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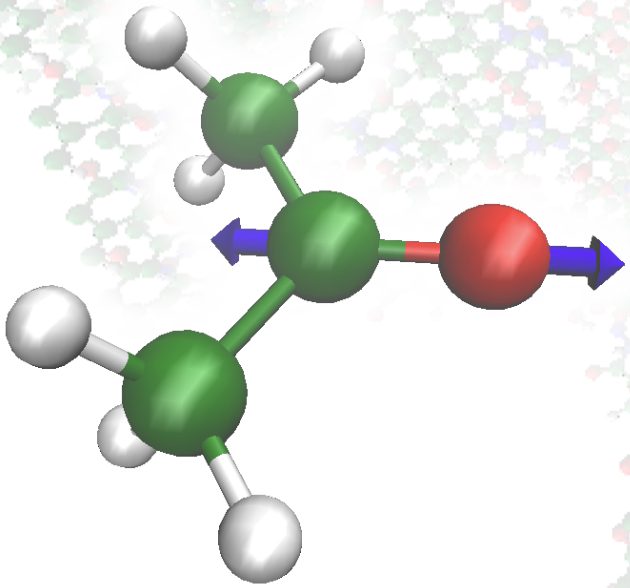
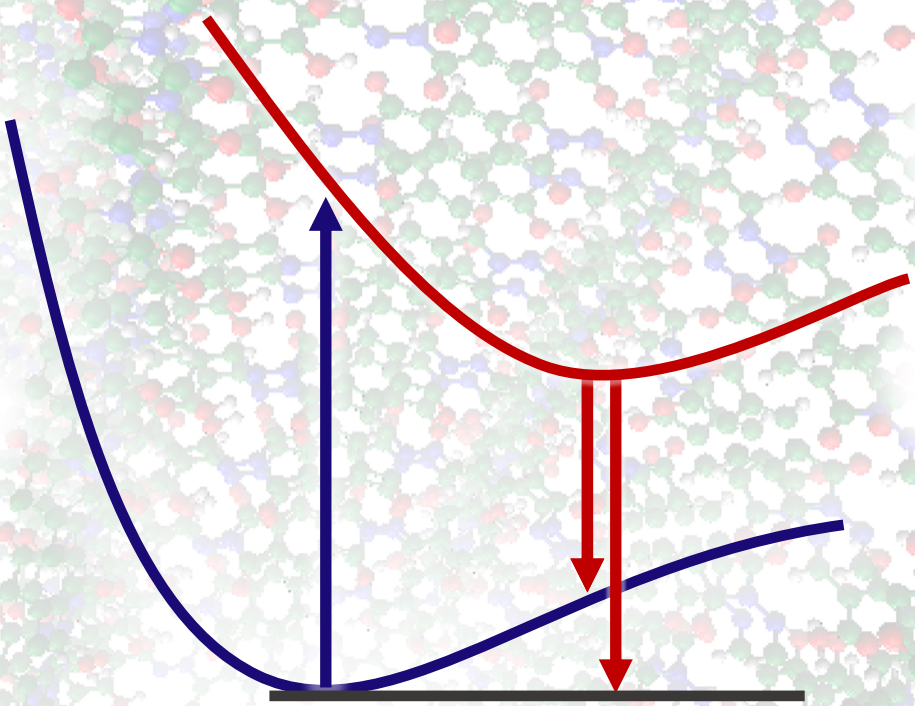
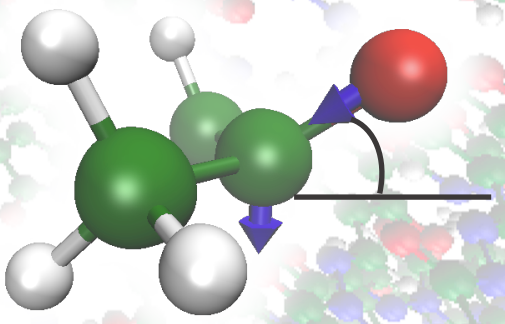
Towards efficient excited-state dynamics with hybrid functional accuracy for large-scale periodic systems

Anna Hehn, Beliz Sertcan, Fabian Belleflamme, Sergey Chulkov,
Matthew Watkins, Jürg Hutter



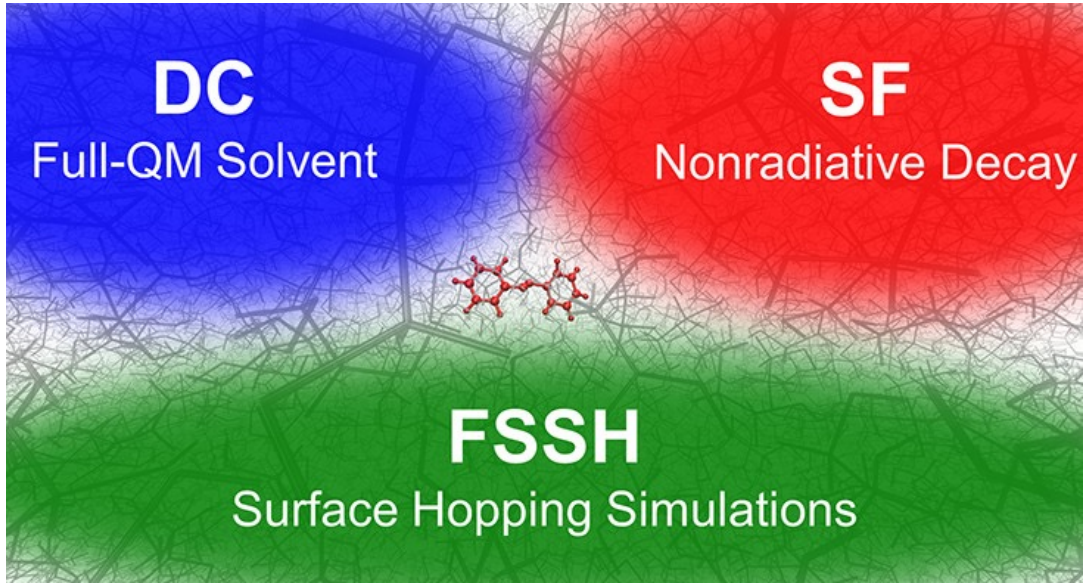




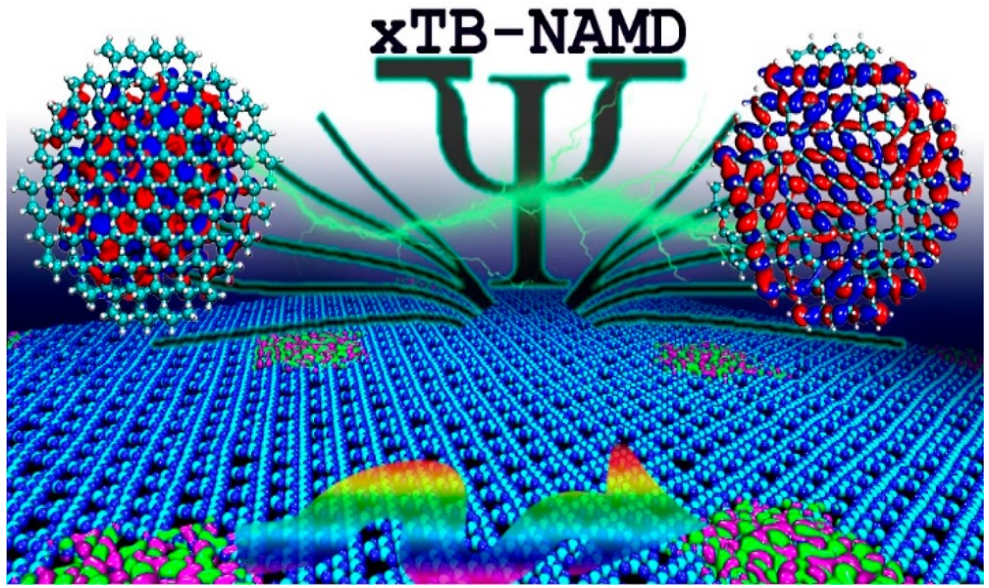
VISTA seminar series

August 17, 2022

Motivation



Divide and Conquer Spin-Flip TD-DFTB + orbital derivative couplings in the DCDFTB Code.
Uratani, Yoshikawa, Nakai, *JCTC 17*, 1290–1300 (**2021**).



Extended Tight-binding + orbital derivative couplings in the Libra code.
Shakiba, Stippell, Li, Akimov, *JCTC* (**2022**).

-> Efficient excited-state properties with hybrid functional accuracy for periodic systems

Theoretical spectroscopy for periodic systems

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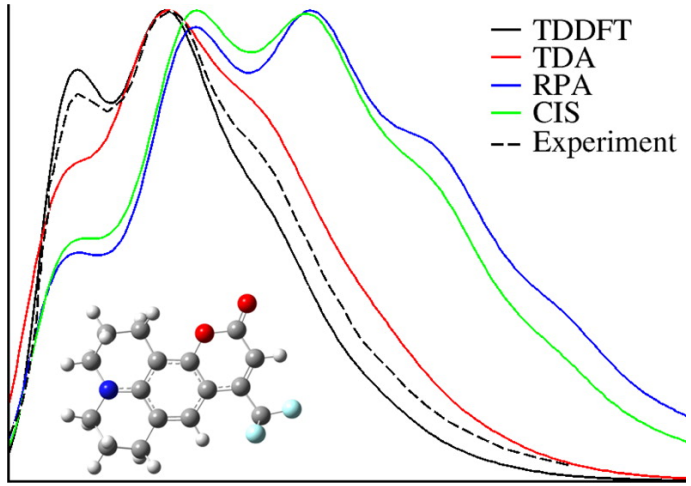
Tamm-Dancoff Approximation (TDA)
adequate model for absorption and fluorescence spectra

Jacquemin et al., *J. Chem. Theory Comput.* 9, 4517, (**2013**).



CP2K **AO-based formalism**

$$\mathbf{AX} = \mathbf{\Omega S X}$$

Projection to ensure $X_{ij\sigma} = 0$

$$\sum_{\kappa k} \left[F_{\mu\kappa\sigma}\delta_{ik} - F_{ik\sigma}S_{\mu\kappa}\right] X_{\kappa k\sigma} + \sum_{\kappa\lambda} Q^{\dagger}_{\mu\kappa\sigma} K_{\kappa\lambda\sigma}[\mathbf{D}^{\mathrm{X}}] C_{\lambda i\sigma} = \sum_{\kappa} \Omega S_{\mu\kappa} X_{\kappa i\sigma}$$

$$K_{\mu\nu\sigma}[\mathbf{D}^{\mathrm{X}}] = \sum_{\kappa\lambda\sigma'} D^{\mathrm{X}}_{\kappa\lambda\sigma'} \left[(\mu\nu|\kappa\lambda) - a_{\mathrm{EX}}\delta_{\sigma\sigma'}(\mu\kappa|\nu\lambda) + f^{\mathrm{XC}}_{\mu\nu\sigma,\kappa\lambda\sigma'}\right]$$

Coulomb

Exchange

XC functional

Approach I:
A robust formulation for exact exchange

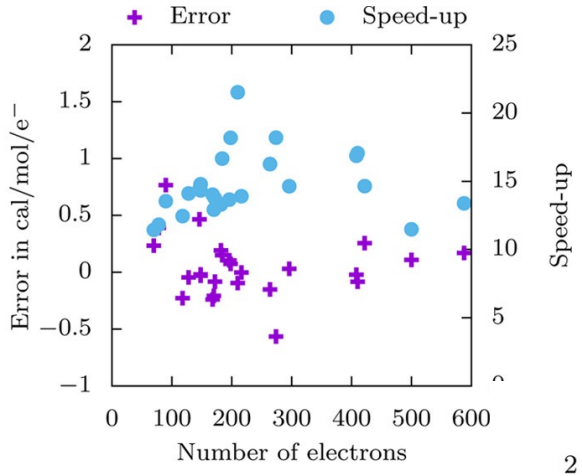
TDDFT

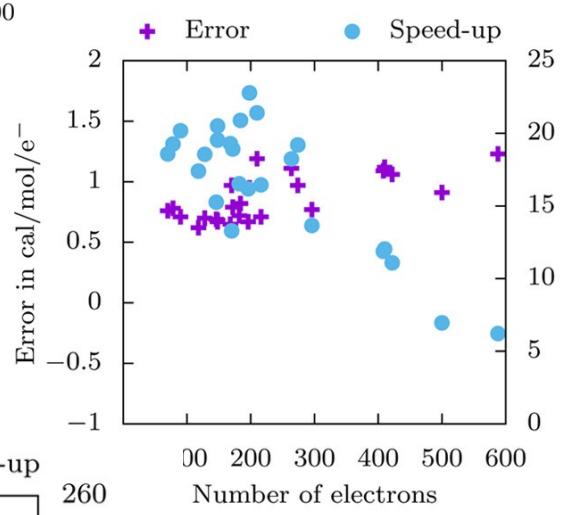
Efficient treatment of exact exchange

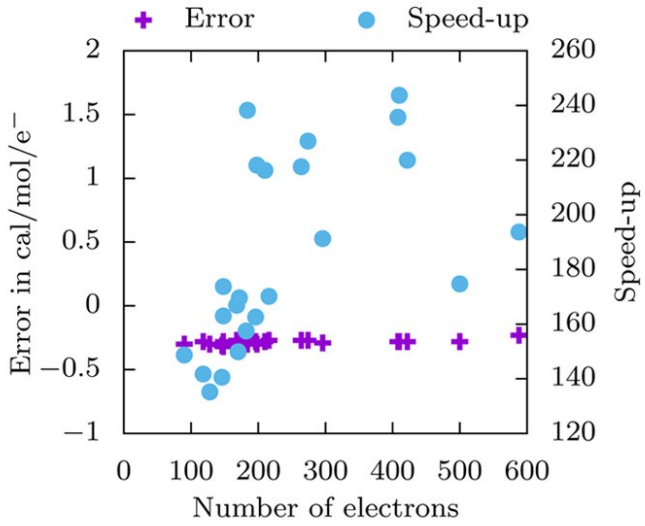
Numerical Integration
Neese, *Chem. Phys.* **(2008)**.

Density fitting
Merlot, *J. Comput. Chem.* **(2013).**

Auxiliary density matrix method (ADMM)
Hutter *et al. J. Chem. Theory Comput.* **(2010).**







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Rebolini *et al., J. Chem. Theory Comput.* (**2016**).

Approach I:
A robust formulation for exact exchange

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State-of-the-art algorithms to reduce the computational cost of exchange:

- Numerical integration (COSX) Neese, *Chem. Phys. 356*, 98 **(2008)**.
- Density fitting (PARI-K) Merlot, *J. Comput. Chem. 34*, 1486 **(2013)**.
- **Auxiliary density matrix method (ADMM)** Guidon *et al. J. Chem. Theory Comput. 6*, 2348 **(2010).**

$$D^{\mathrm{X}}_{\kappa\lambda\sigma}(\mu\kappa|\nu\lambda) \approx \sum_{\hat{\kappa}\hat{\lambda}}\sum_{\hat{\mu}\hat{\nu}} \hat{D}^{\mathrm{X}}_{\hat{\kappa}\hat{\lambda}\sigma}\hat{U}^{\mathrm{T}}_{\hat{\mu}\mu\sigma}(\hat{\mu}\hat{\kappa}|\hat{\nu}\hat{\lambda})\hat{U}_{\hat{\nu}\nu\sigma}$$

exact exchange with small auxiliary density

$$+\left[\sum_{\kappa\lambda} D^{\mathrm{X}}_{\kappa\lambda\sigma} f^{\mathrm{EX}}_{\mu\kappa\sigma,\nu\lambda\sigma} - \sum_{\hat{\kappa}\hat{\lambda}}\sum_{\hat{\mu}\hat{\nu}} \hat{D}^{\mathrm{X}}_{\hat{\kappa}\hat{\lambda}\sigma}\hat{U}^{\mathrm{T}}{}_{\hat{\mu}\mu\sigma} f^{\mathrm{EX}}_{\hat{\mu}\hat{\kappa}\sigma,\hat{\nu}\hat{\lambda}\sigma}\hat{U}_{\hat{\nu}\nu\sigma}\right]$$

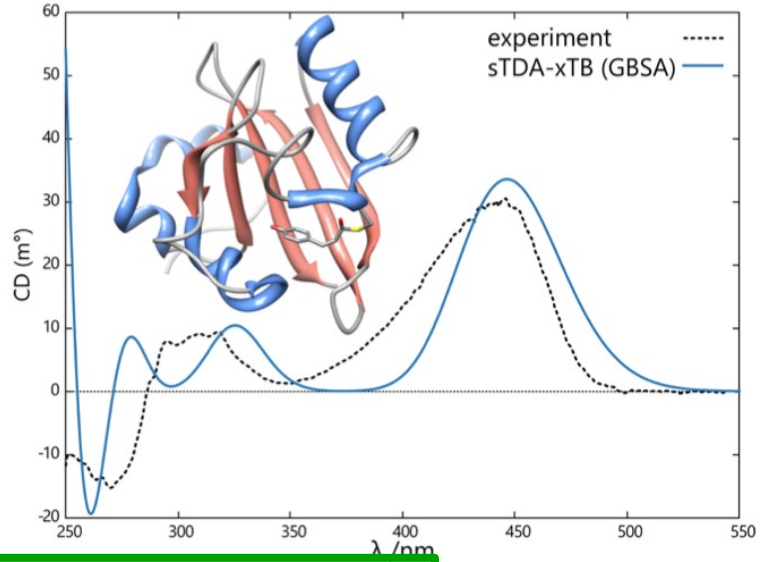
1st order GGA correction term

Possible ADMM variant:
Auxiliary density matrix by projection

$$\hat{\mathbf{D}} = \hat{\mathbf{U}}\mathbf{D}\hat{\mathbf{U}}^{\dagger} \qquad \hat{S}_{\hat{\mu}\hat{\nu}} = \int \hat{\varphi}_{\hat{\mu}}(\mathbf{r})\hat{\varphi}_{\hat{\nu}}(\mathbf{r})\,\mathrm{d}\mathbf{r}$$

$$\hat{\mathbf{U}} = \hat{\mathbf{S}}^{-1}\hat{\mathbf{V}} \qquad \hat{V}_{\hat{\mu}\nu} = \int \hat{\varphi}_{\hat{\mu}}(\mathbf{r})\varphi_{\nu}(\mathbf{r})\,\mathrm{d}\mathbf{r}$$

Approach II:
Semi-empirical tight binding



1. Semi-empirical tight binding

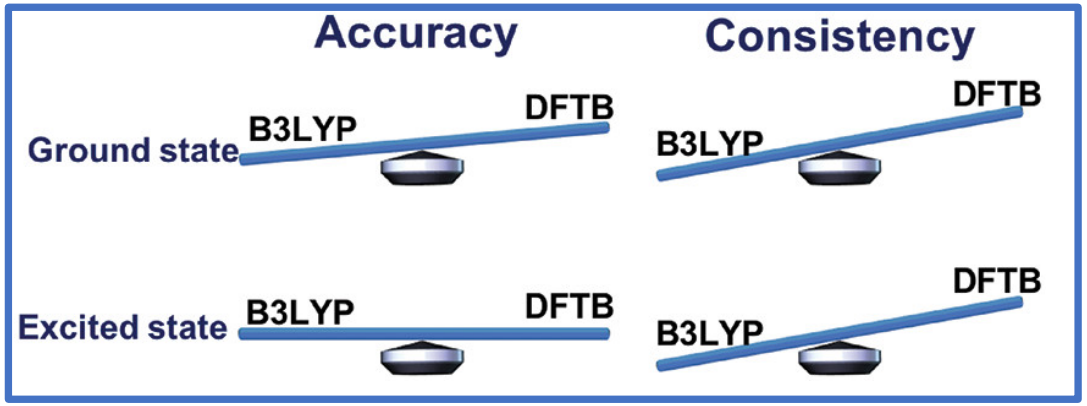
Extensions for excited-state properties

dftb.org

Elstner *et al.*, *J. Chem. Theory Comput.* (**2021**).

TDDFTB Benchmarks

Jacquemin *et al.*, *J. Chem. Theory Comput.* (**2019**).



Global parameters only!

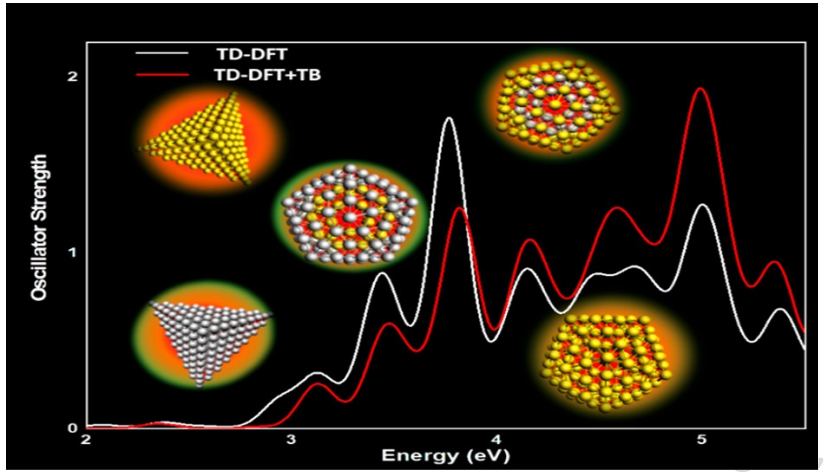
Simplified TDA (sTDA)

Grimme, *J. Chem. Phys.* (**2013**).

TDDFT+TB

Visscher *et al.*, *J. Phys. Chem. C* (**2020**).

SCM Software for Chemistry & Materials



2022

Approach II: Simplified Tamm Dancoff Approximation

$$K_{\mu\nu\sigma}[\mathbf{D}^{\mathrm{X}}] = \sum_{\kappa\lambda\sigma'} D^{\mathrm{X}}_{\kappa\lambda\sigma'} \left[(\mu\nu|\kappa\lambda) - a_{\mathrm{EX}}\delta_{\sigma\sigma'}(\mu\kappa|\nu\lambda) + f^{\mathrm{XC}}_{\mu\nu\sigma,\kappa\lambda\sigma'}\right]$$

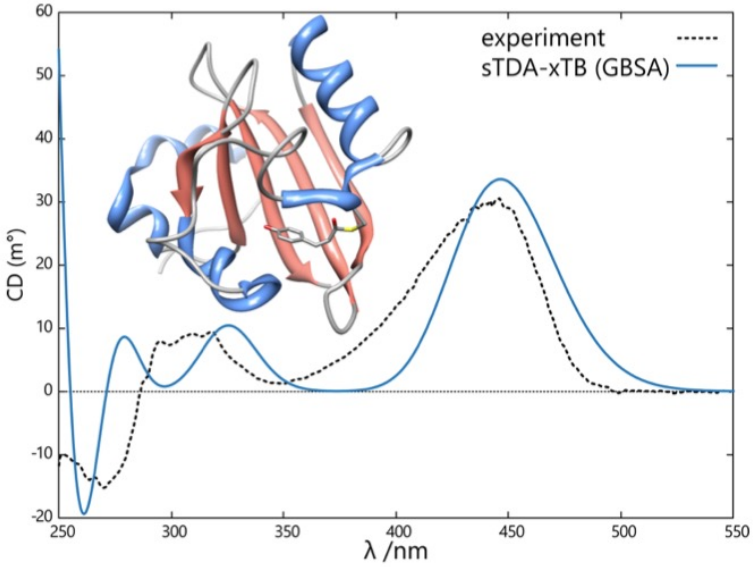
Semi-empirical tight binding reference

1. Approximate two-electron integrals

$$(pq\sigma|rs\sigma')^{\mathrm{sTDA}} = \sum_A \sum_B q^A_{pq\sigma} q^B_{rs\sigma'} \gamma(A,B)$$

$$\gamma(A,B) = \left(\frac{1}{(R_{AB})^{\alpha} + \eta^{-\alpha}}\right)^{1/\alpha}$$

2. Neglect XC kernel



→ **Minimal number of global parameters**

→ **Correct asymptotics for electron repulsion**

→ **System sizes of several hundreds of atoms**

Grimme *J. Chem. Phys.* 138, 244104, **(2013)**.

Treating periodicity within CP2K

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***Γ*-point only**, MOs and integrals are periodically replicated
Ewald summation for Coulomb contributions

Slightly different results in comparison to sTDA code by Grimme !

$$\gamma(A,B) = \left(\frac{1}{(R_{AB})^{\alpha} + \eta^{-\alpha}}\right)^{1/\alpha} \longrightarrow \gamma^{\mathrm{J}}_{\mathrm{PBC}}(A,B) + \frac{1}{R_{AB}}$$

semi-empirical short-range **exact long-range**

$$\gamma^{\mathrm{J}}_{\mathrm{PBC}}(A,B) = \eta \qquad = \left(\frac{1}{(R_{AB})^{\alpha} + \eta^{-\alpha}}\right)^{1/\alpha} \qquad = f(\bar{R})\gamma^{\mathrm{J}}(A,B) - \frac{f(\bar{R})}{R_{AB}}$$

Excited-state properties for ADMM and sTDA: a Lagrangian for AO-based TDDFT

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Lagrange / Z vector formalism to avoid 1st order response:

1. Excitation energies

$$\mathbf{A}\mathbf{X}_n = \mathbf{\Omega}_n \mathbf{S}\mathbf{X}_n \quad \text{with} \quad \mathbf{X}_n^\dagger \mathbf{S}\mathbf{X}_m = \mathbf{1}$$

Geometry dependence of AOs

Lagrangian for state *n*: $L = \Omega + \bar{\mathbf{Z}}\mathbf{F} + \bar{\mathbf{W}}\mathbf{S}$

2. Z vector equation

$$\frac{\partial L}{\partial \mathbf{C}} \rightarrow \mathbf{B}\bar{\mathbf{Z}} = -\mathbf{R}$$

3. Excited-state gradient

$$\frac{\partial L}{\partial \zeta} = \frac{\partial \Omega}{\partial \zeta} + \bar{\mathbf{Z}}\frac{\partial \mathbf{F}}{\partial \zeta} + \bar{\mathbf{W}}\frac{\partial \mathbf{S}}{\partial \zeta}$$

Brillouin condition

$$\sum_{ia\sigma} \bar{Z}_{ia\sigma} F_{ia\sigma} = \sum_{i\mu\nu\sigma} \bar{Z}_{i\nu\sigma} Q^\dagger_{\mu\nu\sigma} F_{\mu i\sigma}$$

$$= \sum_{i\mu\nu\sigma} \bar{Z}_{i\nu\sigma} (F_{\nu\mu\sigma} C_{\mu i\sigma} - S_{\nu\mu} C_{\mu i\sigma} \varepsilon_{i\sigma})$$

Furche, Ahlrichs, *J Chem Phys*, 121, 12772 (**2002**); Hutter, *J Chem Phys*, 118, 3928 (**2003**).

Excited-state properties: a Lagrangian for AO-based TDDFT

University of Zurich[UZH]

Lagrange / Z vector formalism to avoid 1st order response:

1. Excitation energies

$$\mathbf{A}\mathbf{X}_n = \boldsymbol{\Omega}_n \mathbf{S}\mathbf{X}_n \quad \text{with} \quad \mathbf{X}_n^\dagger \mathbf{S}\mathbf{X}_m = \mathbf{1}$$

$$L = \Omega + \bar{\mathbf{Z}}\mathbf{F} + \bar{\mathbf{W}}\mathbf{S}$$

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$$\frac{\partial L}{\partial \mathbf{C}} \rightarrow \mathbf{B}\bar{\mathbf{Z}} = -\mathbf{R}$$

3. Excited-state gradient

$$\frac{\partial L}{\partial \zeta} = \frac{\partial \Omega}{\partial \zeta} + \bar{\mathbf{Z}}\frac{\partial \mathbf{F}}{\partial \zeta} + \bar{\mathbf{W}}\frac{\partial \mathbf{S}}{\partial \zeta}$$

Transformation rules

$$M^{\mathrm{AO}}_{\mu\nu\sigma} = \sum_{\kappa\lambda kl} S_{\mu\kappa} C^{\mathrm{T}}_{\kappa k\sigma} M^{\mathrm{MO}}_{kl\sigma} C_{l\lambda\sigma} S_{\lambda\nu}$$

$$M^{\mathrm{MO}}_{kl\sigma} = \sum_{\kappa\lambda} C^{\mathrm{T}}_{\kappa k\sigma} M^{\mathrm{AO}}_{\kappa\lambda\sigma} C_{\lambda l\sigma}$$

Projection for Lagrange multipliers

$$\frac{\partial L}{\partial \mathbf{C}}\mathbf{C} = 0 \rightarrow \bar{\mathbf{W}} \qquad \frac{\partial L}{\partial \mathbf{C}}\mathbf{Q} = 0 \rightarrow \bar{\mathbf{Z}}$$

Furche, Ahlrichs, *J Chem Phys*, 121, 12772 (**2002**); Hutter, *J Chem Phys*, 118, 3928 (**2003**).

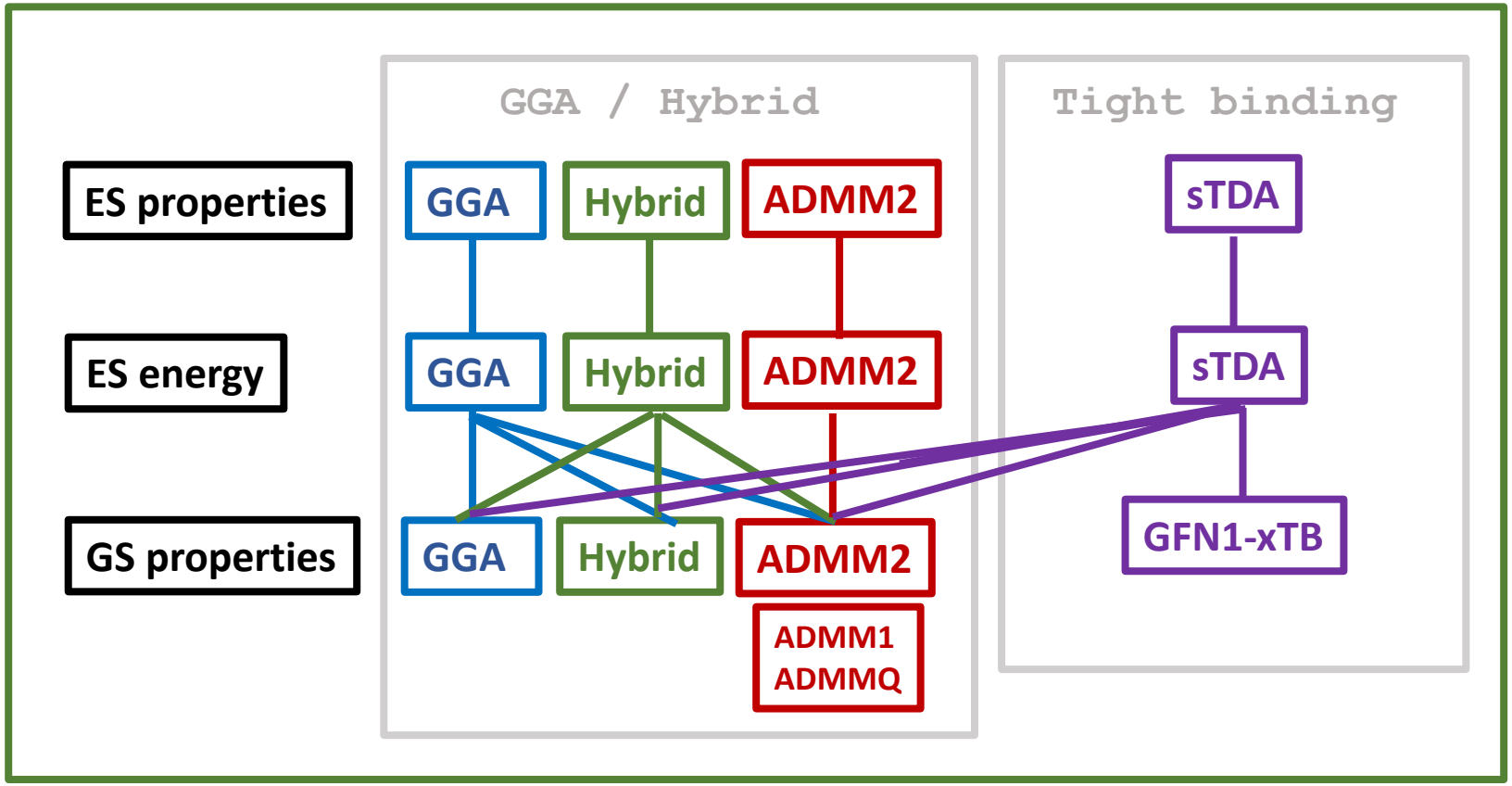
http://www.cp2k.org/

The TDDFT module in CP2K

University of Zurich[UZH]

⟶ Unified TDDFT code for excited-state properties

```
&GLOBAL
 RUN_TYPE GEO_OPT
&END GLOBAL
&PROPERTIES
   &TDDFPT
      KERNEL FULL / sTDA
      NSTATES 10
      MAX_ITER 100
      CONVERGENCE [eV] 1.0e-7
      RKS_TRIPLETS F
   &END TDDFPT
&END PROPERTIES
&DFT
   &EXCITED_STATES T
    STATE 3
   &END EXCITED_STATES
&AUXILIARY_DENSITY_MATRIX_METHOD
&END ADMM
   &XC
    &XC_FUNCTIONAL PBE0
    &END XC_FUNCTIONAL
   &END XC
&END DFT
```



Iannuzzi *et al.*, CHIMIA, 59, 499 **(2005);** Strand *et al. J. Chem. Phys.* 150, 044702 **(2019)**.

I. Accuracy benchmark for molecular systems

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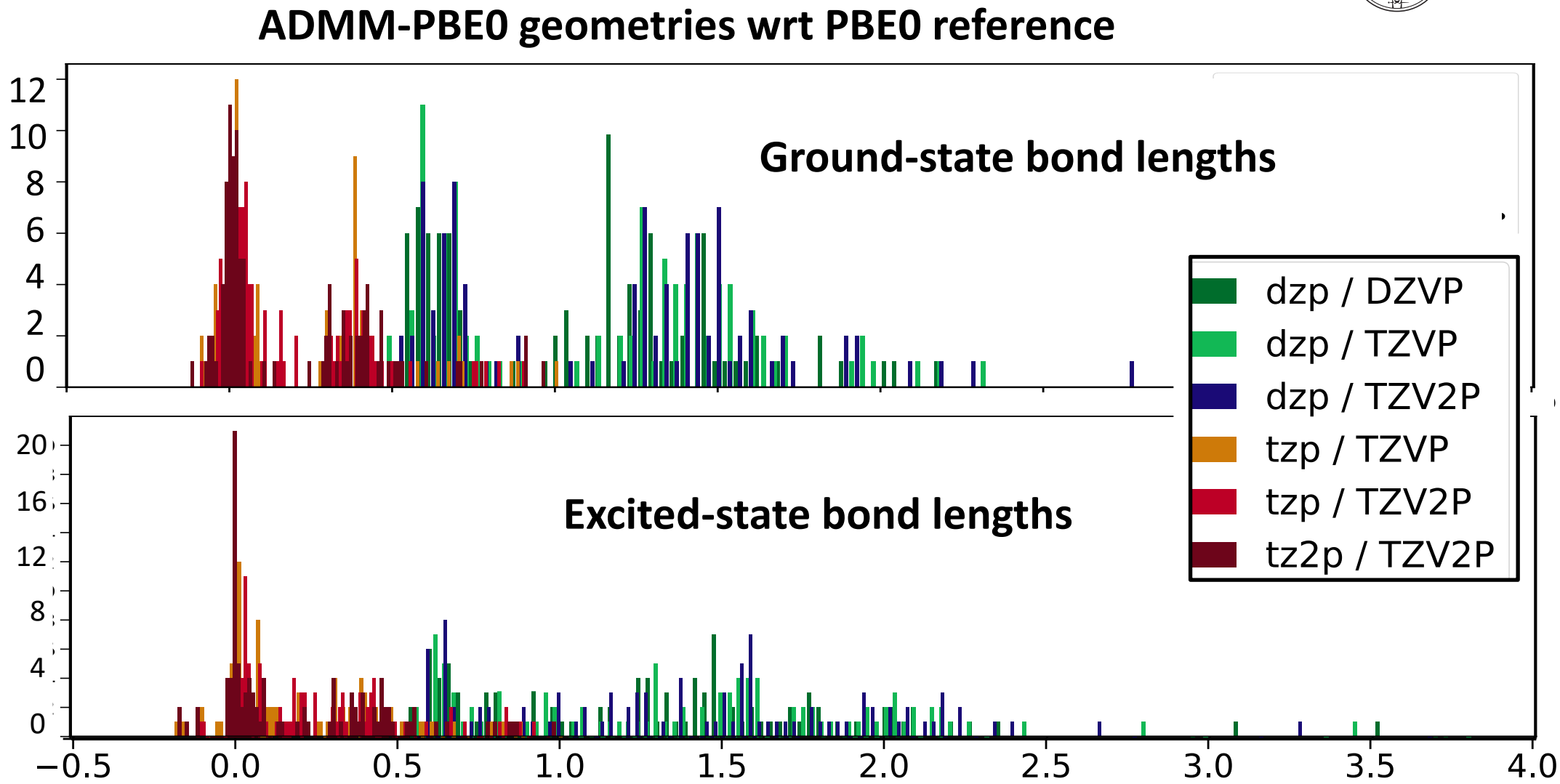


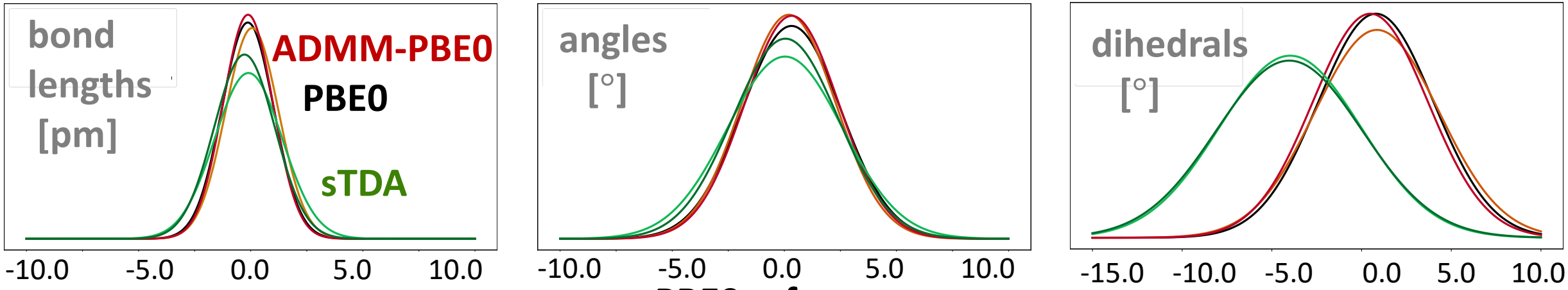
➡ **ADMM error < 0.3 pm | < 0.1° for triple-zeta basis sets**

Jacquemin *et al. J. Chem. Theory Comput. 13,* 6237 **(2017)**.

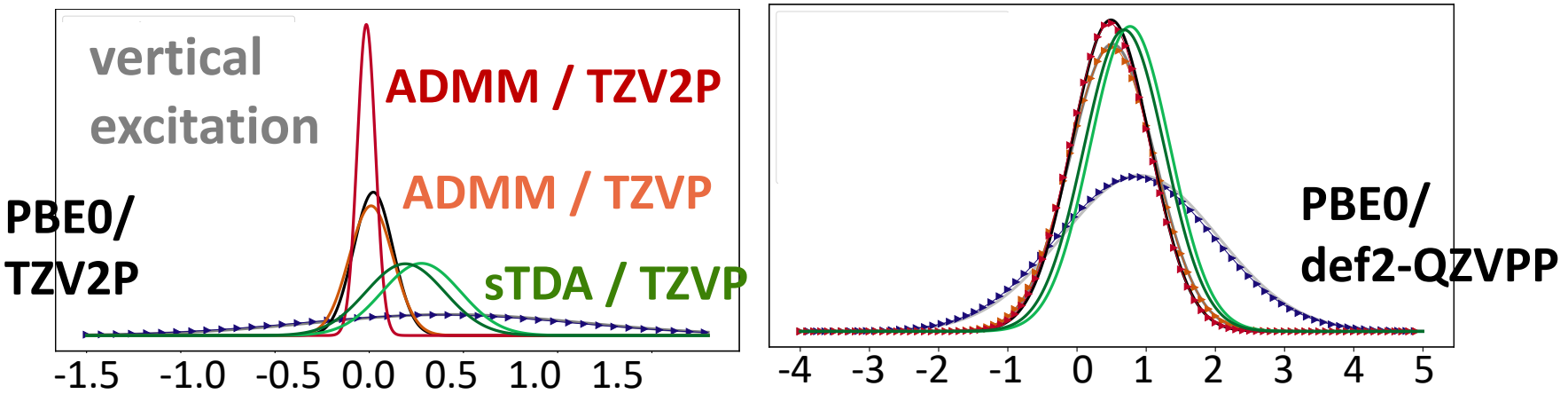
I. Accuracy benchmark for molecular systems

University of Zurich[UZH]

wrt EOM-CCSD reference



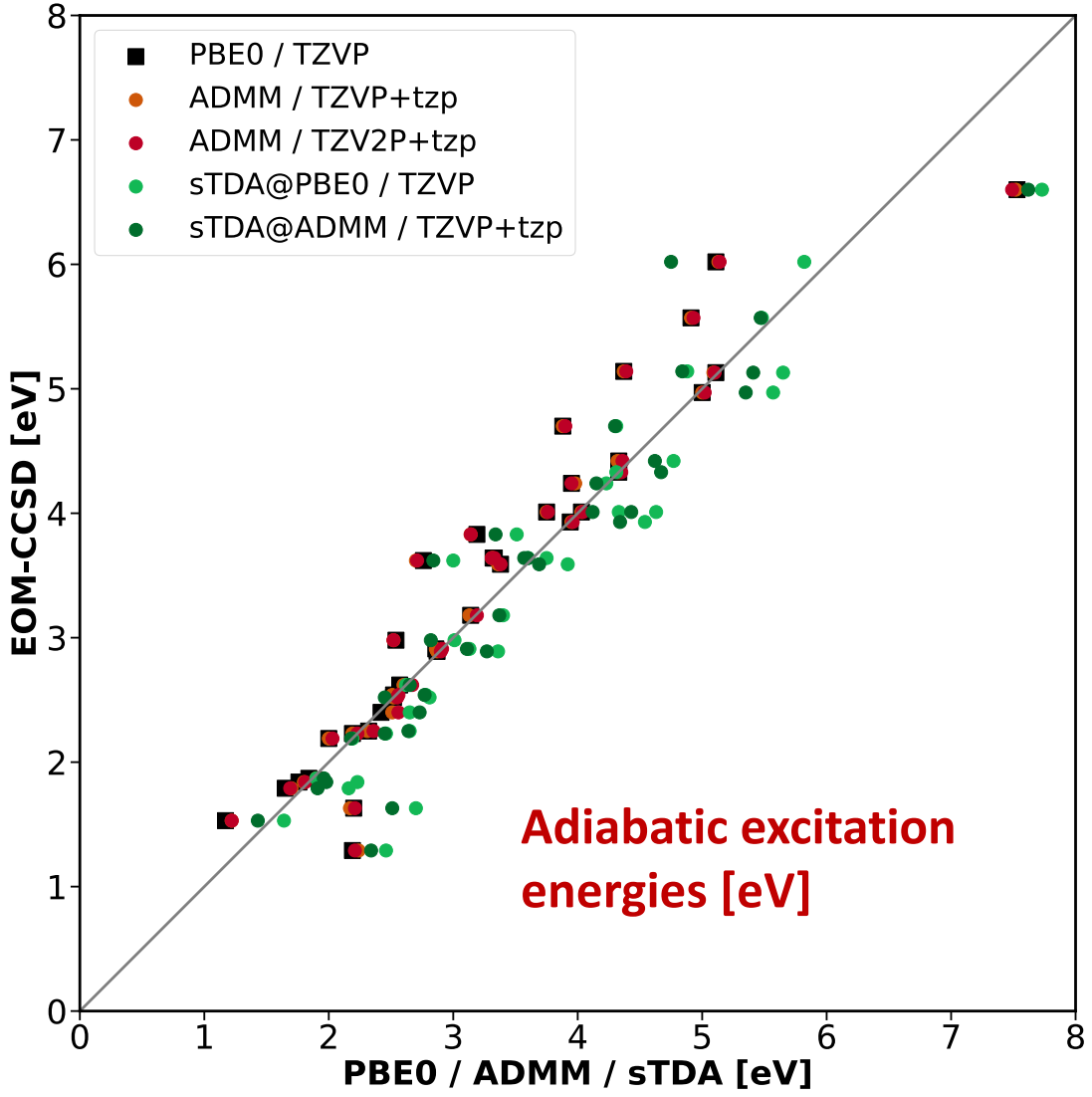
wrt PBE0 reference

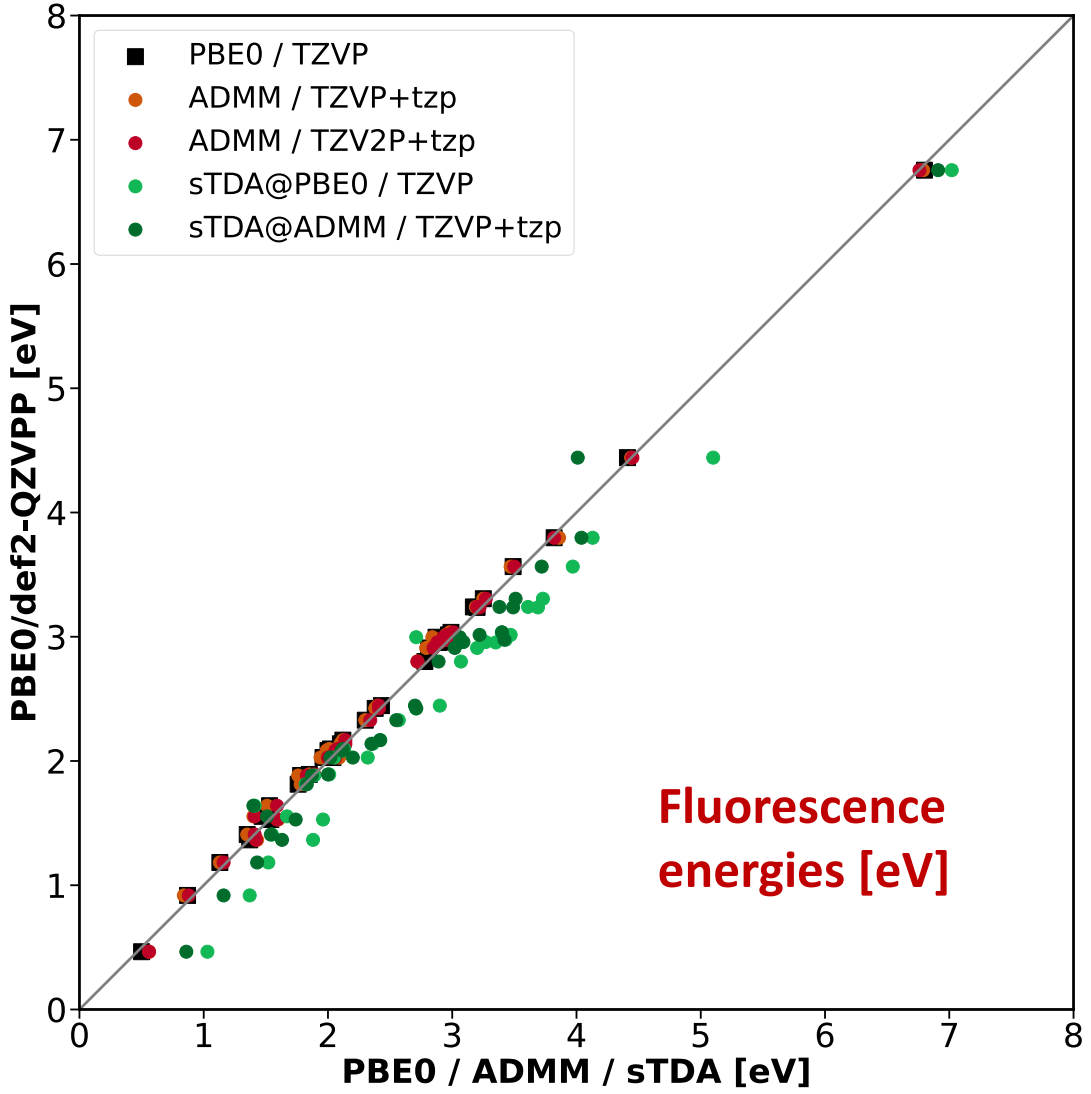


➡ **Error sTDA < 1.1 pm | < 1.6° for triple-zeta basis sets**

PBE0/ADMM < 0.9 pm | < 1.2°

I. Accuracy benchmark for molecular systems





Errors in the range of 0.2 – 0.5 eV

II. Application to periodic systems

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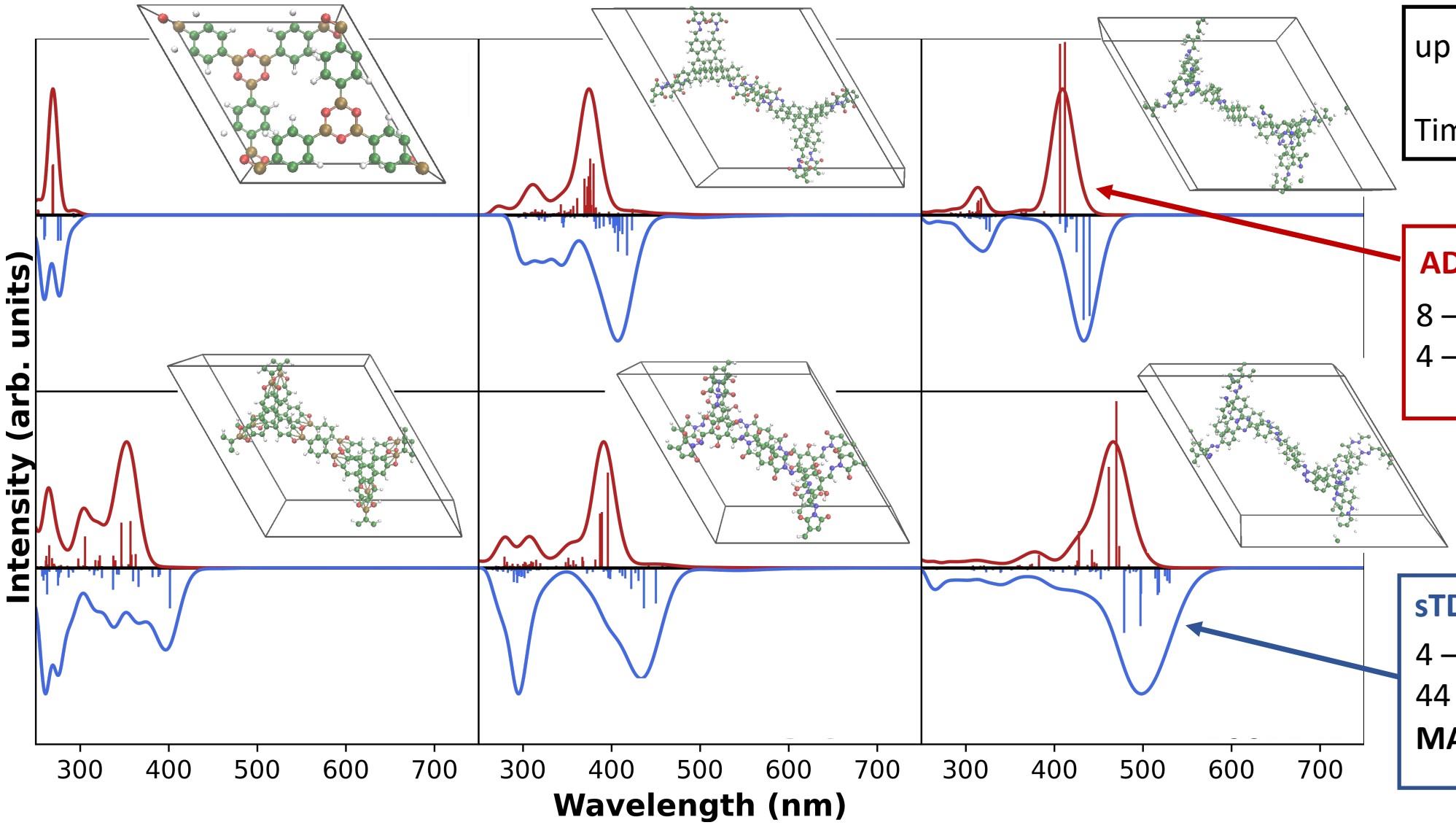

up to 300 atoms
7440 basis functions
Timings for 2304 cores

ADMM-PBE0

8 – 30 min for ES opt step
4 – 10 hrs for 500 ES

sTDA

4 – 10 min for ES opt step
44 mins for 500 ES
MAD of 0.31 – 0.42 eV

gain in efficiency by at least one order of magnitude

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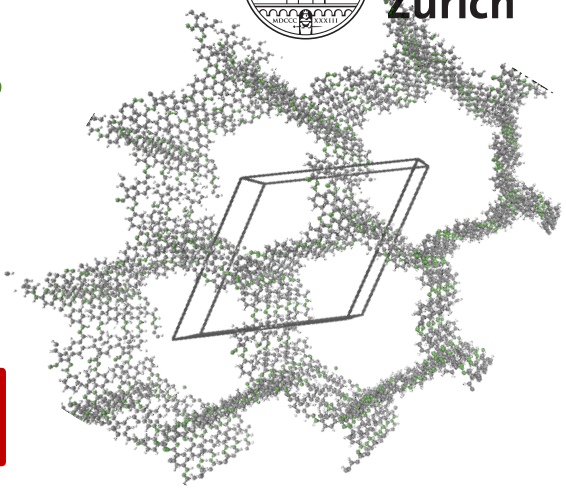
Summary / Outlook: Toward efficient excited-state dynamics

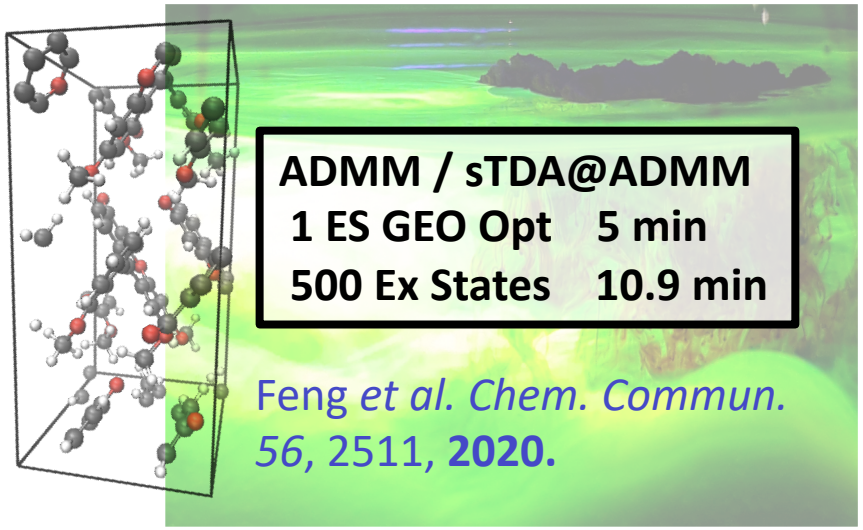


New TDDFT module in CP2K for excited-state properties of periodic systems

GGA / Hybrid functionals

KS – DFT / Tight binding

From hrs to mins!



Auxiliary Density Matrix Method

Speedup by 1 order of magnitude compared to hybrid functional

Accuracy of 0.3 pm / 0.02 – 0.07 eV wrt PBE0 reference

Simplified Tamm-Dancoff Approximation

Speedup by 1 order of magnitude in comparison to ADMM for broad-range spectra

Accuracy of 1.1 pm / 0.2 – 0.5 eV wrt EOM-CCSD reference

J. Chem. Theory Comput. **2022**, 18, 4186.

Summary / Outlook: Towards excited-state dynamics

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Excited-state properties with hybrid functional accuracy

- ADMM-TDDFT
- Semi-empirical sTDA

Periodic boundary conditions

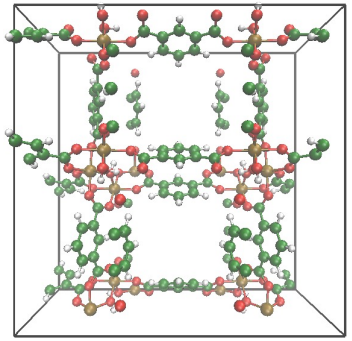
CP2K + NX newtonx.org

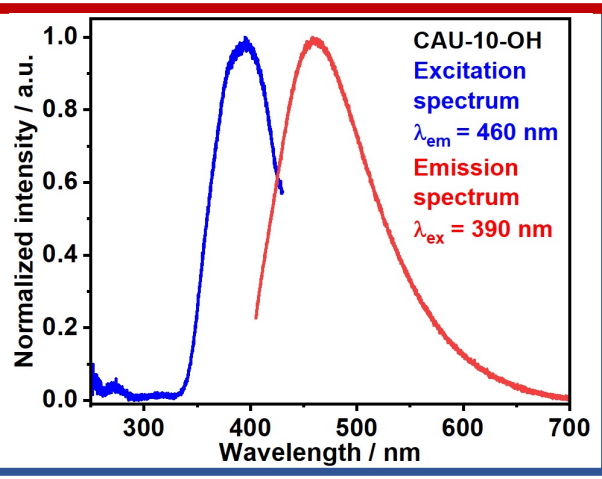
Adiabatic and Nonadiabatic dynamics

On-the-fly velocity Verlet MD
Fewest switches surface hopping
Local diabatization
Decoherence corrections

Barbatti *et al., WIREs: Comp. Mol. Sci.* 4, 26 (**2014**).

Fluorescence CAU10-MOFs





Efficient nonadiabatic couplings

Orbital derivative couplings
Baeck-An couplings

$$\sigma_{MN} \approx \frac{\mathrm{sgn}(\Delta E_{MN})}{2} \sqrt{\frac{1}{\Delta E_{MN}} \frac{\mathrm{d}^2 \Delta E_{MN}}{\mathrm{d}t^2}}$$

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Sergey Chulkov (Uni Lincoln)

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Questions / comments: **Email:** anna.hehn@chem.uzh.ch
Twitter: @anna_hehn

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