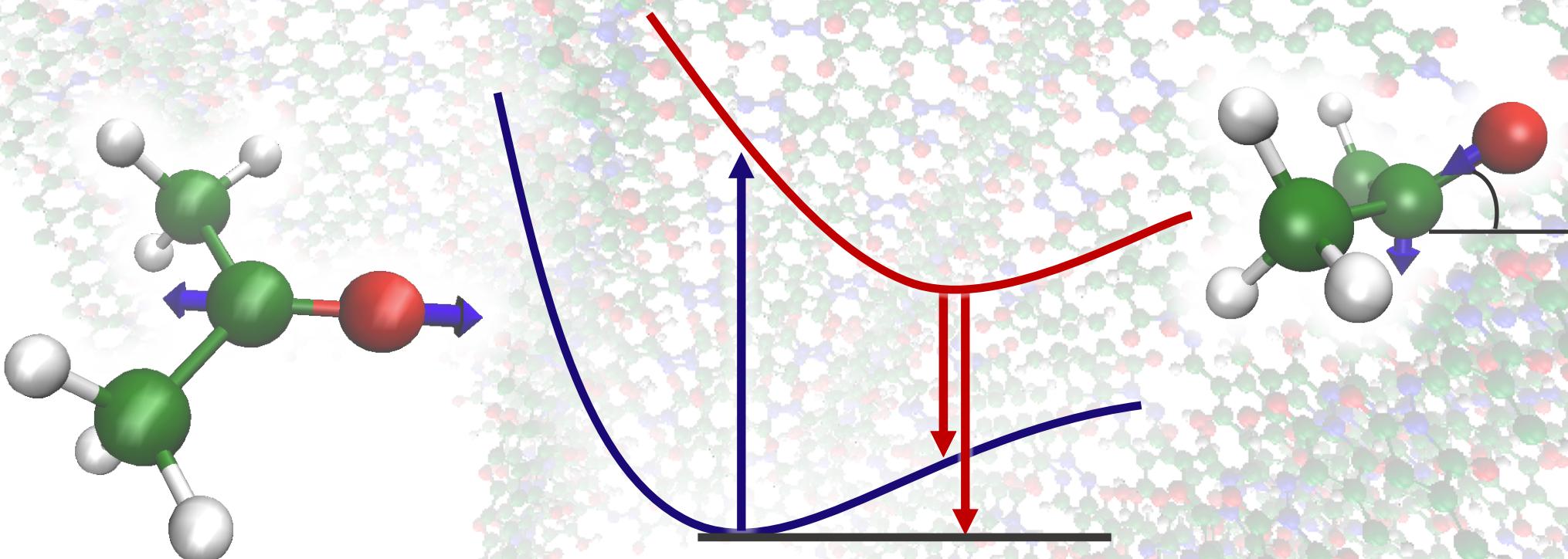


Towards efficient excited-state dynamics with hybrid functional accuracy for large-scale periodic systems

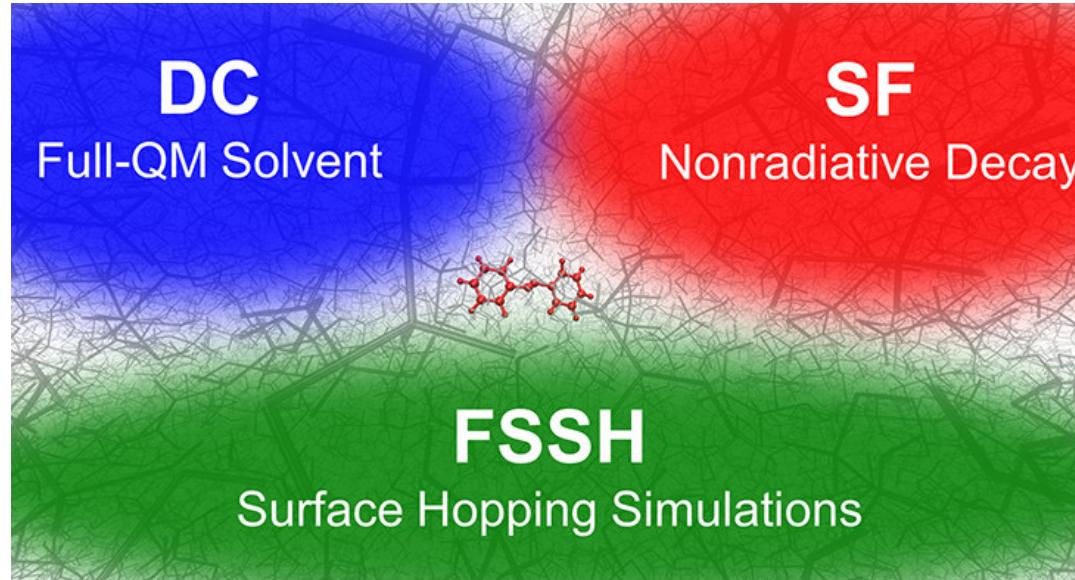
Anna Hehn, Beliz Sertcan, Fabian Belleflamme, Sergey Chulkov,
Matthew Watkins, Jürg Hutter



Motivation

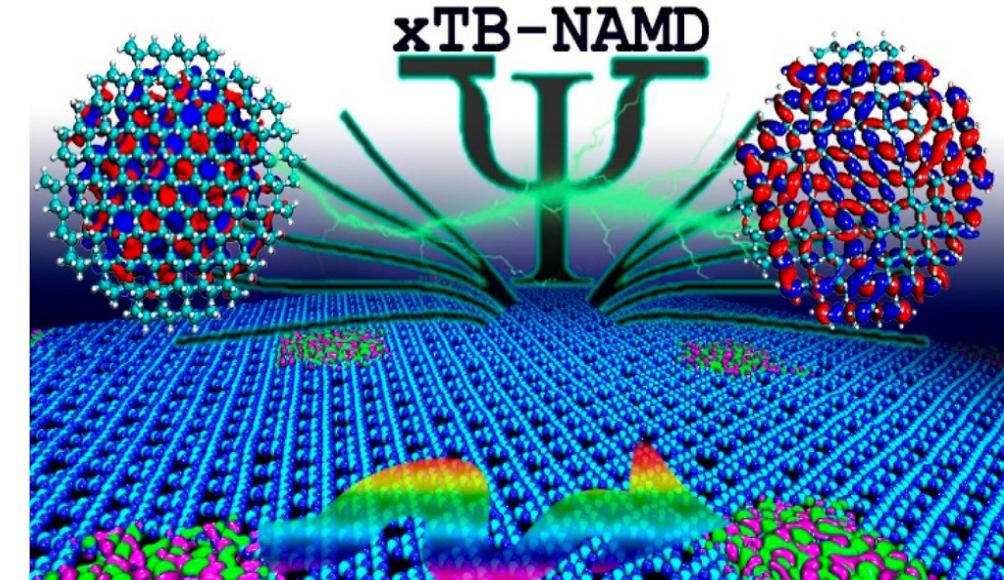


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Divide and Conquer Spin-Flip TD-DFTB + orbital derivative
couplings in the DCDFTB Code.

Uratani, Yoshikawa, Nakai, *JCTC* 17, 1290–1300 (2021).



Extended Tight-binding + orbital derivative
couplings in the Libra code.

Shakiba, Stippell, Li, Akimov, *JCTC* (2022).

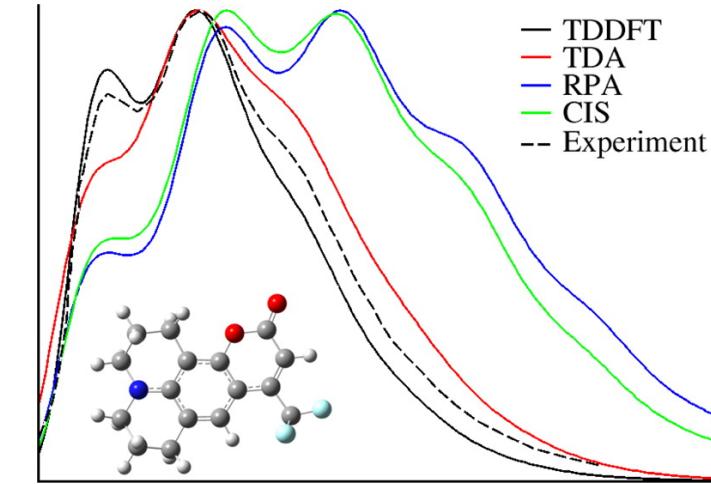
-> Efficient excited-state properties with hybrid functional accuracy for periodic systems

Theoretical spectroscopy for periodic systems

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

$$\mathbf{AX} = \Omega \mathbf{SX}$$

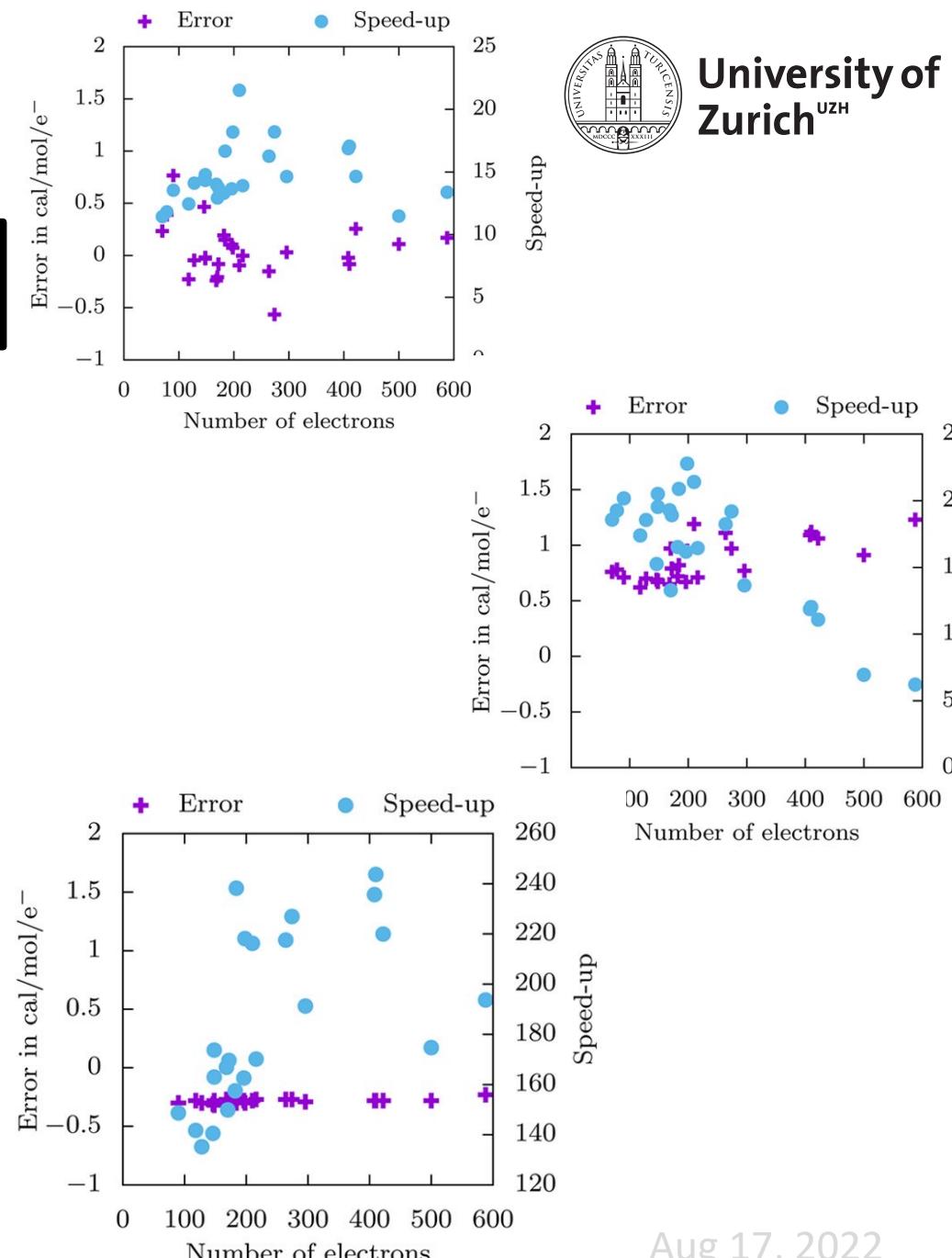
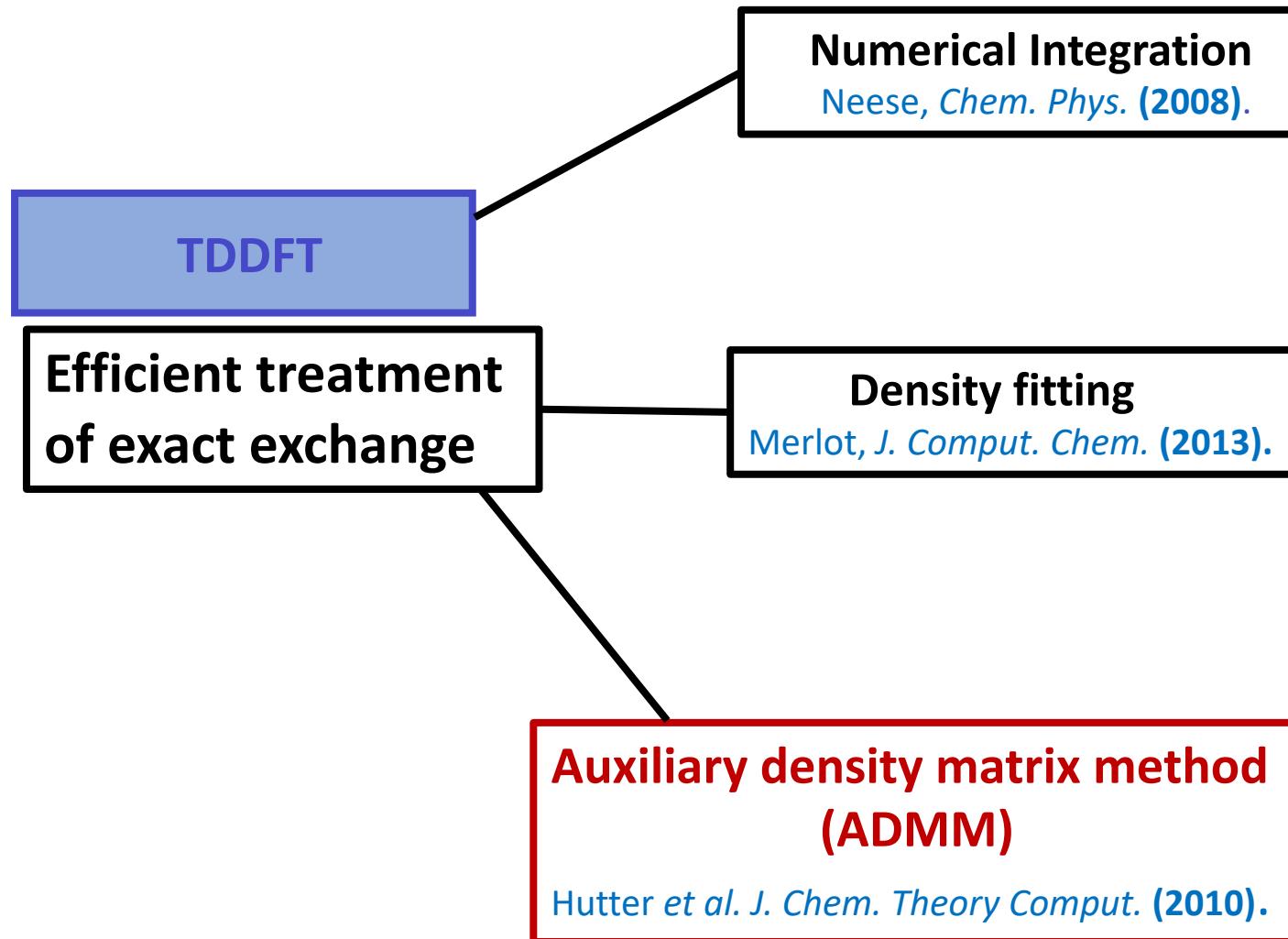
Projection to ensure $X_{ij\sigma} = 0$

$$\sum_{\kappa k} [F_{\mu\kappa\sigma}\delta_{ik} - F_{ik\sigma}S_{\mu\kappa}] X_{\kappa k\sigma} + \sum_{\kappa\lambda} Q_{\mu\kappa\sigma}^\dagger K_{\kappa\lambda\sigma} [\mathbf{D}^x] C_{\lambda i\sigma} = \sum_{\kappa} \Omega S_{\mu\kappa} X_{\kappa i\sigma}$$

$$K_{\mu\nu\sigma}[\mathbf{D}^x] = \sum_{\kappa\lambda\sigma'} D_{\kappa\lambda\sigma'}^x [(\mu\nu|\kappa\lambda) - a_{\text{EX}}\delta_{\sigma\sigma'}(\mu\kappa|\nu\lambda) + f_{\mu\nu\sigma,\kappa\lambda\sigma'}^{\text{XC}}]$$

Coulomb
Exchange
XC functional

Approach I: A robust formulation for exact exchange





Approach I: A robust formulation for exact exchange

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).

$$D_{\kappa\lambda\sigma}^x(\mu\kappa|\nu\lambda) \approx \sum_{\hat{\kappa}\hat{\lambda}} \sum_{\hat{\mu}\hat{\nu}} \hat{D}_{\hat{\kappa}\hat{\lambda}\sigma}^x \hat{U}_{\hat{\mu}\mu\sigma}^T (\hat{\mu}\hat{\kappa}|\hat{\nu}\hat{\lambda}) \hat{U}_{\hat{\nu}\nu\sigma} + \left[\sum_{\kappa\lambda} D_{\kappa\lambda\sigma}^x f_{\mu\kappa\sigma,\nu\lambda\sigma}^{\text{EX}} - \sum_{\hat{\kappa}\hat{\lambda}} \sum_{\hat{\mu}\hat{\nu}} \hat{D}_{\hat{\kappa}\hat{\lambda}\sigma}^x \hat{U}_{\hat{\mu}\mu\sigma}^T f_{\hat{\mu}\hat{\kappa}\sigma,\hat{\nu}\hat{\lambda}\sigma}^{\text{EX}} \hat{U}_{\hat{\nu}\nu\sigma} \right]$$

exact exchange with small auxiliary density
1st order GGA correction term

Possible ADMM variant:
Auxiliary density matrix by projection

$$\hat{\mathbf{D}} = \hat{\mathbf{U}} \mathbf{D} \hat{\mathbf{U}}^\dagger \quad \hat{S}_{\hat{\mu}\hat{\nu}} = \int \hat{\varphi}_{\hat{\mu}}(\mathbf{r}) \hat{\varphi}_{\hat{\nu}}(\mathbf{r}) d\mathbf{r}$$
$$\hat{\mathbf{U}} = \hat{\mathbf{S}}^{-1} \hat{\mathbf{V}} \quad \hat{V}_{\hat{\mu}\nu} = \int \hat{\varphi}_{\hat{\mu}}(\mathbf{r}) \varphi_\nu(\mathbf{r}) d\mathbf{r}$$

Approach II: Semi-empirical tight binding

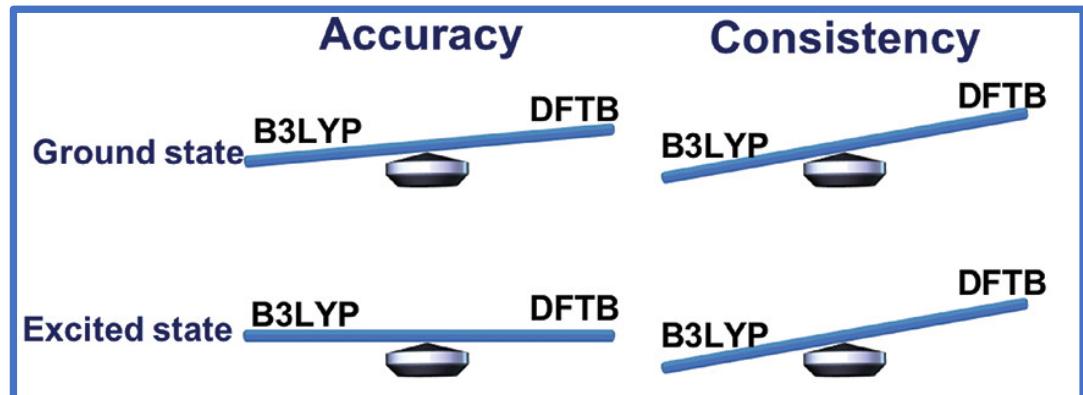
dftb.org

Extensions for
excited-state
properties

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

TDDFTB
Benchmarks

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



1. Semi-empirical tight binding

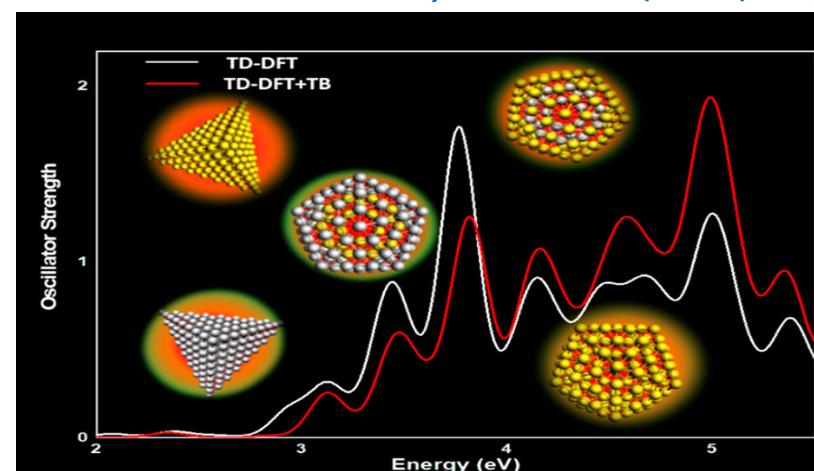
Global parameters only!

Simplified TDA (sTDA)

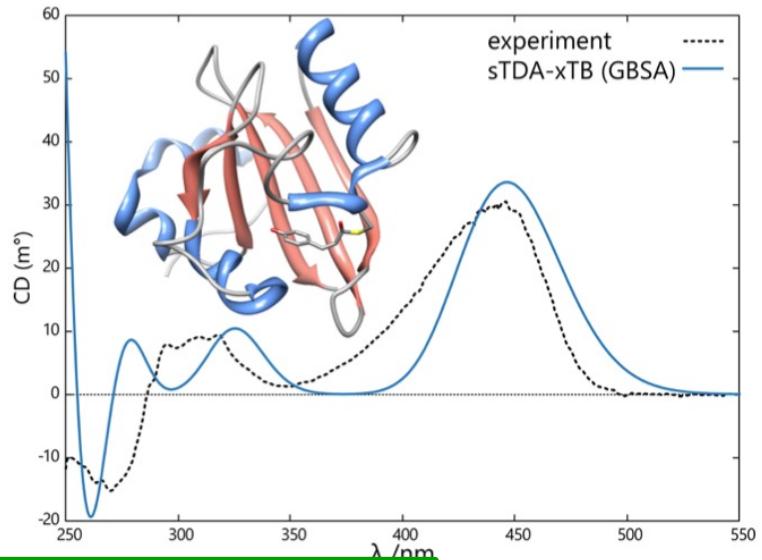
Grimme, *J. Chem. Phys.* (2013).

TDDFT+TB

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



2022



Approach II: Simplified Tamm Dancoff Approximation

$$K_{\mu\nu\sigma}[\mathbf{D}^x] = \sum_{\kappa\lambda\sigma'} D_{\kappa\lambda\sigma'}^x [(\mu\nu|\kappa\lambda) - a_{\text{EX}}\delta_{\sigma\sigma'}(\mu\kappa|\nu\lambda) + f_{\mu\nu\sigma,\kappa\lambda\sigma'}^{\text{XC}}]$$

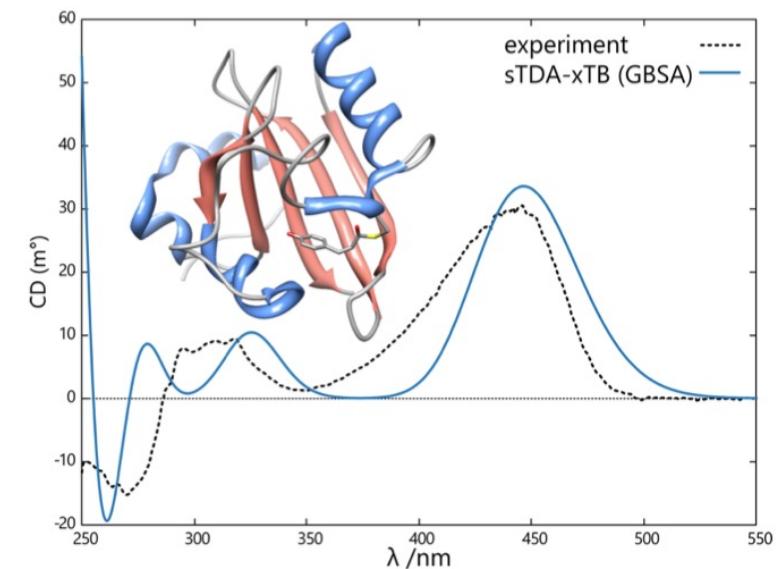
Semi-empirical
tight binding
reference

**1. Approximate two-electron
integrals**

$$(pq\sigma|rs\sigma')^{\text{sTDA}} = \sum_A \sum_B q_{pq\sigma}^A q_{rs\sigma'}^B \gamma(A, B)$$

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

**2. Neglect
XC kernel**



- Minimal number of global parameters
- Correct asymptotics for electron repulsion
- System sizes of several hundreds of atoms

Treating periodicity within CP2K

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

Slightly different results in comparison to sTDA code by Grimme !

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

↗ semi-empirical short-range exact long-range ↘

Figure 1: A plot showing the relationship between the PBC parameter $\gamma_{\text{PBC}}^{\text{J}}(A, B)$ and the distance R_{AB} . The y-axis is labeled $\gamma_{\text{PBC}}^{\text{J}}(A, B)$ and has a value η marked. The x-axis is labeled R_{AB} and has three vertical tick marks: R_{smooth} at a small positive value, R_{cut} at a larger positive value, and R_{AB} at the far right. Below the x-axis, there is a label " $< 10^{-6}$ a.u." indicating the scale for values near zero.

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

$$\mathbf{AX}_n = \Omega_n \mathbf{SX}_n \text{ with } \mathbf{X}_n^\dagger \mathbf{S} \mathbf{X}_m = 1$$

Lagrangian for state n :

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

Geometry dependence of AOs

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

$$\begin{aligned} \sum_{ia\sigma} \bar{Z}_{ia\sigma} F_{ia\sigma} &= \sum_{i\mu\nu\sigma} \bar{Z}_{i\nu\sigma} Q_{\mu\nu\sigma}^\dagger F_{\mu i\sigma} \\ &= \sum_{i\mu\nu\sigma} \bar{Z}_{i\nu\sigma} (F_{\nu\mu\sigma} C_{\mu i\sigma} - S_{\nu\mu} C_{\mu i\sigma} \varepsilon_{i\sigma}) \end{aligned}$$

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



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

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

1. Excitation energies

$$\mathbf{AX}_n = \Omega_n \mathbf{SX}_n \text{ with } \mathbf{X}_n^\dagger \mathbf{S} \mathbf{X}_m = 1$$

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

2. Z vector equation

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

3. Excited-state gradient

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

Transformation rules

$$M_{\mu\nu\sigma}^{\text{AO}} = \sum_{\kappa\lambda kl} S_{\mu\kappa} C_{\kappa k\sigma}^T M_{kl\sigma}^{\text{MO}} C_{l\lambda\sigma} S_{\lambda\nu}$$

$$M_{kl\sigma}^{\text{MO}} = \sum_{\kappa\lambda} C_{\kappa k\sigma}^T M_{\kappa\lambda\sigma}^{\text{AO}} C_{\lambda l\sigma}$$

Projection for Lagrange multipliers

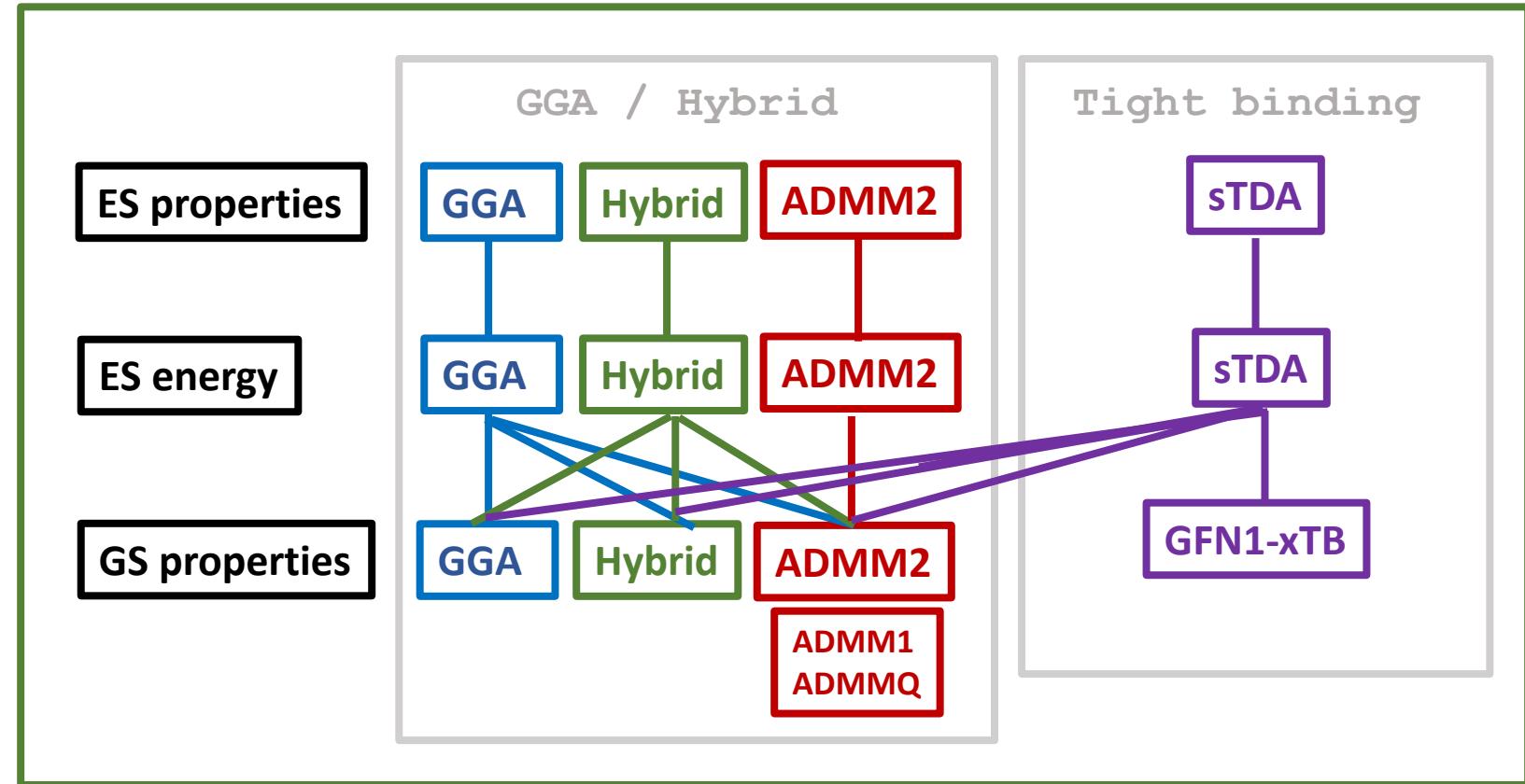
$$\frac{\partial L}{\partial \mathbf{C}} \mathbf{C} = 0 \rightarrow \bar{\mathbf{W}} \quad \frac{\partial L}{\partial \mathbf{C}} \mathbf{Q} = 0 \rightarrow \bar{\mathbf{Z}}$$

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

The TDDFT module in CP2K

→ 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
```



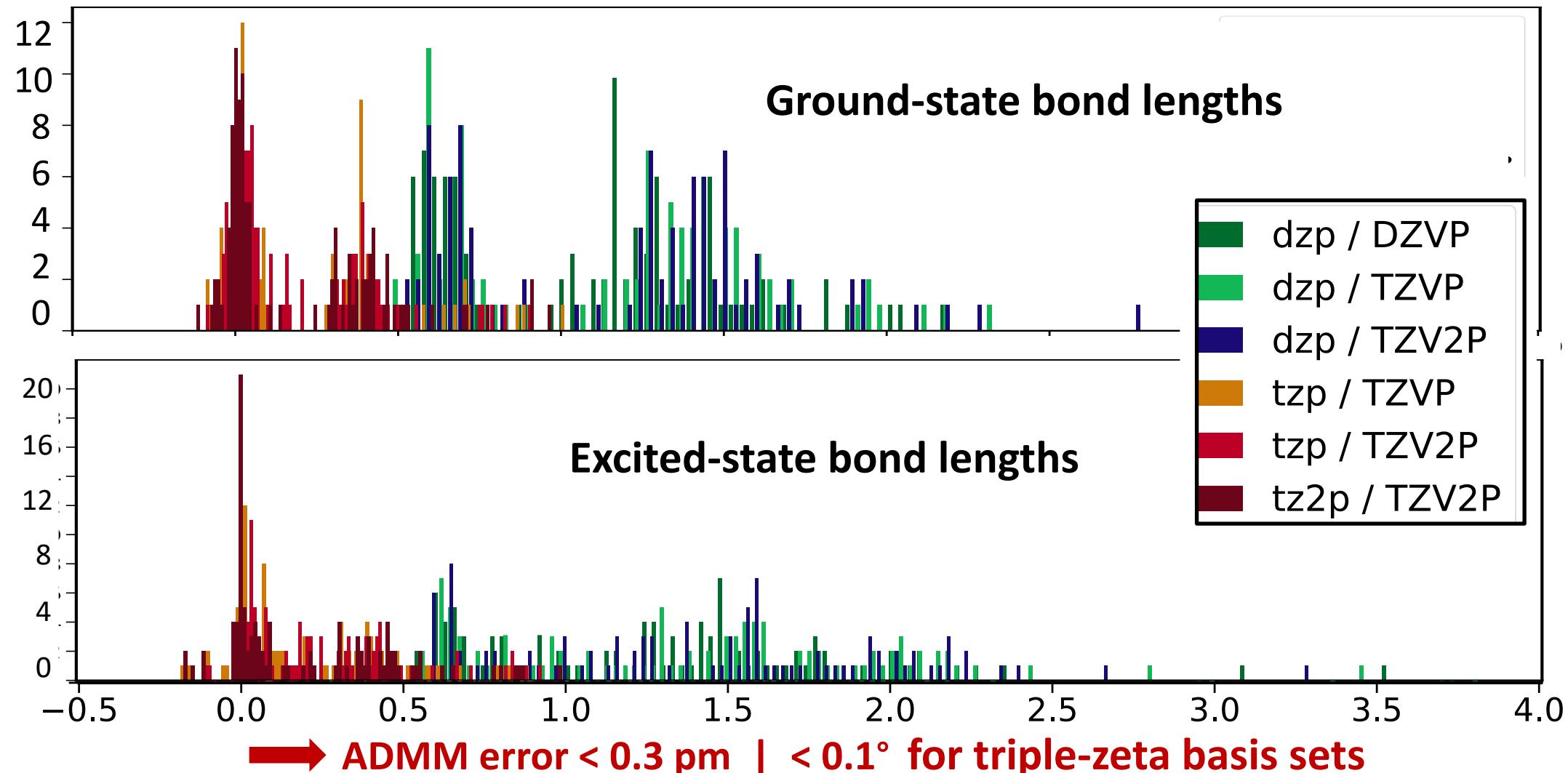
Iannuzzi *et al.*, CHIMIA, 59, 499 (2005); Strand *et al.* J. Chem. Phys. 150, 044702 (2019).

I. Accuracy benchmark for molecular systems

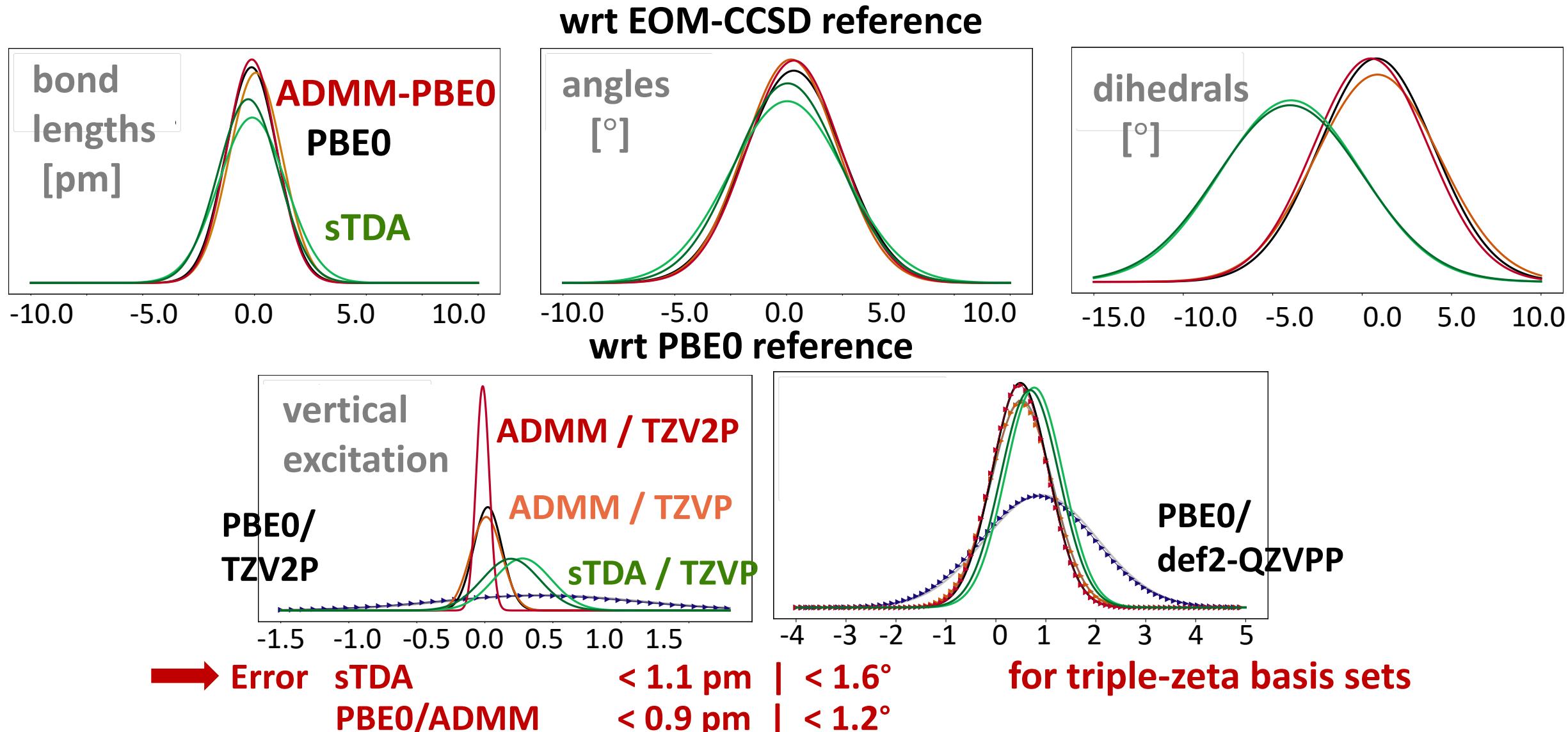


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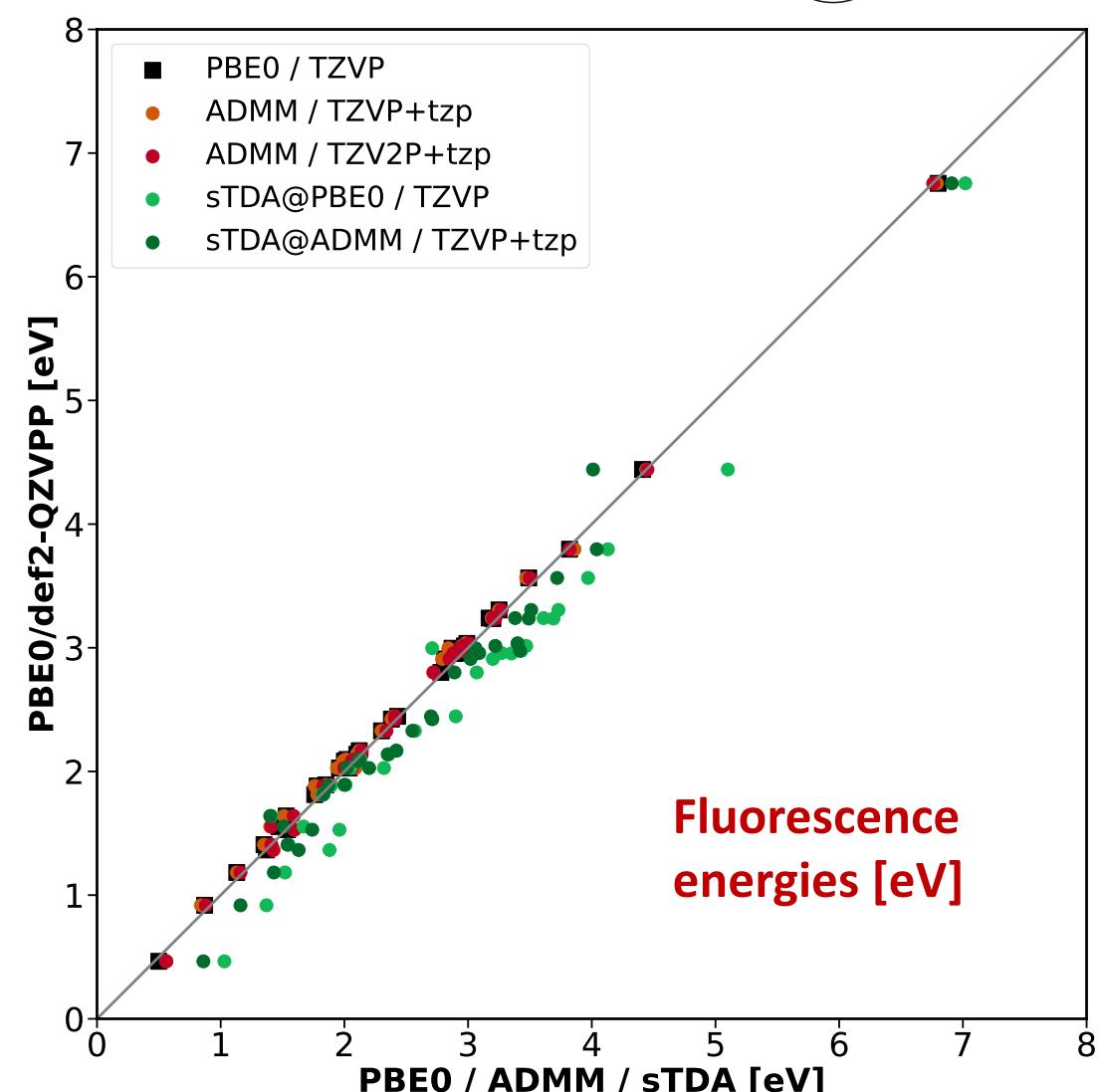
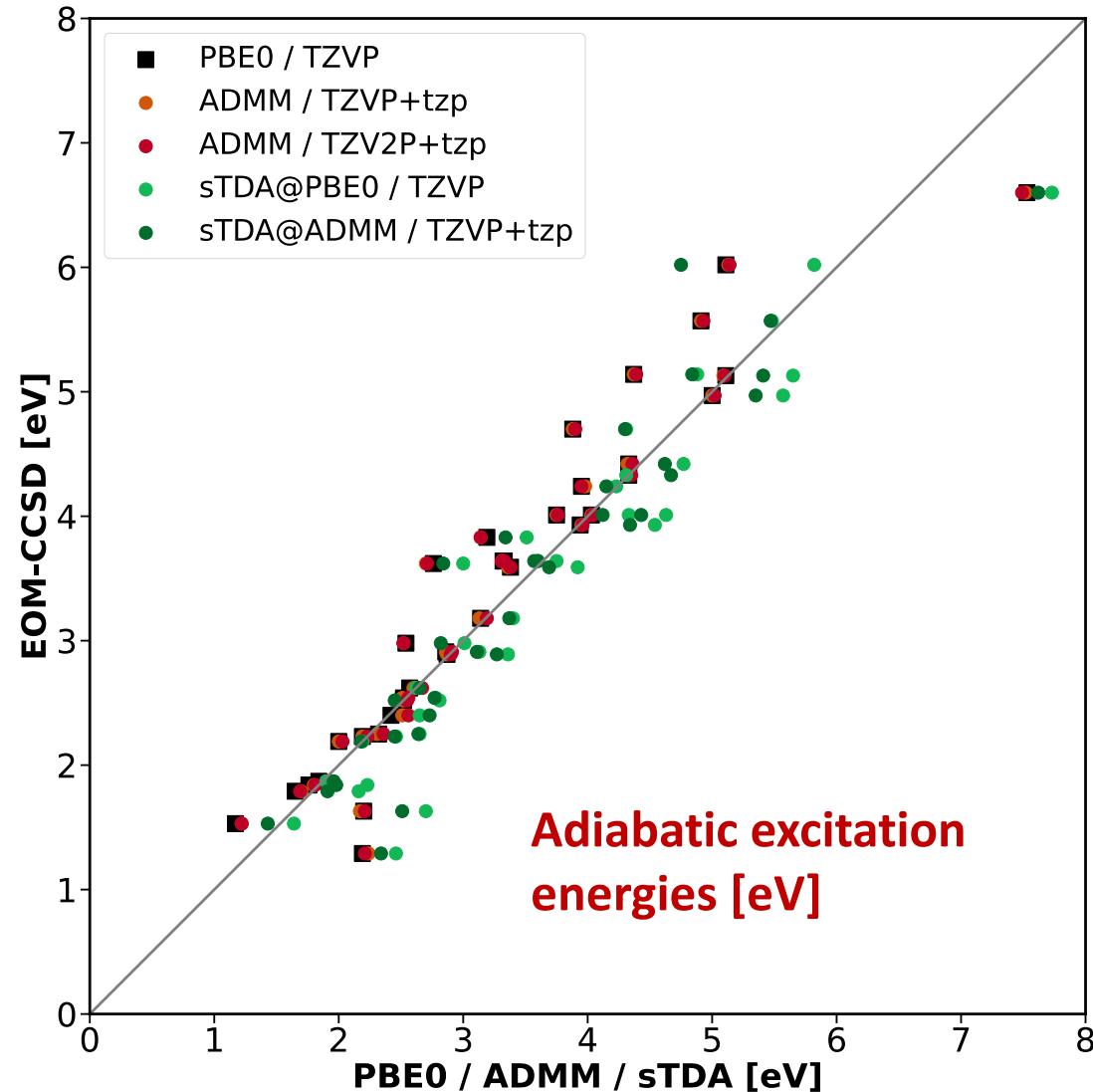
ADMM-PBE0 geometries wrt PBE0 reference



I. Accuracy benchmark for molecular systems

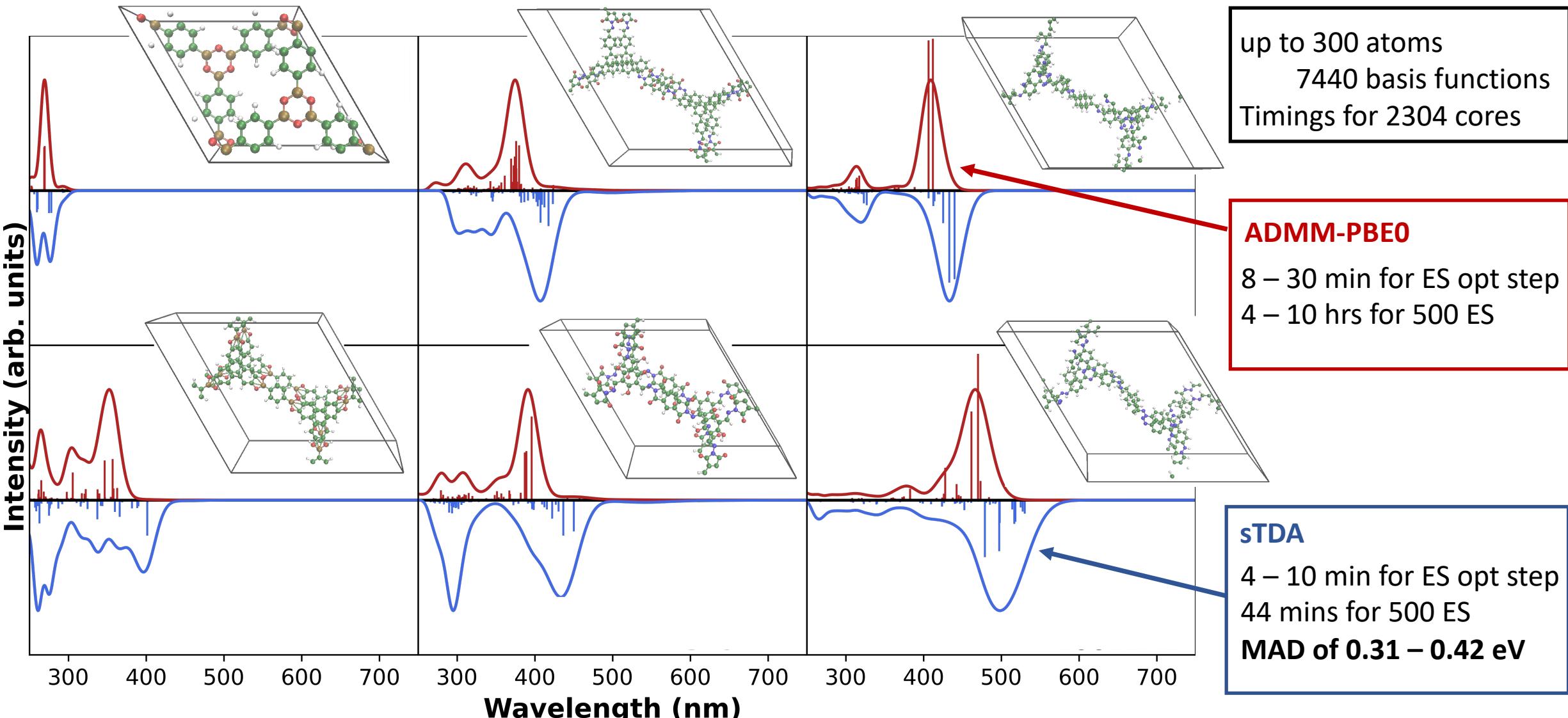


I. Accuracy benchmark for molecular systems

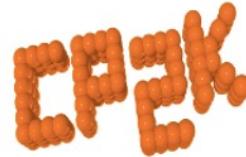


Errors in the range of 0.2 – 0.5 eV

II. Application to periodic systems



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!

ADMM / sTDA@ADMM
1 ES GEO Opt 5 min
500 Ex States 10.9 min

Feng et al. *Chem. Commun.*
56, 2511, 2020.

Auxiliary Density Matrix Method

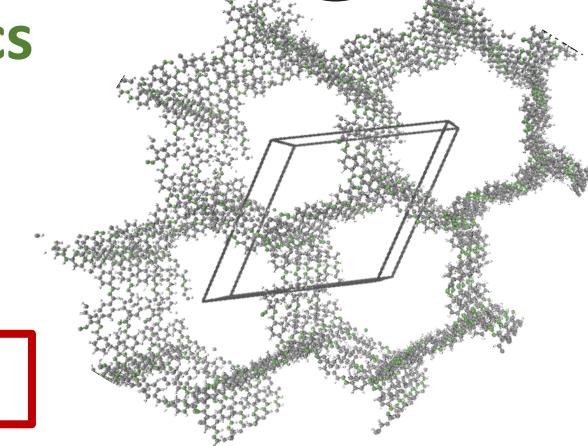
Speedup by 1 order of magnitude compared to hybrid functional

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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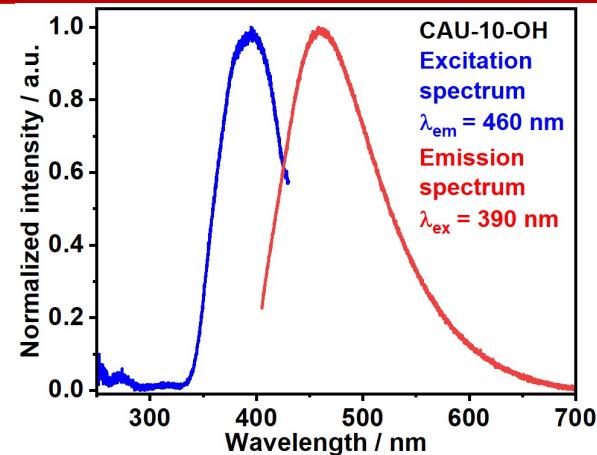
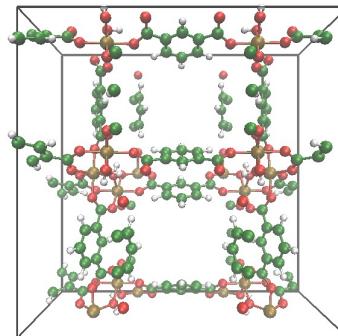
Excited-state properties with
hybrid functional accuracy

ADMM-TDDFT

Semi-empirical sTDA

Periodic boundary
conditions

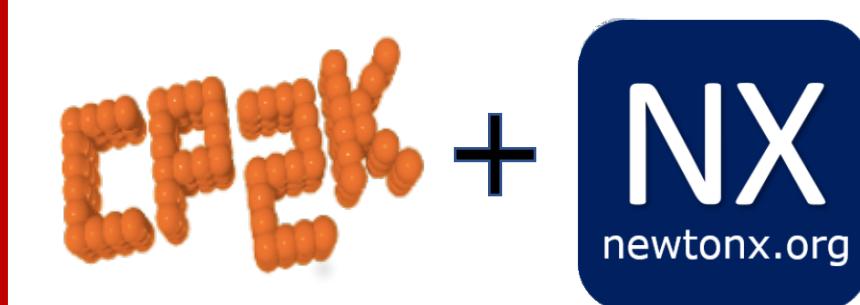
Fluorescence
CAU10-MOFs



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).



Efficient nonadiabatic couplings

Orbital derivative couplings
Baeck-An couplings

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



Acknowledgements

Beliz Sertcan



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Jürg Hutter

Matthew Watkins (Uni Lincoln)



Sergey Chulkov (Uni Lincoln)

Thank you very much for your attention!

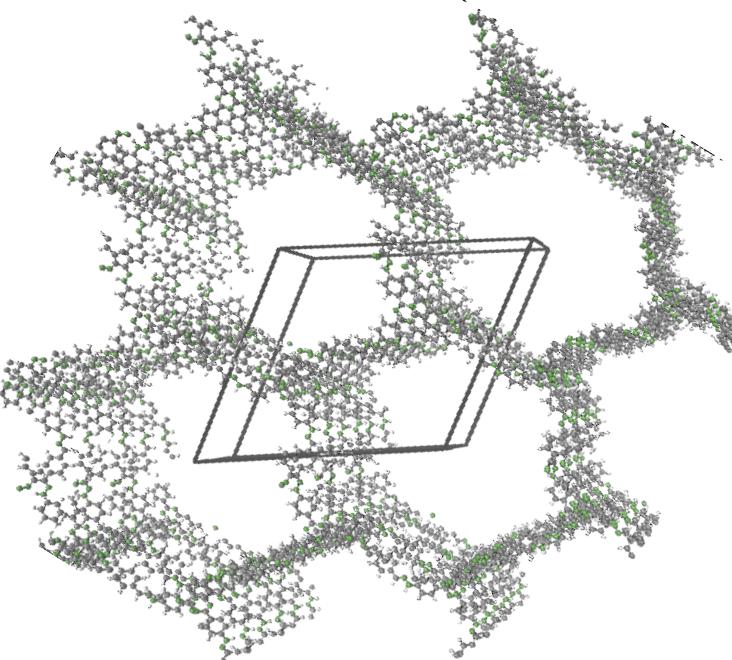
Questions / comments: Email: anna.hehn@chem.uzh.ch
Twitter: [@anna_hehn](https://twitter.com/anna_hehn)

Funding:



MOFdynamics
EU Project No. 798196

II. Application to periodic systems



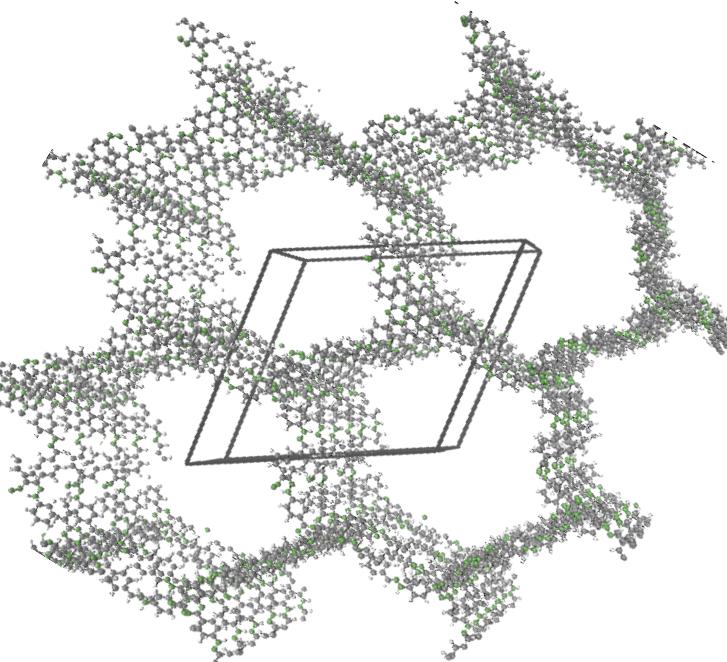
Costs for 36 nodes with 36 MPI tasks / node

	Basis	Cost [ERIs]	Cost [s]	10 Ex	1 ES Opt
PBE0	DZVP	2.0×10^{12} [1.6 TB]		2.1 hrs	21.48 hrs
	TZVP	5.8×10^{12} [4.5 TB]		3.2 hrs	29.56 hrs
ADMM	DZVP+dzp	6.5×10^{10} [50 GB]		21.6 min	12.4 min
	TZVP+tzp	1.4×10^{11} [115 GB]		28.3 min	16.1 min
sTDA	DZVP+dzp	—		2.5 min	4.8 min
	GFN1-xTB	—		15.4 s	10.0 s

Covalent Organic Framework 20611N2
(262 atoms)

→ gain for ADMM in efficiency by at least one order of magnitude
gain for sTDA in case of broad-band excitation spectra

II. Application to periodic systems



Covalent Organic Framework 20611N2
(262 atoms)

