{\text{ext}}(\mathbf{r})}$$

Can also get $n_k(\mathbf{r})$ for the doubly excited states!

A. Baranova and N. T. Maitra, *J. Chem. Theory Comput.*, to appear, 2025

e.g. 1d Harmonic potential: $v_{\text{ext}}(x) = \frac{1}{2}x^2 + \gamma|x|$

via Dressed TDDFT — compute $\frac{\delta\omega_k}{\delta v_{\text{ext}}(\mathbf{r})}$ when one single and one double mix



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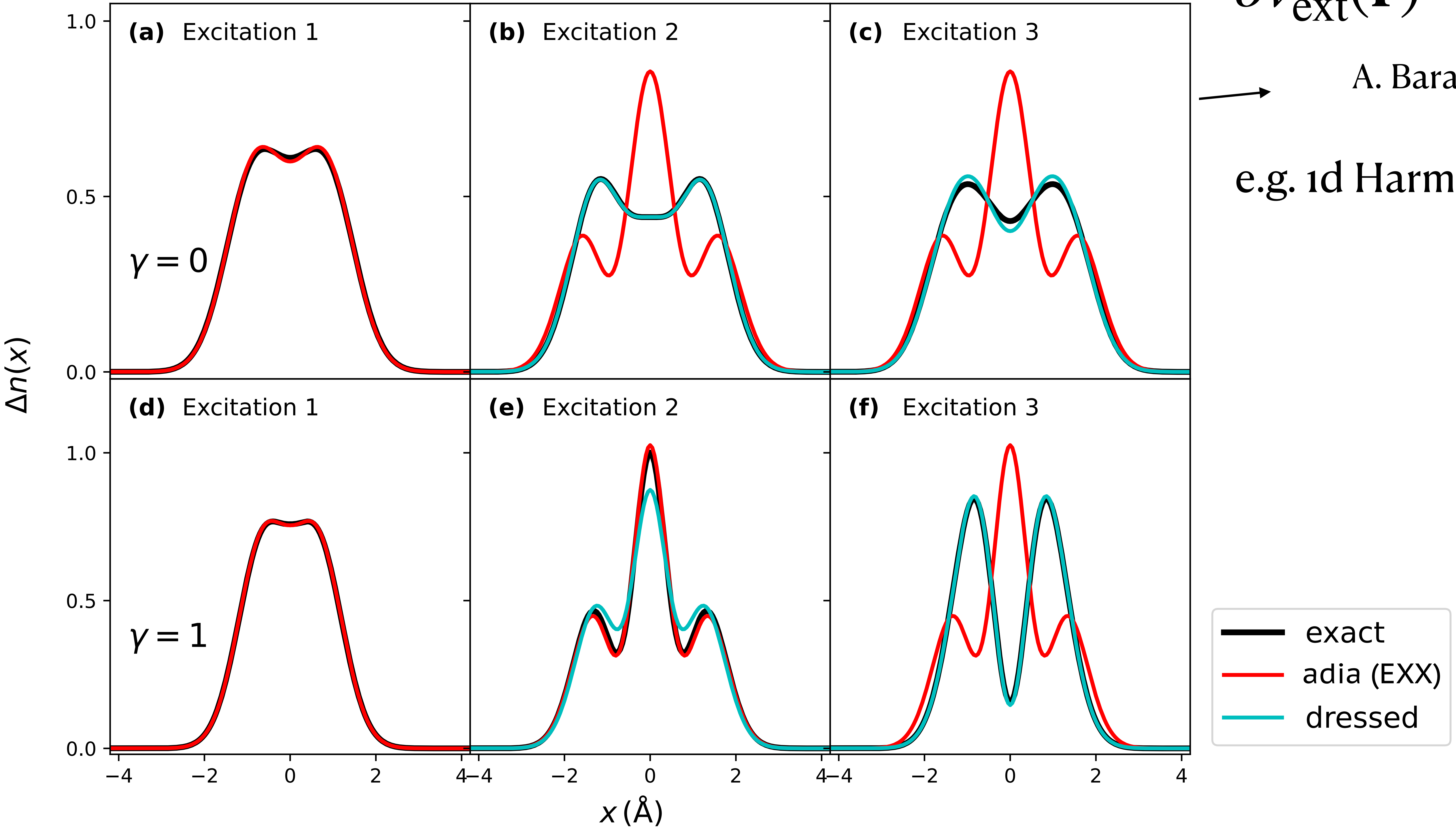

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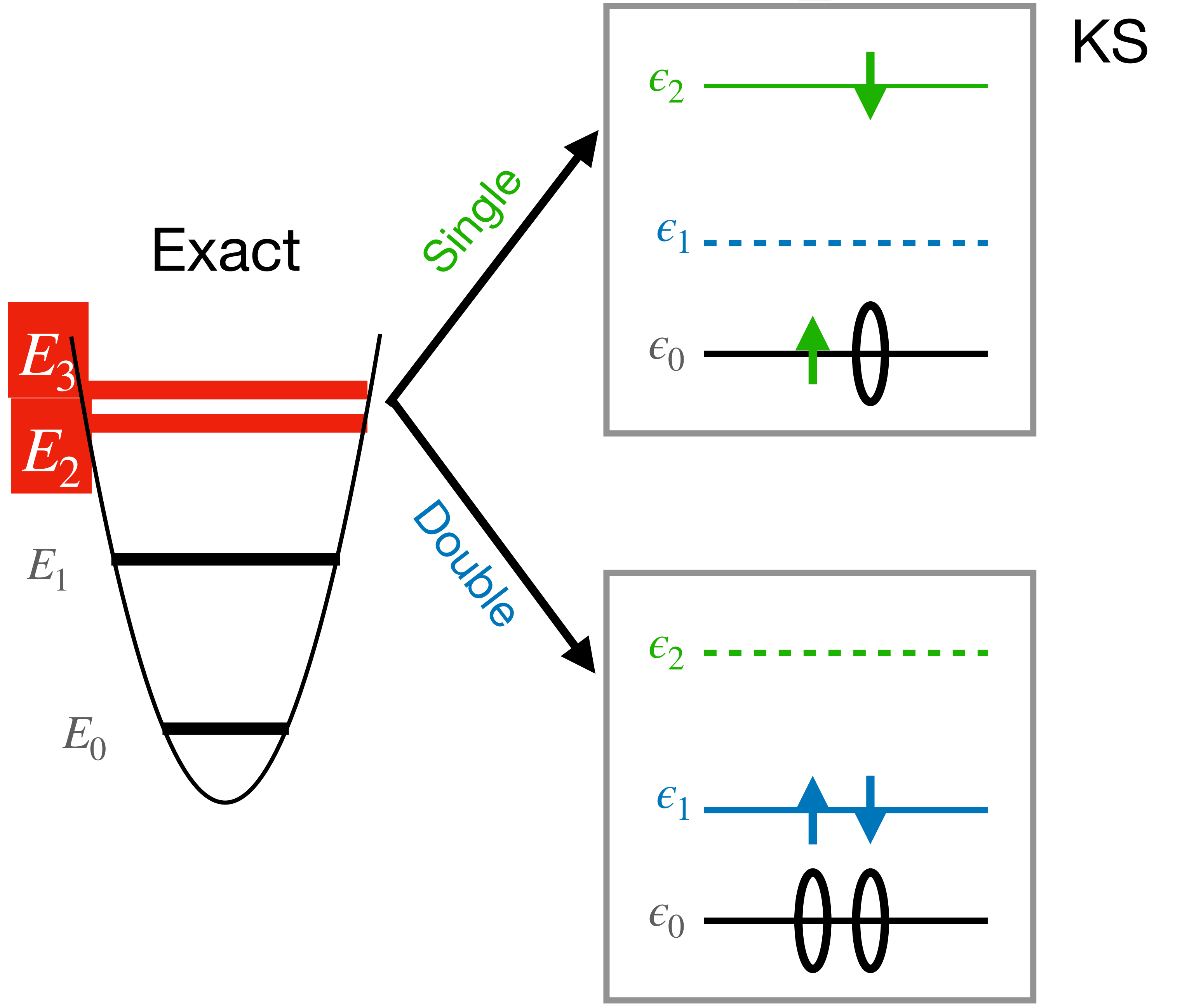
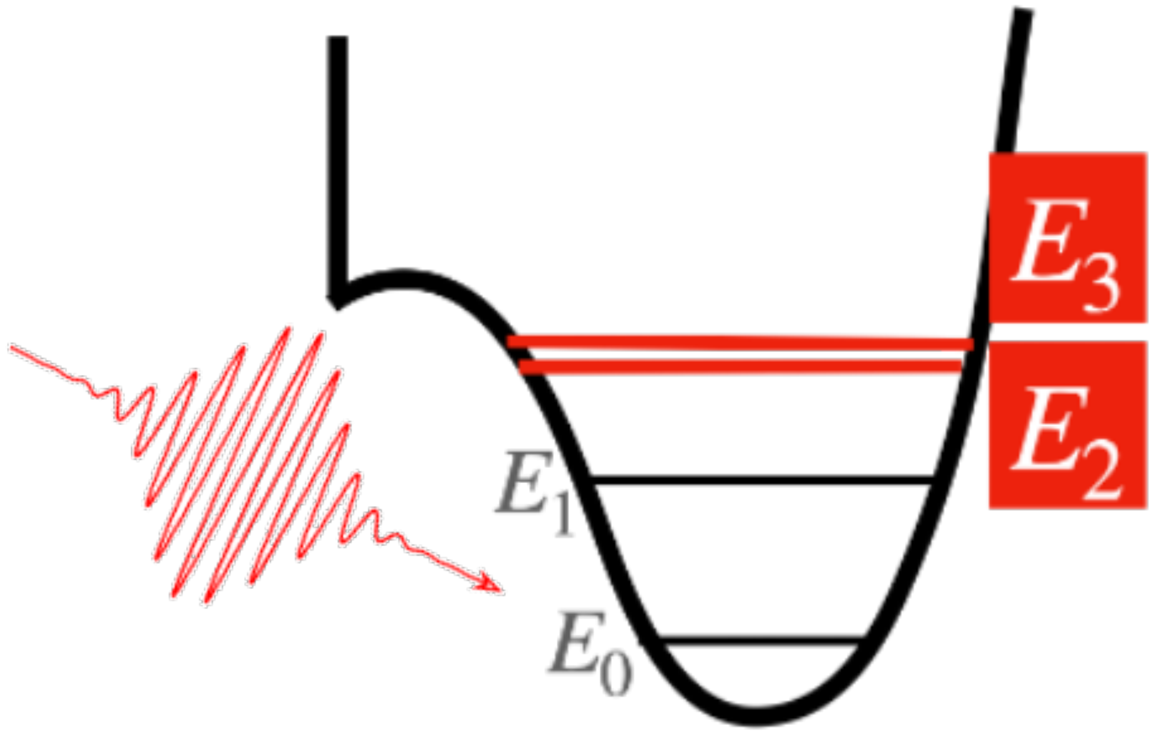


RR-TDDFT via DSMA — Dipole Evolution



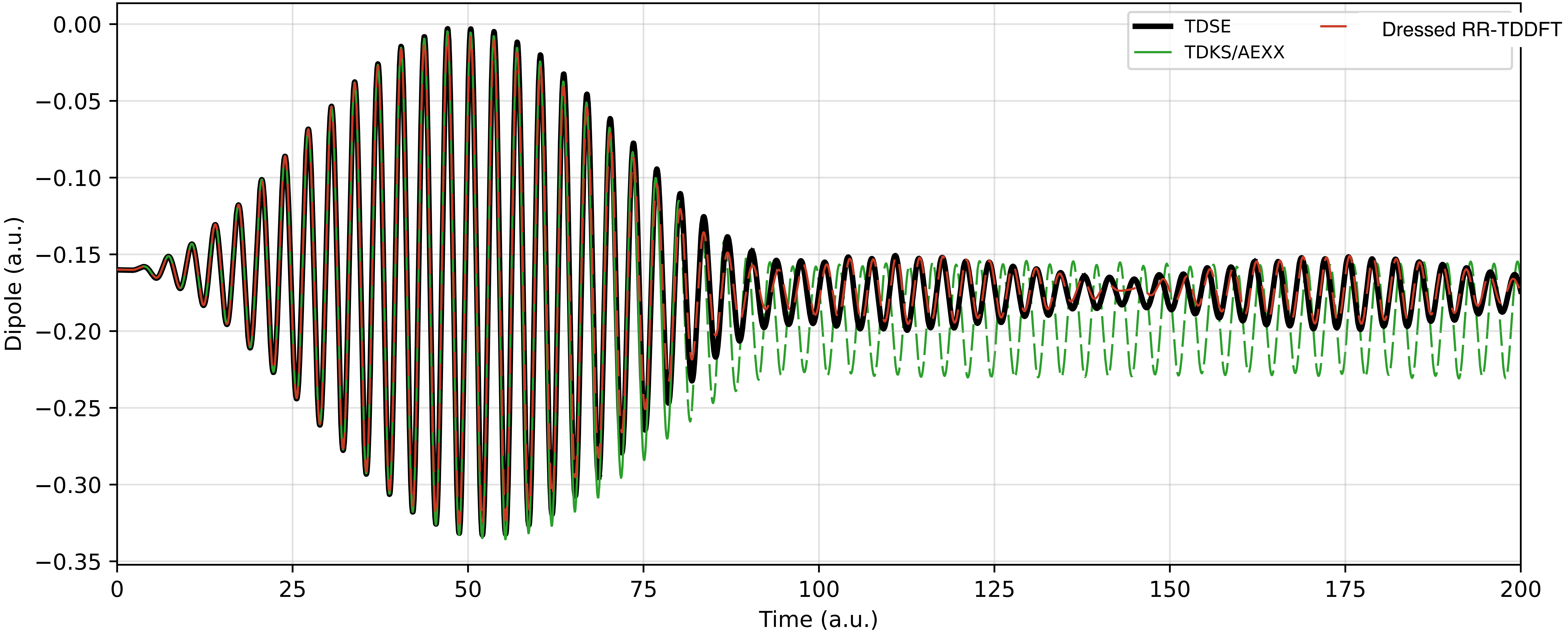
2 electrons in 1d model
potential

$\omega = 1.9$ a.u.

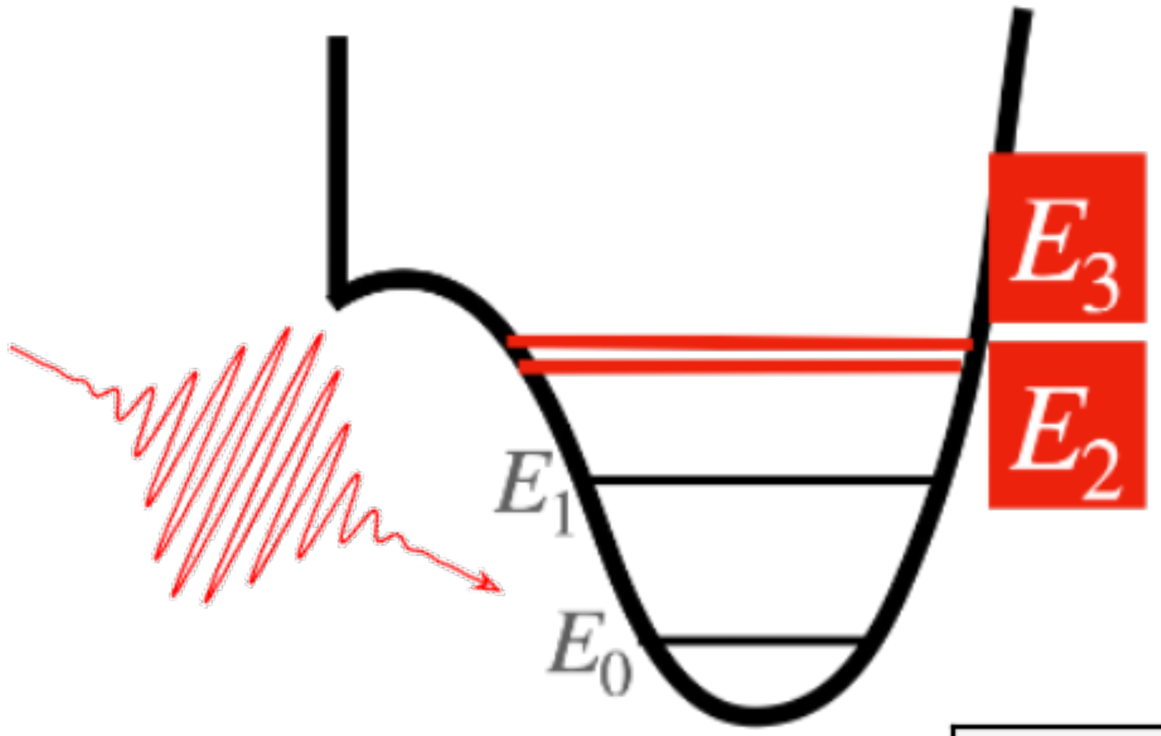
$$\varepsilon(t) = \begin{cases} 0.3\sin^2\left(\frac{\pi t}{100}\right)\sin(\omega t) \\ 0 \quad t > 100 \text{ a. u.} \end{cases}$$

driving pulse with $\omega = 1.9$ a.u.

Dhyey Ray



RR-TDDFT via DSMA — Density Evolution



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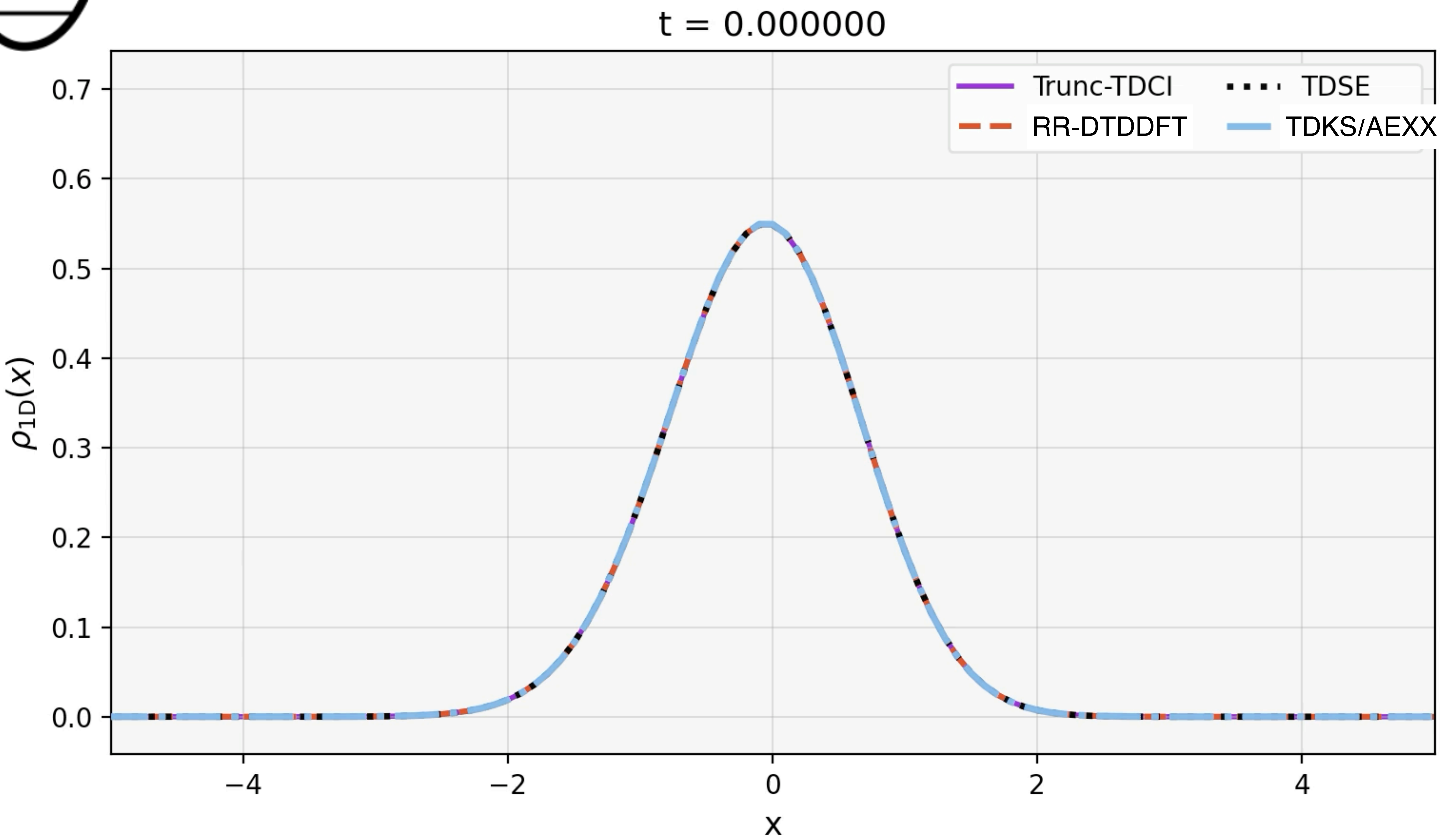


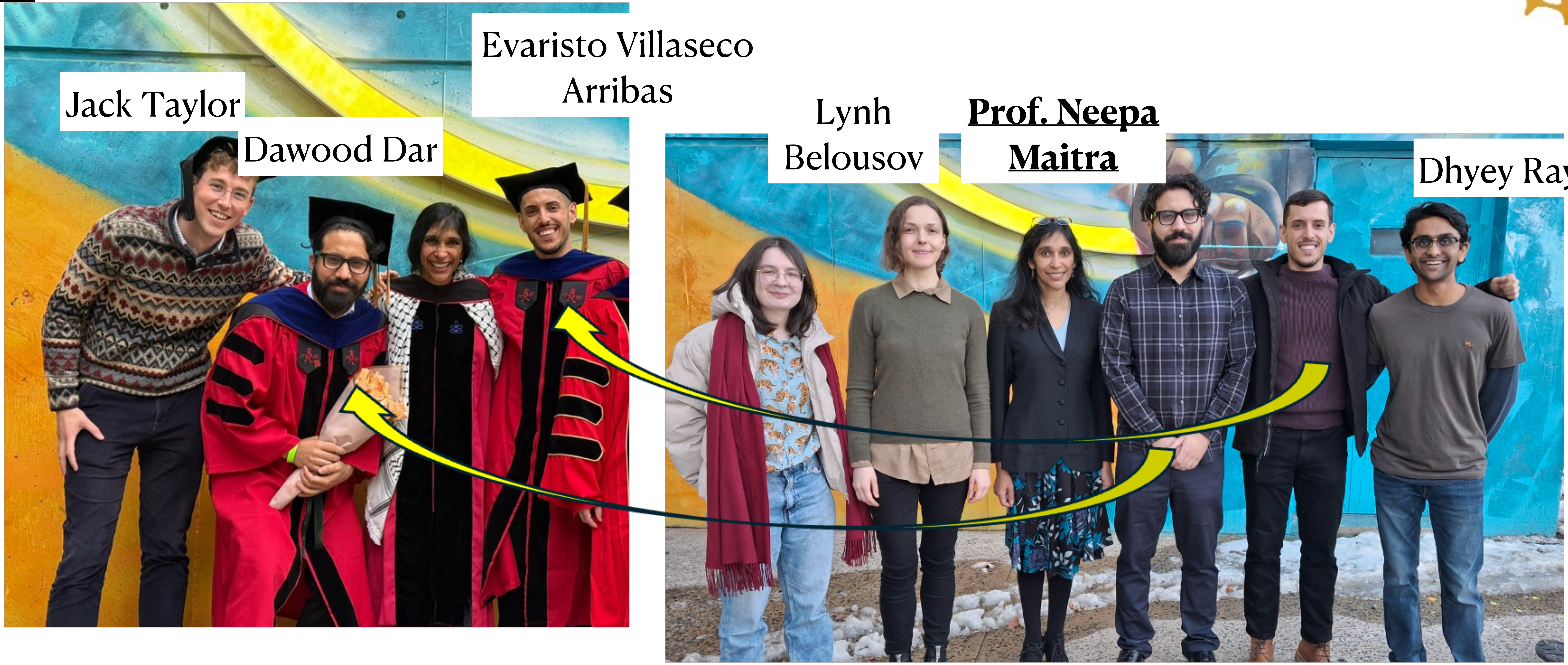
Conclusions

- RR-TDDFT enables TDDFT to be used as confidently and reliably for non-perturbative dynamics from the ground-state as it is for response properties

- RR-TDDFT outperforms TDKS under the same adiabatic approximation because it only needs xc functionals to be evaluated near ground states.

- RR-TDDFT can harness non-adiabatic functionals developed in the response-regime to describe the non-perturbative dynamics of the systems involving double excitations
  - Requires deriving densities of excited states, which can be done with available non-adiabatic approximations for the double excitations

Acknowledgements



Jack Taylor

Dawood Dar

Evaristo Villaseco Arribas

Lynh Belousov

Prof. Neepa Maitra

Dhyey Ray

Thank you for listening!

Dressed TDDFT kernel

$$\Omega(\omega)_{qq'} = \nu_q^2\delta_{qq'} + 4\sqrt{\nu_q\nu_{q'}}f_{\mathrm{HXC}qq'}(\omega)$$

$$f^{\mathrm{DTDDF}}_{\mathrm{XC}qq'}(\omega) = f^{\mathrm{adia}}_{\mathrm{XC}qq'} + X_{qq'}(\omega)$$

Different “flavors” of DTDDFT:

$$X^0_{qq'}(\omega) = \frac{H_{qD}H_{Dq'}}{4\sqrt{\nu_q\nu_{q'}}}\left[1+\frac{\left(H_{qq'}+H_{DD}-2H_{00}\right)^2}{\omega^2-\left(H_{DD}-H_{00}\right)^2}\right]$$

$$X^{\mathrm{s}}_{qq'}(\omega) = \frac{H_{qD}H_{Dq'}}{4\sqrt{\nu_q\nu_{q'}}}\left[1+\frac{\left(\nu_q+\nu_D\right)\left(\nu_{q'}+\nu_D\right)}{\omega^2-\nu_D^2}\right]$$

$$X^{\mathrm{a}}_{\mathrm{w}}(\omega) = \frac{H_{qD}H_{Dq'}}{4\sqrt{\nu_q\nu_{q'}}}\left[1+\frac{\left(\Omega^A_q+\Omega^A_{s1}+\Omega^A_{s2}\right)\left(\Omega^A_{q'}+\Omega^A_{s1}+\Omega^A_{s2}\right)}{\omega^2-\left(\Omega^A_{s1}+\Omega^A_{s2}\right)^2}\right]$$

For one single + one double characters in the excitation — Dressed Small Matrix Approximation

$$\omega^2 = \nu_q^2 + 4\nu_q f_{\mathrm{HXC}q}(\omega)$$

$$f^{\mathrm{DSMA}_0}_{\mathrm{xc}qq}(\omega) = f^{\mathrm{adia}}_{\mathrm{xc}qq} + \frac{\left|H_{qD}\right|^2}{4\nu_q}\left(1+\frac{\left(H_{qq}+H_{DD}-2H_{00}\right)^2}{\left[\omega^2-\left(\left(H_{DD}-H_{00}\right)^2+H_{qD}^2\right)\right]}\right)$$

Excited State Densities via Dressed TDDFT

For one single + one double characters in the excitation:

$$\omega^2 = \nu_q^2 + 4\nu_q f_{\mathrm{HXC}q}(\omega)$$

$$f^{\mathrm{DSMA}^*}_{\mathrm{xc}qq}(\omega) = f^{\mathrm{adia}}_{\mathrm{xc}qq} + \frac{\left|H_{qD}\right|^2}{4\nu_q}\left(1 + \frac{\left(\omega^{\mathrm{adia}} + (H_{DD} - H_{00})\right)^2}{\left[\omega^2 - \left(\left(H_{DD} - H_{00}\right)^2 + H_{qD}^2\right)\right]}\right)$$

$$n_k(\mathbf{r}) = n_0(\mathbf{r}) + \Delta n_k(\mathbf{r}) \nearrow = \frac{\delta\omega_k}{\delta v_{\mathrm{ext}}(\mathbf{r})}$$

$$\Delta n_\pm \approx G_\pm^2 \frac{\omega^{\mathrm{adia}}}{\omega_\pm} \Delta n^{\mathrm{adia}}(r)$$

Single excitation
character

$$+(1 - G_\pm^2)\frac{H_{dd} - H_{00}}{\omega_\pm}\frac{\delta\left(H_{dd} - H_{00}\right)}{\delta v_{\mathrm{ext}}(r)}$$

Double excitation
character

$$+\frac{1}{2\omega_\pm}\left(\frac{\delta H_{qd}^2}{\delta v_{\mathrm{ext}}(r)} \pm 2G_+G_-\frac{\delta}{\delta v_{\mathrm{ext}}(r)}\left[H_{qd}\left(\omega^{\mathrm{adia}} + \left(H_{dd} - H_{00}\right)\right)\right]\right)$$

Coupling
term

Excited State Densities via Dressed TDDFT

$$\Delta n_\pm \approx G_\pm^2 \frac{\omega^{\text{adia}}}{\omega_\pm} \Delta n^{\text{adia}}(r)$$

Single excitation
character

$$+(1-G_\pm^2)\frac{H_{dd}-H_{00}}{\omega_\pm}\frac{\delta\left(H_{dd}-H_{00}\right)}{\delta v_{\text{ext}}(r)}$$

Double excitation
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$$+\frac{1}{2\omega_\pm}\left(\frac{\delta H_{qd}^2}{\delta v_{\text{ext}}(r)} \pm 2G_+G_-\frac{\delta}{\delta v_{\text{ext}}(r)}\left[H_{qd}\left(\omega^{\text{adia}}+\left(H_{dd}-H_{00}\right)\right)\right]\right)$$

Coupling
term

$$\Phi_{mn}(\mathbf{x}) = \phi_m(\mathbf{x})\phi_n(\mathbf{x})$$

Evaluating Hamiltonian matrix elements (Slater-Condon selection rules applied)

One-body integrals $\frac{\delta}{\delta v_{\text{ext}}(\mathbf{r})}\left\langle \phi_r \middle| \hat{h} \middle| \phi_s \right\rangle = \Phi_{rs}(\mathbf{r}) + \int d^3x \left\{ \sum_{p\neq r}^{\infty} \frac{\left\langle \phi_p \middle| \hat{h} \middle| \phi_s \right\rangle}{\epsilon_r - \epsilon_p}\Phi_{pr}(\mathbf{x}) + \sum_{p\neq s}^{\infty} \frac{\left\langle \phi_r \middle| \hat{h} \middle| \phi_p \right\rangle}{\epsilon_s - \epsilon_p}\Phi_{ps}(\mathbf{x}) \right\} \left(I - f_{\text{Hxc}}\chi_{\text{S}}\right)^{-1}(\mathbf{x},\mathbf{r}),$

Two-body integrals
$$\frac{\delta}{\delta v_{\text{ext}}(\mathbf{r})}\left(\phi_r\phi_s \mid \phi_m\phi_n\right) = \int d^3x \left\{ \sum_{p\neq r}^{\infty} \frac{\left(\phi_p\phi_s \mid \phi_m\phi_n\right)}{\epsilon_r-\epsilon_p}\Phi_{pr}(\mathbf{x}) + \sum_{p\neq s}^{\infty} \frac{\left(\phi_r\phi_p \mid \phi_m\phi_n\right)}{\epsilon_s-\epsilon_p}\Phi_{ps}(\mathbf{x}) \right.$$
$$\left. + \sum_{p\neq m}^{\infty} \frac{\left(\phi_r\phi_s \mid \phi_p\phi_n\right)}{\epsilon_m-\epsilon_p}\Phi_{pm}(\mathbf{x}) + \sum_{p\neq n}^{\infty} \frac{\left(\phi_r\phi_s \mid \phi_m\phi_p\right)}{\epsilon_n-\epsilon_p}\Phi_{pn}(\mathbf{x}) \right\} \left(I - f_{\text{HXC}}\chi_{\text{S}}\right)^{-1}(\mathbf{x},\mathbf{r}),$$

Transition densities

From ground to excited state

$$\left|G_k\right|^2 = \frac{\omega_k \left| \overbrace{\left\langle \Psi_0 \right| \hat{n} \left| \Psi_k \right\rangle}^{\rho_{0k}} \right|^2}{v_q \left| \left\langle \Phi_0 \right| \hat{n} \left| \Phi_q \right\rangle \right|^2},$$

Available from Dressed TDDFT

From excited to excited state

$$\rho_{jk}(\mathbf{r}) = \left\langle \Psi_j \left| \hat{n} \right| \Psi_k \right\rangle$$

— approximation required