

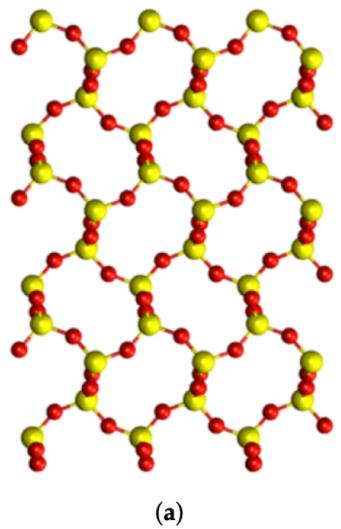
# Post-DFT / HF Methods for the Condensed Phase with CP2K

Developments for excited states within TDDFT



# Current application range for theoretical spectroscopy

**Absorption spectroscopy** on oxygen vacancies  
in phases of  $\text{SiO}_2$

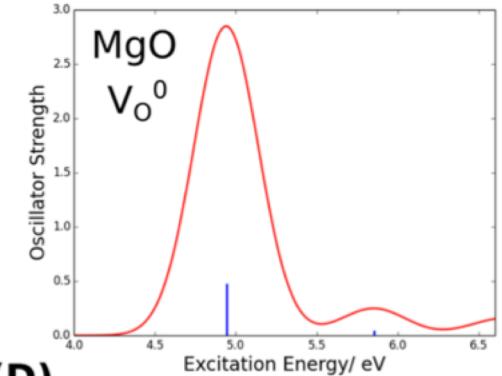


Shluger et. al.,  
Materials 16, 1382 (2023).

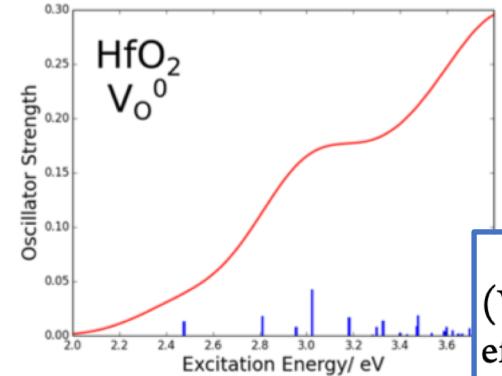
Strand et. al., J. Chem. Phys.  
150, 044702 (2019).

in binary metal oxides

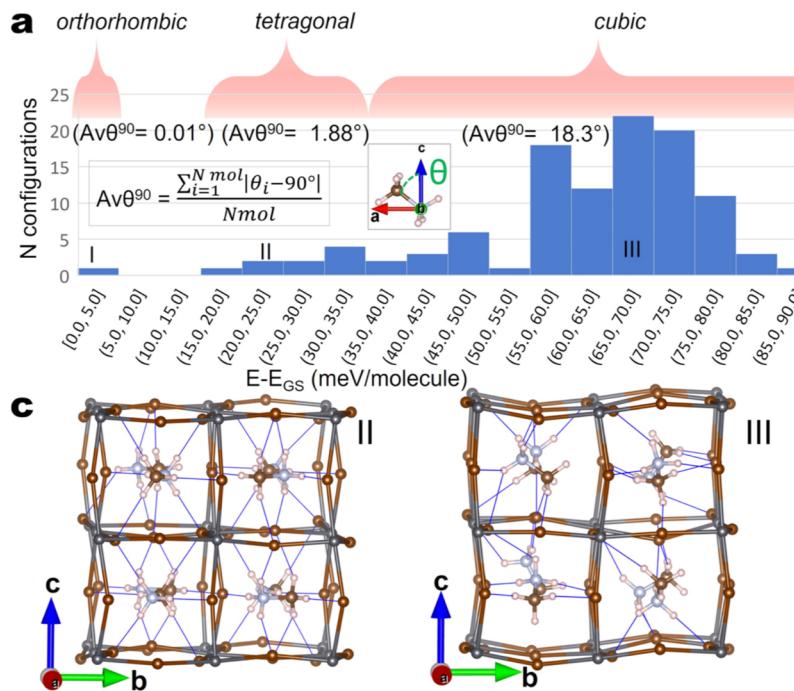
(A)



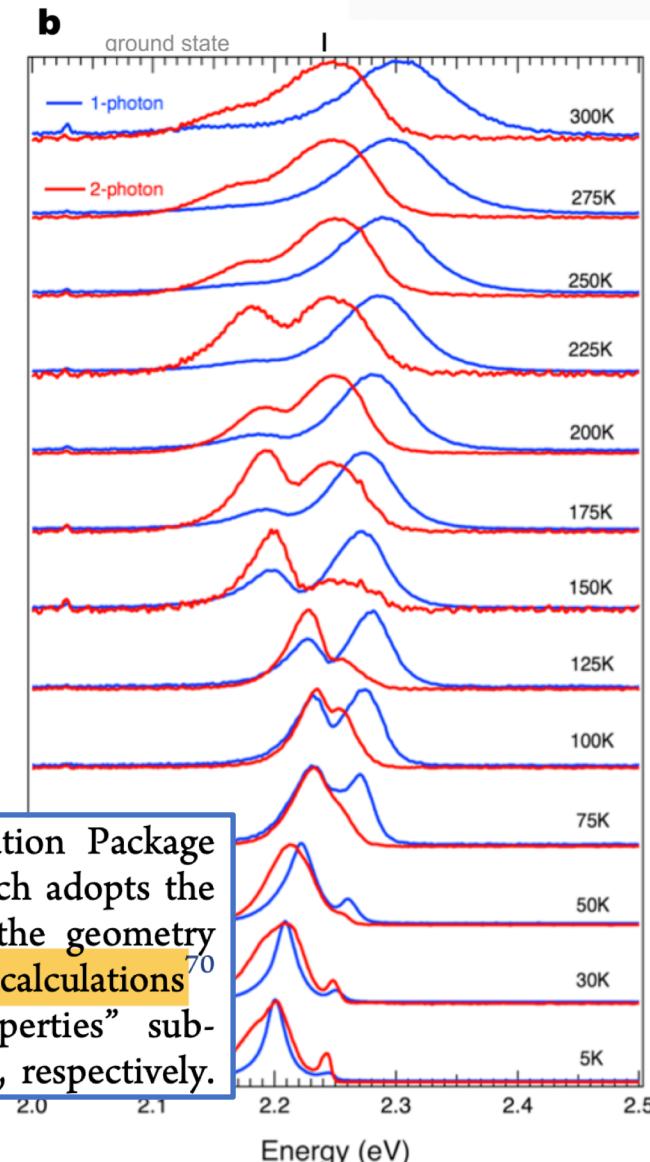
(D)



**Luminescence** of hybrid lead halide perovskites



Saleh et. al., Chem. Mater. 33, 8524 (2021).

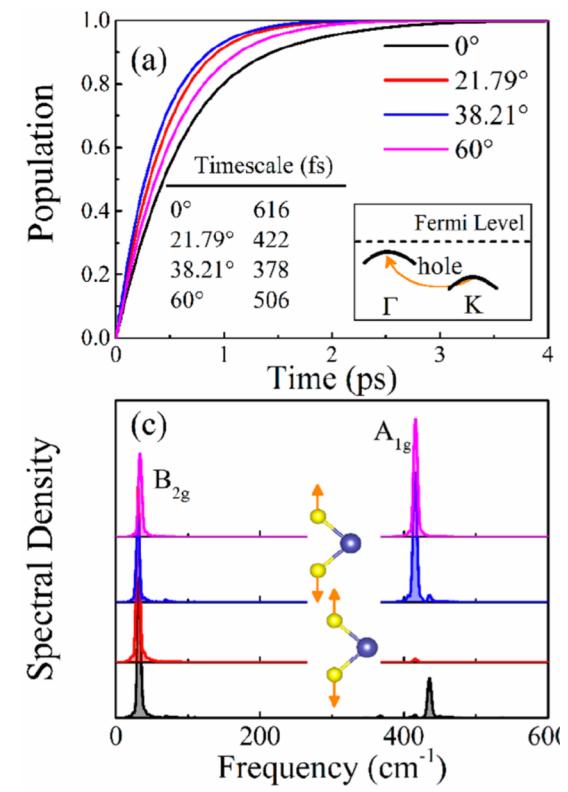
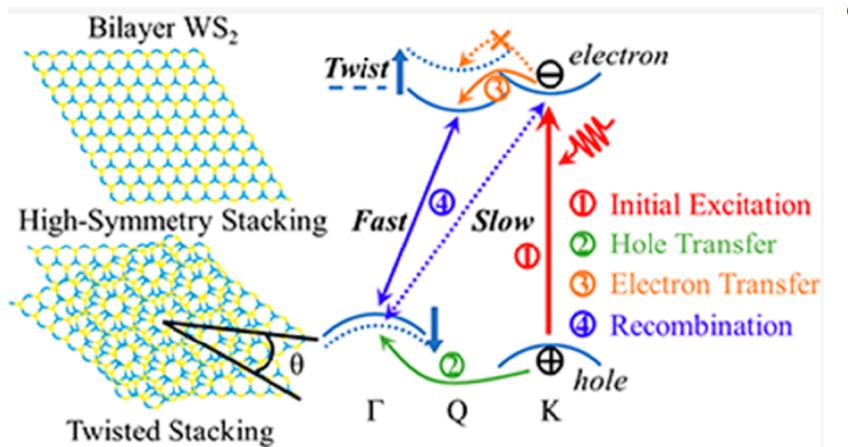
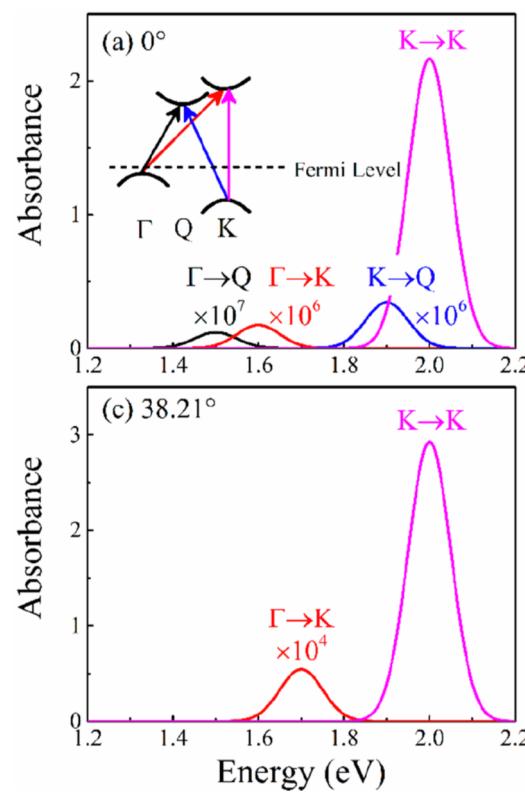


**DFT Calculations.** Both Vienna Ab initio Simulation Package (VASP)<sup>68</sup> and cp2k<sup>69</sup> codes were exploited. Cp2k, which adopts the efficient Gaussian plane-wave method, was used for the geometry optimization of large cells and for time-dependent DFT calculations (“Dynamics of Methylammonium and Optical Properties” subsection). The plane-wave cutoffs were 125 and 200 Ry, respectively.

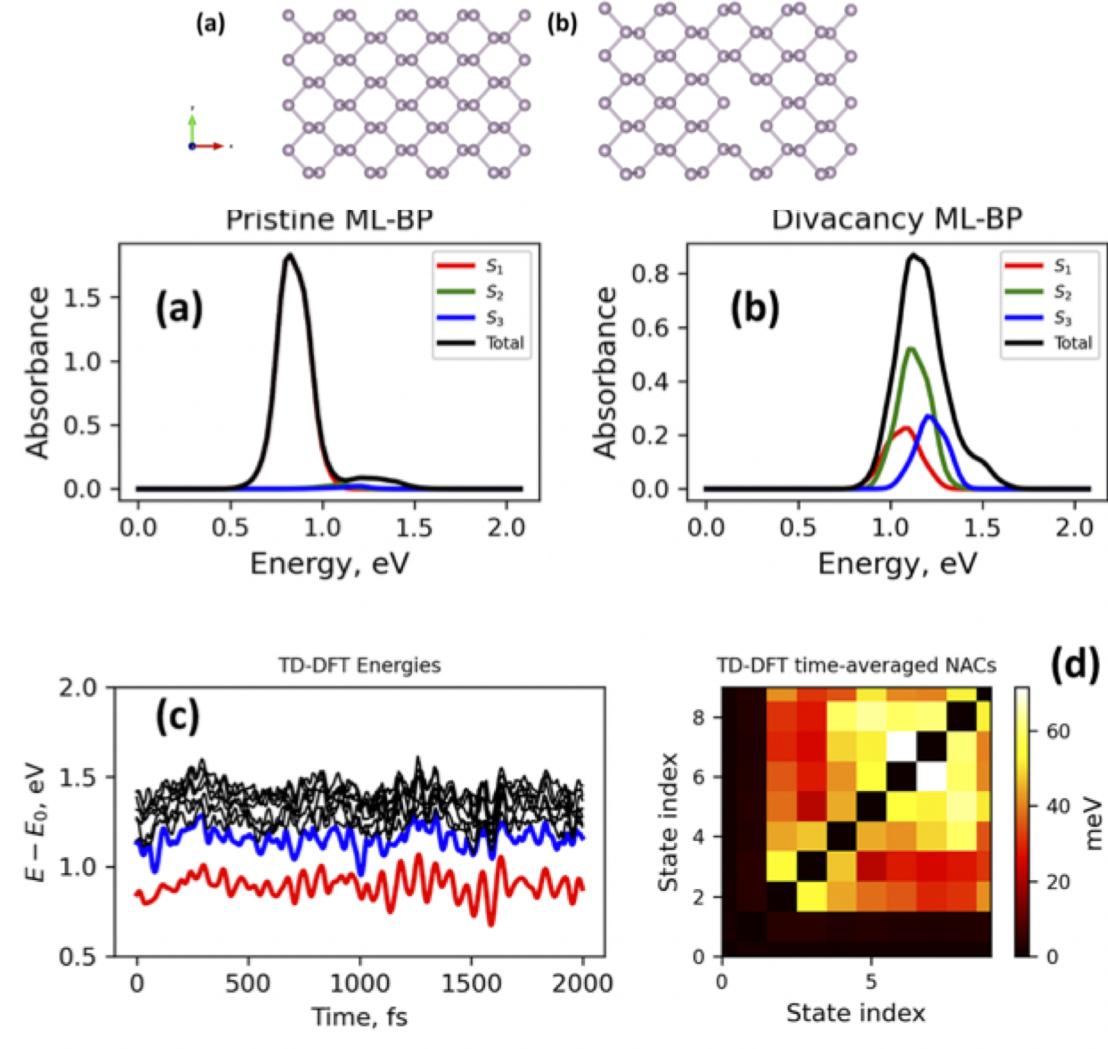
# Current application range for theoretical spectroscopy ... ... and the promising future!

**Charge carrier transfer and rekombination in bilayer WS<sub>2</sub>**

Prezhdo et. al.,  
*J. Am. Chem. Soc.* 145,  
22826 (2023).



**Excited-state dynamics in monolayer black phosphorus**



Akimov et. al., *J. Chem. Phys.* 155, 134106 (2021).

# Tailoring the Swiss Army Knife for efficient absorption and emission spectroscopy



1. Approximate hybrid density functional accuracy → Absorption spectroscopy
2. Excited-state nuclear gradients → Emission spectroscopy
3. Gaussian and Augmented Plane Wave → local defects
4. Perturbative spin-orbit coupling → Phosphorescence
5. CP2K-NewtonX interface → Towards non-adiabatic molecular dynamics

# Tailoring the Swiss Army Knife for efficient absorption and emission spectroscopy



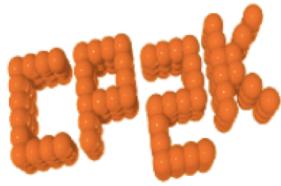
1. Approximate hybrid density functional accuracy → Absorption spectroscopy
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# Tailoring the Swiss Army Knife for efficient absorption and emission spectroscopy



1. Approximate hybrid density functional accuracy → Absorption spectroscopy
2. Excited-state nuclear gradients → Emission spectroscopy
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# An efficient setup for absorption spectroscopy



**Mixed Gaussian and plane wave (GPW)**

Coulomb and XC energy computed with plane wave representation

$$\rho(r) = \sum_{\alpha\beta} P_{\alpha\beta} \varphi_{\alpha}(r) \varphi_{\beta}(r) \approx \sum_{\mathbf{G}} \rho(\mathbf{G}) e^{-i\mathbf{G} \times r}$$

$$P_{\alpha\beta} = \sum_i f_i C_{\alpha i} C_{\beta i}$$

$$V_H(\mathbf{G}) = 4\pi \frac{\rho(\mathbf{G})}{\mathbf{G}^2}$$

Poisson solver

Lippert, Hutter, Parrinello, *Mol. Phys.* 92, 477 (1997); Goedecker, Teter, Hutter, *Phys. Rev. B* 54, 1703 (1996).

Sternheimer equations

Tamm-Dancoff approximation

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

Virtual space via projection operators

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

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

Coulomb

Exchange

XC

Iannuzzi, Chassaing, Wallman, Hutter, *CHIMIA* 59, 499 (2005); Strand, Chulkov, Watkins, Shluger, *J. Chem. Phys.* 150, 044702 (2019).



# Input section to compute absorption spectra

→ TDDFT tutorial on how to compute excitation energies for acetone  
<https://manual.cp2k.org/trunk/methods/properties/index.html>

## Properties

- Optical Spectroscopy
  - Time-Dependent DFT
  - Bethe-Salpeter Equation
- X-Ray Spectroscopy
  - X-Ray Absorption from  $\Delta$ SCF
  - X-Ray Absorption from TDDFT
  - X-Ray Absorption from  $\delta$ -Kick
  - X-Ray Ab-Initio Correction Scheme
  - X-Ray Resonant Excitation
- Infrared Spectroscopy
- Raman Spectroscopy
- Bandstructure from GW
- Nuclear Magnetic Resonance
- STM Images
- RESP Charges

## The LR-TDDFT input section

To compute absorption spectra, parameters defining the LR-TDDFT computation specified in the **TDDFPT** subsection. Furthermore, **RUN\_TYPE** has to be set to **E** underlying KS ground-state reference has to be specified in the **DFT** section.

The most important keywords and subsections of **TDDFPT** are:

- **KERNEL**: option for the kernel matrix **K** to choose between the full kernel for functionals and the simplified TDA kernel
- **NSTATES**: number of excitation energies to be computed
- **CONVERGENCE**: threshold for the convergence of the Davidson algorithm
- **RKS\_TRIPLETS**: option to switch from the default computation of singlet exci triplet excitation energies
- **RESTART**: the keyword enables the restart of the TDDFPT computation if a co restart file (.tdwfn) exists
- **WFN\_RESTART\_FILE\_NAME**: for a restart of the TDDFPT computation, the n file has to be specified using this keyword

To compute excited-state gradients and thus corresponding fluorescence spectra to be optimized furthermore has to be specified by adding the subsection **EXCITE** section **DFT**.

## Subsections

- DIPOLE\_MOMENTS
- LINRES
- LRIGPW
- MGRID
- PRINT
- SOC
- STDA
- XC

## Keywords

- SECTION\_PARAMETERS
- ADMM\_KERNEL\_CORRECTION\_SYMMETRIC
- ADMM\_KERNEL\_XC\_CORRECTION
- AUTO\_BASIS
- CONVERGENCE
- DO\_LRIGPW
- EOS\_SHIFT
- EV\_SHIFT
- KERNEL
- MAX\_ITER
- MAX\_KV
- MIN\_AMPLITUDE
- NLUMO
- NPROC\_STATE
- NSTATES
- OE\_CORR
- ORTHOGONAL\_EPS
- RESTART
- RKS\_TRIPLETS
- WFN\_RESTART\_FILE\_NAME

→ TDDFT tutorial on how to compute excitation energies for acetone

```
&GLOBAL
PROJECT S20Acetone
RUN_TYPE ENERGY
PREFERRED_DIAG_LIBRARY SL
PRINT_LEVEL medium
&END GLOBAL
&FORCE_EVAL
METHOD Quickstep
&PROPERTIES
  &TDDFPT
    KERNEL FULL
    NSTATES 10
    MAX_ITER 100
    CONVERGENCE [eV] 1.0e-7
    RKS_TRIPLETS F
  &END TDDFPT
  &END PROPERTIES
&DFT
```

Several trivial keywords:

# excited states  $N$ ?

Convergence threshold?

Spin multiplicity for closed-shell  
electronic configurations?

$$\mathbf{AX}^N = \boldsymbol{\Omega}^N \mathbf{SX}^N$$

$$\sum_{\kappa k} [F_{\mu k \sigma} \delta_{ik} - F_{ik \sigma} S_{\mu \kappa}] X_{\kappa k \sigma}^N$$

$$+ \sum_{\kappa \lambda} Q_{\mu \kappa}^T K_{\kappa \lambda \sigma}^N [\mathbf{D}^x] C_{\lambda i \sigma} = \sum_{\kappa} \boldsymbol{\Omega}^N S_{\mu \kappa} X_{\kappa i \sigma}^N$$



# Input section to compute absorption spectra



→ TDDFT tutorial on how to compute excitation energies for acetone

```
&GLOBAL
PROJECT S20Acetone
RUN_TYPE ENERGY
PREFERRED_DIAG_LIBRARY SL
PRINT_LEVEL medium
&END GLOBAL
&FORCE_EVAL
METHOD Quickstep
&PROPERTIES
  &TDDFPT
    KERNEL FULL
    NSTATES 10
    MAX_ITER 100
    CONVERGENCE [eV] 1.0e-7
    RKS_TRIPLETS F
  &END TDDFPT
  &END PROPERTIES
&DFT
```

Several trivial keywords:

# excited states  $N$ ?

Convergence threshold?

Spin multiplicity for closed-shell  
electronic configurations?

choose  
appropriately wrt  
remaining settings

```
&DFT
  &QS
    METHOD GPW
    EPS_DEFAULT 1.0E-17
    EPS_PGF_ORB 1.0E-20
  &END QS
  &SCF
    SCF_GUESS restart
    &OT
      PRECONDITIONER FULL_ALL
      MINIMIZER DIIS
    &END OT
    &OUTER_SCF
      MAX_SCF 900
      EPS_SCF 1.0E-7
    &END OUTER_SCF
    MAX_SCF 10
    EPS_SCF 1.0E-7
  &END SCF
  POTENTIAL_FILE_NAME POTENTIAL_UZH
  BASIS_SET_FILE_NAME BASIS_MOLOPT_UZH
  BASIS_SET_FILE_NAME BASIS_ADMM_UZH
  &MGRID
    CUTOFF 800
    REL_CUTOFF 80
  &END MGRID
  &AUXILIARY_DENSITY_MATRIX_METHOD
    METHOD BASIS_PROJECTION
    EXCH_SCALING_MODEL NONE
    EXCH_CORRECTION_FUNC NONE
    ADMM_PURIFICATION_METHOD NONE
  &END AUXILIARY_DENSITY_MATRIX_METHOD
  &POISSON
    PERIODIC NONE
    POISSON_SOLVER WAVELET
  &END
  &XC
    XC_FUNCTIONAL PBE0
  &END XC_FUNCTIONAL
  &END XC
&END DFT
```

→ TDDFT tutorial on how to compute excitation energies for acetone

```
&GLOBAL
PROJECT S20Acetone
RUN_TYPE ENERGY
PREFERRED_DIAG_LIBRARY SL
PRINT_LEVEL medium
&END GLOBAL
&FORCE_EVAL
METHOD Quickstep
&PROPERTIES
  &TDDFPT
    KERNEL FULL
    NSTATES 10
    MAX_ITER 100
    CONVERGENCE [eV] 1.0e-7
    RKS_TRIPLETS F
  &END TDDFPT
  &END PROPERTIES
&DFT
```

Several trivial keywords:

# excited states  $N$ ?

Convergence threshold?

Spin multiplicity for closed-shell electronic configurations?

Singlet and triplet excitation energies and amplitudes for closed-shell references

$$\mathbf{AX}^N = \boldsymbol{\Omega}^N \mathbf{SX}^N$$

$$\sum_{\kappa k} [F_{\mu k \sigma} \delta_{ik} - F_{ik \sigma} S_{\mu \kappa}] X_{\kappa k \sigma}^N$$

$$+ \sum_{\kappa \lambda} Q_{\mu \kappa}^T K_{\kappa \lambda \sigma}^N [\mathbf{D}^x] C_{\lambda i \sigma} = \sum_{\kappa} \boldsymbol{\Omega}^N S_{\mu \kappa} X_{\kappa i \sigma}^N$$

Spin adaptation

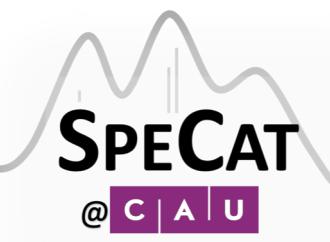
$$\mathbf{U} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

$$\mathbf{U}^T \boldsymbol{\Omega}_{\sigma \sigma'}^N \mathbf{U} = \begin{pmatrix} \Omega_{\alpha \alpha}^N + \Omega_{\alpha \beta}^N & 0 \\ 0 & \Omega_{\alpha \alpha}^N - \Omega_{\alpha \beta}^N \end{pmatrix} = \begin{pmatrix} \Omega_{\text{sing}}^N & 0 \\ 0 & \Omega_{\text{trip}}^N \end{pmatrix}$$

$$\mathbf{U} \mathbf{X}_{\sigma}^N = \begin{pmatrix} \frac{1}{\sqrt{2}} (\mathbf{X}_{\alpha}^N + \mathbf{X}_{\beta}^N) \\ \frac{1}{\sqrt{2}} (\mathbf{X}_{\alpha}^N - \mathbf{X}_{\beta}^N) \end{pmatrix} = \begin{pmatrix} \mathbf{X}_{\text{sing}}^N \\ \mathbf{X}_{\text{trip}}^N \end{pmatrix}$$



# Different TDDFT kernel options



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

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

```
&GLOBAL
PROJECT S20Acetone
RUN_TYPE ENERGY
PREFERRED_DIAG_LIBRARY SL
PRINT_LEVEL medium
&END GLOBAL
&FORCE_EVAL
METHOD Quickstep
&PROPERTIES
&TDDFPT
KERNEL FULL
NSTATES 10
MAX_ITER 100
CONVERGENCE [eV] 1.0e-7
RKS_TRIPLETS F
&END TDDFPT
&END PROPERTIES
&EFT
```

## I. Auxiliary density matrix method (ADMM)

→ Introducing small auxiliary basis for exact exchange

$$D_{\kappa \lambda \sigma}^x (\mu \kappa | \nu \lambda) \approx \hat{D}_{\hat{\kappa} \hat{\lambda} \sigma}^x U_{\hat{\mu} \mu \sigma}^T (\hat{\mu} \hat{\kappa} | \hat{\nu} \hat{\lambda}) U_{\hat{\nu} \nu \sigma} + D_{\kappa \lambda \sigma}^x f_{\mu \kappa \sigma, \nu \lambda \sigma}^{\text{EX}} - \hat{D}_{\hat{\kappa} \hat{\lambda} \sigma}^x U_{\hat{\mu} \mu \sigma}^T f_{\hat{\mu} \hat{\kappa} \sigma, \hat{\nu} \hat{\lambda} \sigma}^{\text{EX}} U_{\hat{\nu} \nu \sigma}$$

1st order GGA correction term

### Keywords

- `ADMM_PURIFICATION_METHOD`
- `ADMM_TYPE`
- `BLOCK_LIST`
- `EPS_FILTER`
- `EXCH_CORRECTION_FUNC`
- `EXCH_SCALING_MODEL`
- `METHOD`
- `OPTX_A1`
- `OPTX_A2`
- `OPTX_GAMMA`

← Own subsections with keyword list →

## II. Simplified Tamm Dancoff Approx. (sTDA)

→ Approx. Coulomb and Exchange *and* neglect XC

$$(pq|rs) \approx \sum_A \sum_B q_{pq}^A q_{rs}^B \gamma(A, B)$$

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

### Keywords

- `COULOMB_SR_CUT`
- `COULOMB_SR_EPS`
- `DO_EWALD`
- `DO_EXCHANGE`
- `EPS_TD_FILTER`
- `FRACTION`
- `MATAGA_NISHIMOTO_CEXP`
- `MATAGA_NISHIMOTO_XEXP`

# Different TDDFT kernel options

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

## I. Auxiliary density matrix method (ADMM)

→ Introducing small auxiliary basis for exact exchange

$$D_{\kappa \lambda \sigma}^x(\mu \kappa | \nu \lambda) \approx \hat{D}_{\hat{\kappa} \hat{\lambda} \sigma}^x U_{\hat{\mu} \mu \sigma}^T (\hat{\mu} \hat{\kappa} | \hat{\nu} \hat{\lambda}) U_{\hat{\nu} \nu \sigma} + D_{\kappa \lambda \sigma}^x f_{\mu \kappa \sigma, \nu \lambda \sigma}^{\text{EX}} - \hat{D}_{\hat{\kappa} \hat{\lambda} \sigma}^x U_{\hat{\mu} \mu \sigma}^T f_{\hat{\mu} \hat{\kappa} \sigma, \hat{\nu} \hat{\lambda} \sigma}^{\text{EX}} U_{\hat{\nu} \nu \sigma}$$

1st order GGA correction term

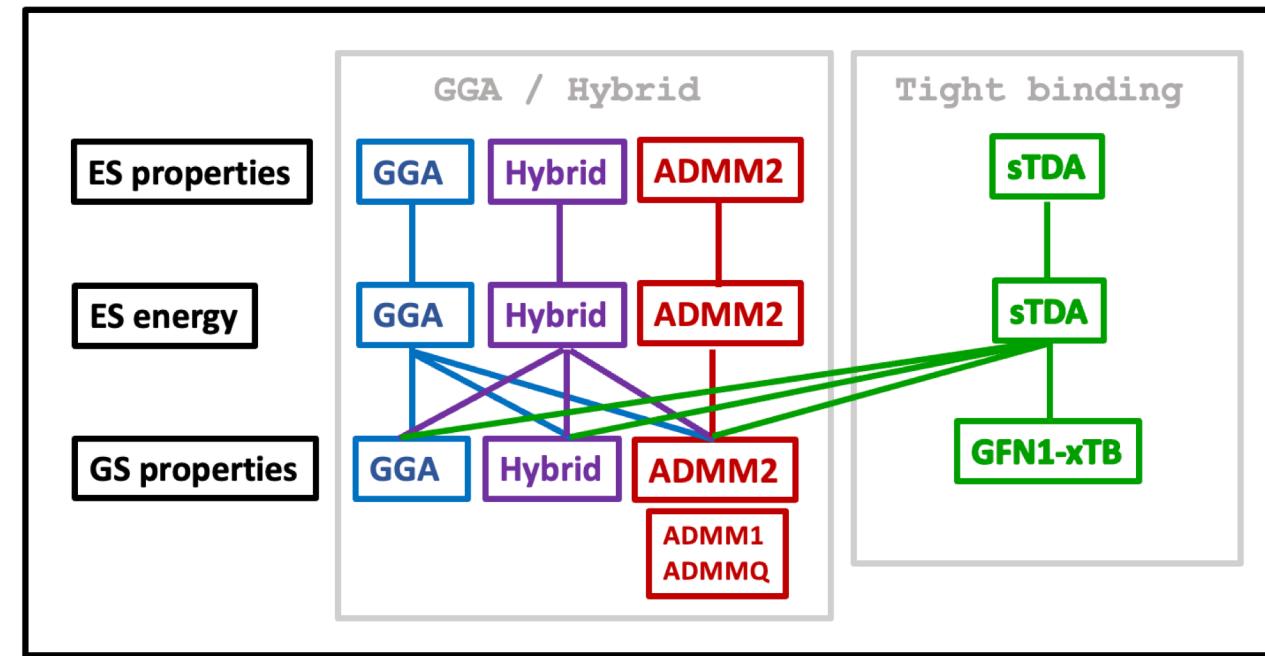
→ No density purification! Only type ADMM2.

$$E_{\text{EX}}[\mathbf{D}] = E_{\text{EX}}[\hat{\mathbf{D}}] + (E_{\text{EX}}[\mathbf{D}] - E_{\text{EX}}[\hat{\mathbf{D}}])$$

$$\mathbf{F}[\mathbf{D}] \approx \mathbf{F}^{\text{ADMM}}[\mathbf{D}] + \hat{\mathbf{U}}^T \hat{\mathbf{F}}^{\text{ADMM}}[\hat{\mathbf{D}}] \hat{\mathbf{U}}$$

Only restricted options for ADMM in TDDFT!

→ Equivalent setup for ES and GS!



$$\check{\mathbf{M}}^\zeta = \check{\mathbf{U}}^\zeta \check{\mathbf{M}} \check{\mathbf{U}}^T + \check{\mathbf{U}} \check{\mathbf{M}}^\zeta \check{\mathbf{U}}^T + \check{\mathbf{U}} \check{\mathbf{M}} (\check{\mathbf{U}}^T)^\zeta,$$

# Different TDDFT kernels

$$\sum_{\kappa k} [F_{\mu \kappa \sigma} \delta_{ik} - F_{ik\sigma} S_{\mu \kappa}] X_{\kappa k}$$

## I. Auxiliary density matrix method (ADMM)

→ Introducing small auxiliary basis for exact exchange

$$D_{\kappa \lambda \sigma}^x(\mu \kappa | \nu \lambda) \approx \hat{D}_{\hat{\kappa} \hat{\lambda} \sigma}^x U_{\hat{\mu} \mu \sigma}^T (\hat{\mu} \hat{\kappa} | \hat{\nu} \hat{\lambda}) U_{\hat{\nu} \nu \sigma} + D_{\kappa \lambda \sigma}^x f_{\mu \kappa \sigma, \nu \lambda \sigma}^{\text{EX}} - \hat{D}_{\hat{\kappa} \hat{\lambda} \sigma}^x U_{\hat{\mu} \mu \sigma}^T f_{\hat{\mu} \hat{\kappa} \sigma, \hat{\nu} \hat{\lambda} \sigma}^{\text{EX}} U_{\hat{\nu} \nu \sigma}$$

1st order GGA correction term

→ No density purification! Only type **ADMM2**.

$$E_{\text{EX}}[\mathbf{D}] = E_{\text{EX}}[\hat{\mathbf{D}}] + (E_{\text{EX}}[\mathbf{D}] - E_{\text{EX}}[\hat{\mathbf{D}}])$$

$$\mathbf{F}[\mathbf{D}] \approx \mathbf{F}^{\text{ADMM}}[\mathbf{D}] + \hat{\mathbf{U}}^T \hat{\mathbf{F}}^{\text{ADMM}}[\hat{\mathbf{D}}] \hat{\mathbf{U}}$$

## ADMM2 input section:

```
&FORCE_EVAL
```

```
&PROPERTIES
```

```
&TDDFPT
```

```
KERNEL FULL
```

```
&END TDDFPT
```

```
&END PROPERTIES
```

1. order contributions

```
&DFT
```

```
&AUXILIARY_DENSITY_MATRIX_METHOD
```

```
METHOD BASIS_PROJECTION
```

```
EXCH_CORRECTION_FUNC NONE / PBEX
```

```
ADMM_PURIFICATION_METHOD NONE
```

```
EXCH_SCALING_MODEL NONE
```

```
&END AUXILIARY_DENSITY_MATRIX_METHOD
```

```
...
```

```
&END DFT
```

```
&END FORCE_EVAL
```

with appropriate auxiliary basis

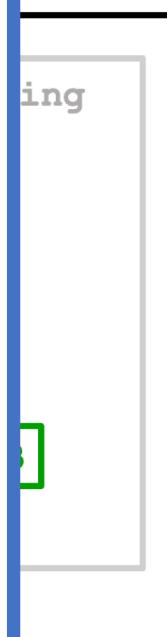
```
&KIND H
```

```
BASIS_SET AUX_FIT admm-dzp-q1
```

```
BASIS_SET ORB ccGRB-D-q1
```

```
POTENTIAL GTH-PBEO-q1
```

```
&END KIND
```



TDDFT section!



## Different TDDFT kernel options

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

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

### II. Simplified Tamm Dancoff Approx. (sTDA)

→ Approx. Coulomb and Exchange *and* neglect XC

$$(pq|rs) \approx \sum_A \sum_B q_{pq}^A q_{rs}^B \gamma(A, B)$$

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

#### Keywords

- COULOMB\_SR\_CUT
- COULOMB\_SR\_EPS
- DO\_EWALD
- DO\_EXCHANGE
- EPS\_TD\_FILTER
- FRACTION
- MATAGA\_NISHIMOTO\_CEXP
- MATAGA\_NISHIMOTO\_XEXP

Kernel  $K$

$$K_{\kappa \lambda \sigma} [\mathbf{D}^x] C_{\lambda i \sigma} = \sum_{\kappa} \Omega S_{\mu \kappa} X_{\kappa i \sigma}$$



$$\sum_{\lambda} K_{\mu \lambda \sigma}^{\text{sTDA}} [\mathbf{D}^x] C_{\lambda i \sigma} = \sum_{AB} (1-s) \gamma^J(A, B) \tilde{C}_{\mu i \sigma}^B \sum_{\lambda_A l \sigma'} \tilde{C}_{\lambda_A l \sigma'} \tilde{X}_{\lambda_A l \sigma'}$$

**Sternheimer formulation**

$$q_{ij\sigma}^A = \sum_{\kappa_A} \tilde{C}_{\kappa_A i \sigma}^T \tilde{C}_{\kappa_A j \sigma}$$

$$\tilde{C}_{\mu i \sigma} = \sum_{\eta} S_{\mu \eta}^{1/2} C_{\eta i \sigma},$$

$$\tilde{C}_{\mu i \sigma}^A = \sum_{\eta_A} S_{\mu \eta_A}^{1/2} \tilde{C}_{\eta_A i \sigma}$$

approximating both Coulomb and exchange

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

$$\gamma^{\text{EX}}(A, B) = \left( \frac{1}{(R_{AB})^\beta + (a_{\text{EX}} \eta)^{-\beta}} \right)^{1/\beta} \quad \text{MATAGA_NISHIMOTO_XEXP}$$

global exact exchange scaling parameter

```

<
INTEGER, PARAMETER, PRIVATE :: nelem = 103
! H
! Li Be
! Na Mg
! K Ca Sc
! Rb Sr Y
! Cs Ba La Ce-Lu
! Fr Ra Ac Th Pa U
      He
      B C N O F Ne
      Al Si P S Cl Ar
      Ga Ge As Se Br Kr
      In Sn Sb Te I Xe
      Tl Pb Bi Po At Rn
      No Lr 103
      Ti V Cr Mn Fe Co Ni Cu Zn
      Zr Nb Mo Tc Ru Rh Pd Ag Cd
      Hf Ta W Re Os Ir Pt Au Hg
      Np Pu Am Cm Bk Cf Es Fm Md
REAL(KIND=dp), DIMENSION(1:nelem), PARAMETER, PRIVATE:: hardness = &
(/6.4299544220_dp, 12.544911890_dp, & ! 2 H-He
 2.3745866560_dp, 3.4967633530_dp, 4.6190089720_dp, 5.7409789220_dp, &
 6.8624665290_dp, 7.9854357010_dp, 9.1064753720_dp, 10.23034050_dp, & ! 8 !
 2.444141360_dp, 3.0146513830_dp, 3.5849070740_dp, 4.15513090_dp, &
 4.7258039740_dp, 5.2959792410_dp, 5.8661864840_dp, 6.4366187140_dp, & ! 8 !
 2.3273178360_dp, 2.7587238140_dp, 2.8581921140_dp, 2.9578300430_dp, &
 3.0573410060_dp, 3.1567254290_dp, 3.2563827230_dp, 3.3559314050_dp, &
 3.4556091170_dp, 3.5550133130_dp, 3.6544183480_dp, 3.7541601450_dp, &
 4.1855197930_dp, 4.6166272460_dp, 5.0662145070_dp, 5.4794960970_dp, &
 5.9110996450_dp, 6.3418467680_dp, & ! 18 K-Kr
 2.1204582570_dp, 2.5373700480_dp, 2.6335468980_dp, 2.7297528930_dp, &
 2.8259738860_dp, 2.9221296040_dp, 3.0183708780_dp, 3.1145981770_dp, &
 3.210756280_dp, 3.3069474480_dp, 3.4031948570_dp, 3.4993761390_dp, &
 3.9163692460_dp, 4.3332332190_dp, 4.7500787860_dp, 5.1669793270_dp, &
 5.5838871020_dp, 6.000897330_dp, & ! 18 Rb-Xe
 0.6829150240_dp, 0.9200946840_dp, 1.1570887860_dp, 1.39427570_dp, &
 1.6314731730_dp, 1.8684389980_dp, 2.1056577930_dp, 2.3426646420_dp, &
 2.5798149820_dp, 2.8170264230_dp, 3.0540365330_dp, 3.2911692310_dp, &
 3.5282971610_dp, 3.7655249290_dp, 4.0025547030_dp, 4.2394783410_dp, &
 4.4765830210_dp, 4.7065224490_dp, 4.9508466940_dp, 5.1879311720_dp, &
 5.4256076210_dp, 5.6619144310_dp, 5.900042920_dp, 6.1367145320_dp, &
 6.3741299770_dp, 6.6102656130_dp, 1.7043485810_dp, 1.9413526120_dp, &
 2.178491510_dp, 2.4158121060_dp, 2.6527780840_dp, 2.8899554570_dp, & ! 32 !
 0.9882529880_dp, 1.2819499970_dp, 1.3497250380_dp, 1.4175257380_dp, &
 1.9368567520_dp, 2.2305576050_dp, 2.5241204960_dp, 3.0436128480_dp, &
 3.4168675260_dp, 3.4049844440_dp, 3.9244199680_dp, 4.2180813280_dp, &
 4.5115926320_dp, 4.8050928950_dp, 5.0989816210_dp, 5.3926054620_dp, &
 5.4606987930_dp/) ! 17 Fr-Lr
>

REAL(KIND=dp), DIMENSION(2), PARAMETER, PRIVATE:: alpha = (/1.420_dp, 0.480_dp/)
REAL(KIND=dp), DIMENSION(2), PARAMETER, PRIVATE:: beta = (/0.200_dp, 1.830_dp/)

```

## sTDA parameters in the code

1. Global scaling via  $a_{\text{EX}}$

DO\_EXCHANGE

FRACTION

2. Hardness  $\eta$

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

MATAGA\_NISHIMOTO\_CEXP

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

MATAGA\_NISHIMOTO\_XEXP

global exact exchange scaling parameter

3. Default parameters are computed as

$$\alpha = \alpha_1 + a_{\text{EX}}\alpha_2$$

$$\beta = \beta_1 + a_{\text{EX}}\beta_2$$

→ Check sTDA publications  
and manual for  
different parameterizations!

e.g.

functional	$a_x$	$\alpha$	$\beta$
CAM-B3LYP	0.38	0.90	1.86
LC-BLYP	0.53	4.50	8.00
$\omega$ B97	0.61	4.41	8.00
$\omega$ B97X	0.56	4.58	8.00
$\omega$ B97X-D3	0.51	4.51	8.00

[https://www.chemie.uni-bonn.de/grimme/de/software/stda/stda\\_manual.pdf](https://www.chemie.uni-bonn.de/grimme/de/software/stda/stda_manual.pdf)

→ Balanced amount of exact exchange for GS and ES!

```

<
INTEGER, PARAMETER, PRIVATE :: nelem = 103
! H
! Li Be
! Na Mg
! K Ca Sc
! Rb Sr Y
! Cs Ba La Ce-Lu
! Fr Ra Ac Th Pa U
      He
      B C N O F Ne
      Al Si P S Cl Ar
      Ga Ge As Se Br Kr
      In Sn Sb Te I Xe
      Tl Pb Bi Po At Rn
      No Lr 103
      Ti V Cr Mn Fe Co Ni Cu Zn
      Zr Nb Mo Tc Ru Rh Pd Ag Cd
      Hf Ta W Re Os Ir Pt Au Hg
      Np Pu Am Cm Bk Cf Es Fm Md
REAL(KIND=dp), DIMENSION(1:nelem), PARAMETER, PRIVATE:: hardness = &
(/6.4299544220_dp, 12.544911890_dp, & ! 2 H-He
 2.3745866560_dp, 3.4967633530_dp, 4.6190089720_dp, 5.7409789220_dp, &
 6.8624665290_dp, 7.9854357010_dp, 9.1064753720_dp, 10.23034050_dp, & ! 8 !
 2.444141360_dp, 3.0146513830_dp, 3.5849070740_dp, 4.15513090_dp, &
 4.7258039740_dp, 5.2959792410_dp, 5.8661864840_dp, 6.4366187140_dp, & ! 8 !
 2.3273178360_dp, 2.7587238140_dp, 2.8581921140_dp, 2.9578300430_dp, &
 3.0573410060_dp, 3.1567254290_dp, 3.2563827230_dp, 3.3559314050_dp, &
 3.4556091170_dp, 3.5550133130_dp, 3.6544183480_dp, 3.7541601450_dp, &
 4.1855197930_dp, 4.6166272460_dp, 5.0662145070_dp, 5.4794960970_dp, &
 5.9110996450_dp, 6.3418467680_dp, & ! 18 K-Kr
 2.1204582570_dp, 2.5373700480_dp, 2.6335468980_dp, 2.7297528930_dp, &
 2.8259738860_dp, 2.9221296040_dp, 3.0183708780_dp, 3.1145981770_dp, &
 3.210756280_dp, 3.3069474480_dp, 3.4031948570_dp, 3.4993761390_dp, &
 3.9163692460_dp, 4.3332332190_dp, 4.7500787860_dp, 5.1669793270_dp, &
 5.5838871020_dp, 6.000897330_dp, & ! 18 Rb-Xe
 0.6829150240_dp, 0.9200946840_dp, 1.1570887860_dp, 1.39427570_dp, &
 1.6314731730_dp, 1.8684389980_dp, 2.1056577930_dp, 2.3426646420_dp, &
 2.5798149820_dp, 2.8170264230_dp, 3.0540365330_dp, 3.2911692310_dp, &
 3.5282971610_dp, 3.7655249290_dp, 4.0025547030_dp, 4.2394783410_dp, &
 4.4765830210_dp, 4.7065224490_dp, 4.9508466940_dp, 5.1879311720_dp, &
 5.4256076210_dp, 5.6619144310_dp, 5.900042920_dp, 6.1367145320_dp, &
 6.3741299770_dp, 6.6102656130_dp, 1.7043485810_dp, 1.9413526120_dp, &
 2.178491510_dp, 2.4158121060_dp, 2.6527780840_dp, 2.8899554570_dp, & ! 32 !
 0.9882529880_dp, 1.2819499970_dp, 1.3497250380_dp, 1.4175257380_dp, &
 1.9368567520_dp, 2.2305576050_dp, 2.5241204960_dp, 3.0436128480_dp, &
 3.4168675260_dp, 3.4049844440_dp, 3.9244199680_dp, 4.2180813280_dp, &
 4.5115926320_dp, 4.8050928950_dp, 5.0989816210_dp, 5.3926054620_dp, &
 5.4606987930_dp/) ! 17 Fr-Lr
>

REAL(KIND=dp), DIMENSION(2), PARAMETER, PRIVATE:: alpha = (/1.420_dp, 0.480_dp/)
REAL(KIND=dp), DIMENSION(2), PARAMETER, PRIVATE:: beta = (/0.200_dp, 1.830_dp/)

```

## sTDA parameters in the code

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FRACTION

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

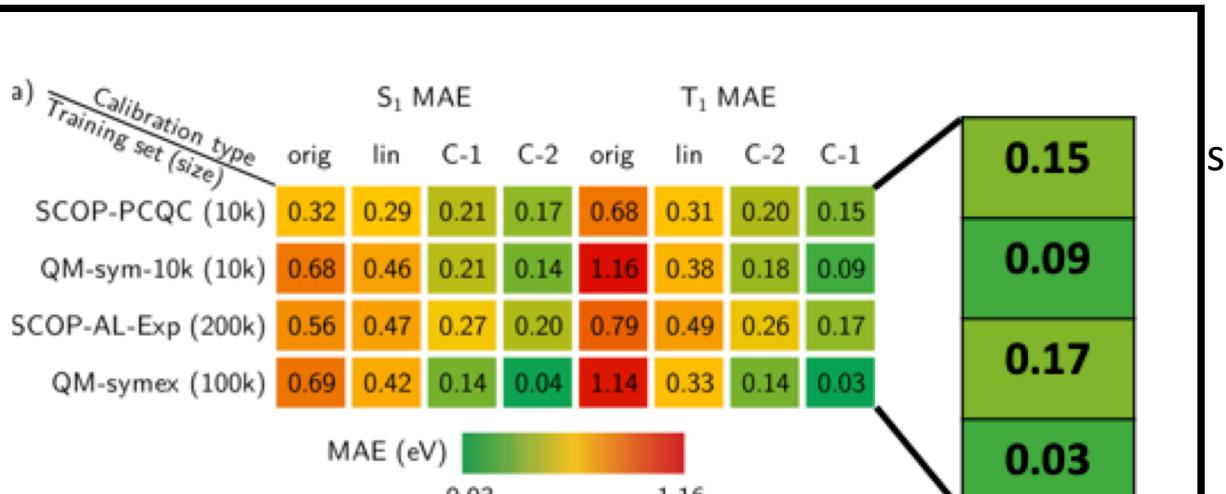
MATAGA\_NISHIMOTO\_CEXP

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

MATAGA\_NISHIMOTO\_XEXP

global exact exchange scaling parameter

3. Default parameters are computed as



Walsh et al. J. Chem. Phys. 156, 134116 (2022).

→ Balanced amount of exact exchange for GS and ES!

## Main idea for excited state method sTDA

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

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

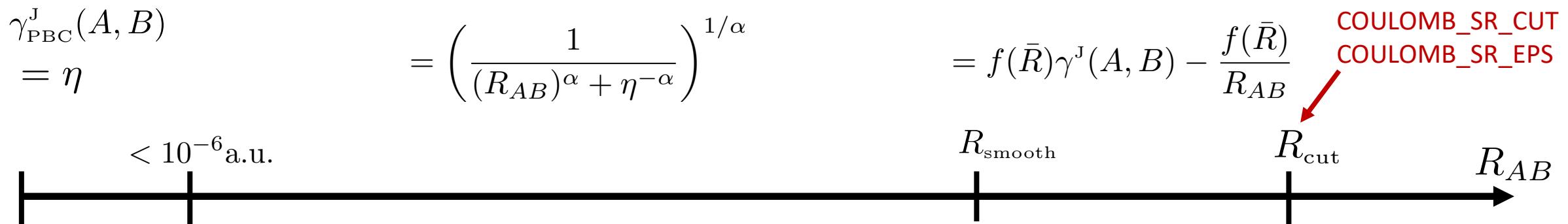
## extended to periodic boundary conditions

$$\gamma_{\text{PBC}}^{\text{J}}(A, B) + \frac{1}{R_{AB}}$$

semi-empirical short-range      exact long-range

$\Gamma$ -point only, MOs and integrals are periodically replicated

Ewald summation for Coulomb contributions  $\longrightarrow$  Default for DO\_EWALD keyword is FALSE!



# Different TDDFT kernel options

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

## II. Simplified Tamm Dancoff Approx. (sTDA)

→ Approx. Coulomb and Exchange *and* neglect XC

$$(pq|rs) \approx \sum_A \sum_B q_{pq}^A q_{rs}^B \gamma(A, B)$$

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

### Keywords

- COULOMB\_SR\_CUT
- COULOMB\_SR\_EPS
- DO\_EWALD
- DO\_EXCHANGE
- EPS\_TD\_FILTER
- FRACTION
- MATAGA\_NISHIMOTO\_CEXP
- MATAGA\_NISHIMOTO\_XEXP

Different definitions wrt original sTDA implementation ( X vs. C ) !

**Be very careful with the default settings! Switch on Ewald if required!**

### sTDA input section:

```
&FORCE_EVAL
  &PROPERTIES
    &TDDFPT
      KERNEL sTDA
      &STDA
        FRACTION 0.25
        DO_EWALD T
      &END STDA
    &END TDDFPT
  &END DFT
&END FORCE_EVAL
```

```
&XC
  &XC_FUNCTIONAL
    &GGA_C_PBE
  &END GGA_C_PBE
  &GGA_X_PBE
    SCALE 0.75
  &END GGA_X_PBE
  &END XC_FUNCTIONAL
  &HF
    FRACTION 0.25
    &HF_INFO ON
  &END
  &INTERACTION_POTENTIAL
    POTENTIAL_TYPE TRUNCATED
    CUTOFF_RADIUS 4.0
    T_C_G_DATA t_c_g.dat
  &END
  &SCREENING
    EPS_SCHWARZ 1.0E-8
    SCREEN_ON_INITIAL_P FALSE
  &END
  &END HF
&END XC
```



# Output of a TDDFT computation



→ TDDFT tutorial on how to compute excitation energies for acetone

TDDFPT Initial Guess				
State number	Occupied orbital	→	Virtual orbital	Excitation energy (eV)
1	12		13	6.63336
2	11		13	9.62185
3	10		13	10.34045
4	9		13	10.78846
5	8		13	11.05691
6	12		14	12.07194
7	7		13	12.42370
8	6		13	12.63557
9	12		15	12.65312
10	5		13	12.68633

Excitation analysis				
State number	Occupied orbital		Virtual orbital	Excitation amplitude
1	4.67815 eV			
		12	13	0.998438
2	8.73074 eV			
		10	13	0.995560
		6	13	0.087643
3	9.17033 eV			
		9	13	0.993356
		7	13	0.075589
4	9.70094 eV			
		11	13	-0.893130
		12	16	0.297568
		5	13	0.260022

— TDDFPT run converged in 10 iteration(s)

R-TDDFPT states of multiplicity 1

Transition dipoles calculated using velocity formulation

State number	Excitation energy (eV)	Transition dipole (a.u.)			Oscillator strength (a.u.)
		x	y	z	
TDDFPT  1	4.67815	2.4840E-08	-1.9187E-08	5.9673E-08	5.21038E-16
TDDFPT  2	8.73074	-8.1610E-09	1.0502E-08	9.1823E-08	1.84132E-15
TDDFPT  3	9.17033	1.6661E-02	2.4911E-08	-9.2612E-08	6.23670E-05
TDDFPT  4	9.70094	-2.3716E-09	7.2323E-07	7.0660E-01	1.18663E-01
TDDFPT  5	9.88658	-3.1922E-08	-4.1476E-01	1.0768E-06	4.16669E-02
TDDFPT  6	10.70094	0.51625E-09	1.02055E-01	1.01225E-07	1.01555E-02

Further keywords:

NLUMO

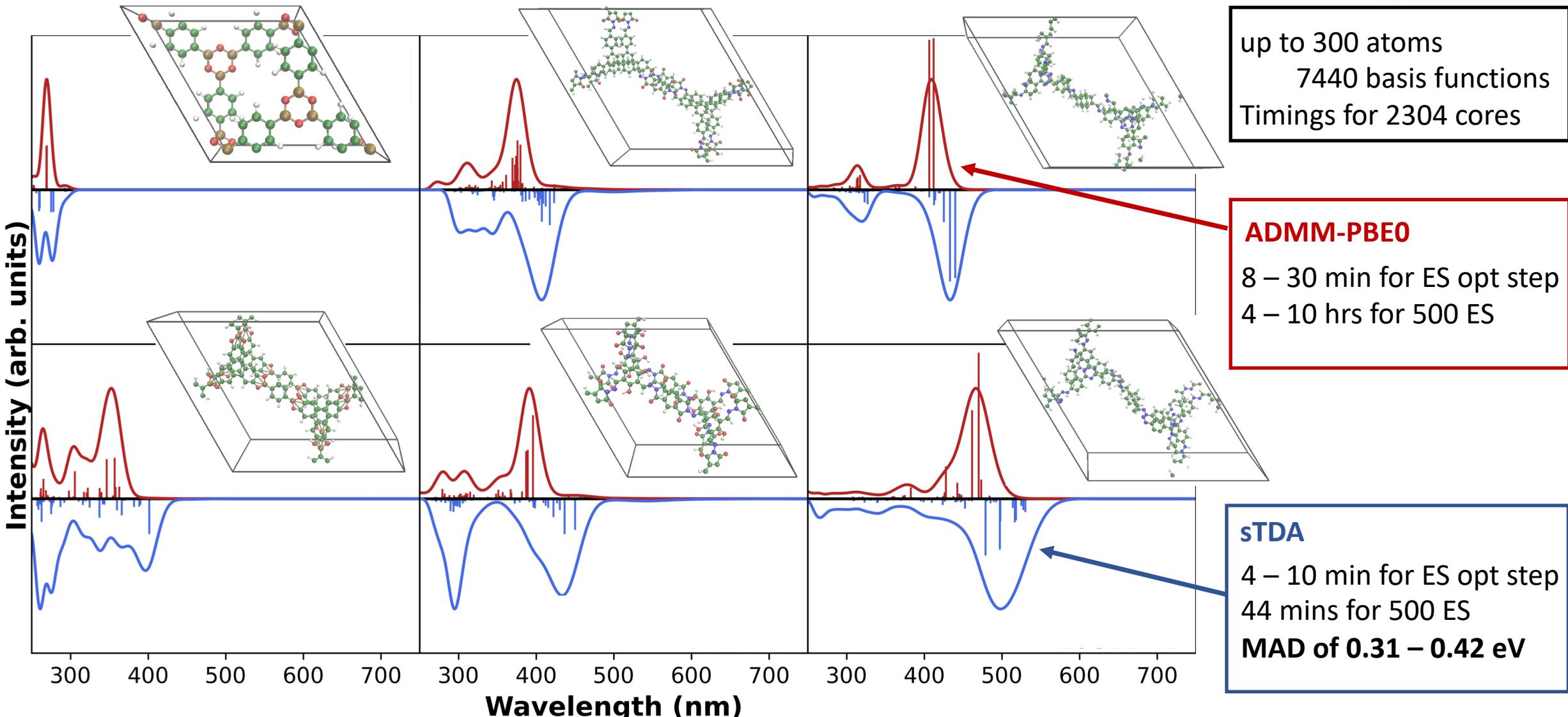
EV\_SHIFT  $F_{\mu\nu\sigma}^{\Delta \text{VIR}} = F_{\mu\nu\sigma} + \frac{1}{2} \sum_{\kappa} \Delta^{\text{VIR}} (Q_{\kappa\mu\sigma}^T S_{\kappa\nu} + S_{\mu\kappa} Q_{\kappa\nu\sigma})$

DIPOLE\_MOMENTS DIPOLE\_FORM (BERRY, LENGTH, VELOCITY)

....  $i(\varepsilon_i - \varepsilon_j) \langle \phi_i | \hat{r}_\zeta | \phi_j \rangle = \langle \phi_i | \hat{p}_\zeta | \phi_j \rangle + i \langle \phi_i | [V_{\text{nl}}, \hat{r}_\zeta] | \phi_j \rangle$

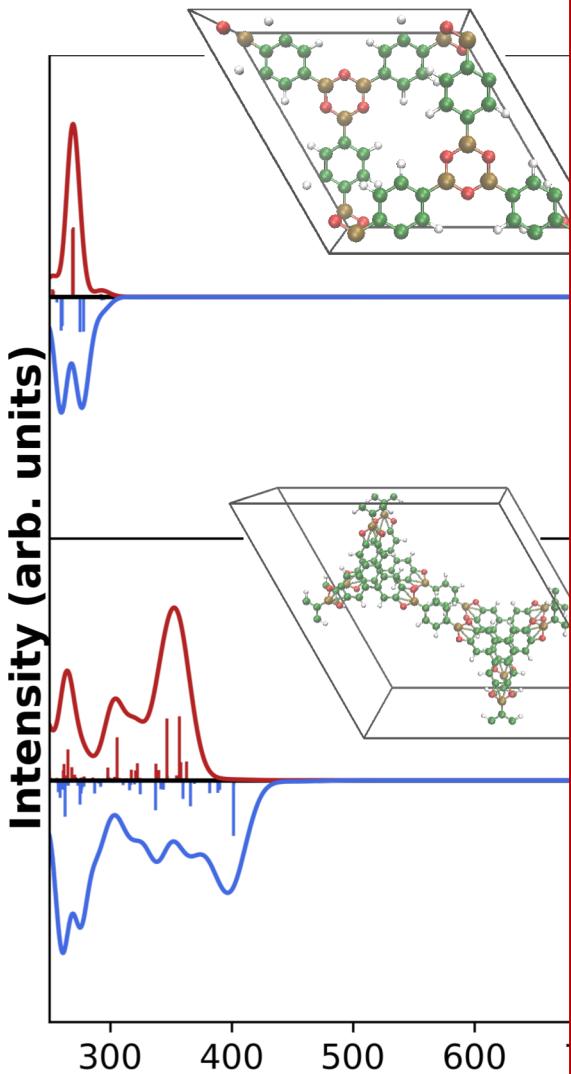


# Application on covalent-organic framework materials





# Application on covalent-organic framework materials



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## Excited-state properties for extended systems: efficient hybrid density functional methods

Anna-Sophia Hehn<sup>1\*</sup>, Beliz Sertcan<sup>1\*</sup>, Fabian Belleflamme<sup>1\*</sup>, Sergey K. Chulkov<sup>2\*</sup>, Matthew B. Watkins<sup>2</sup>, Jürg Hutter<sup>1\*</sup>

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2 School of Mathematics and Physics, University of Lincoln, Brayford Pool, Lincoln LN67TS, United Kingdom

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DOI [10.24435/materialscloud:gw-kq](https://doi.org/10.24435/materialscloud:gw-kq) [version v1]

Publication date: Jun 17, 2022

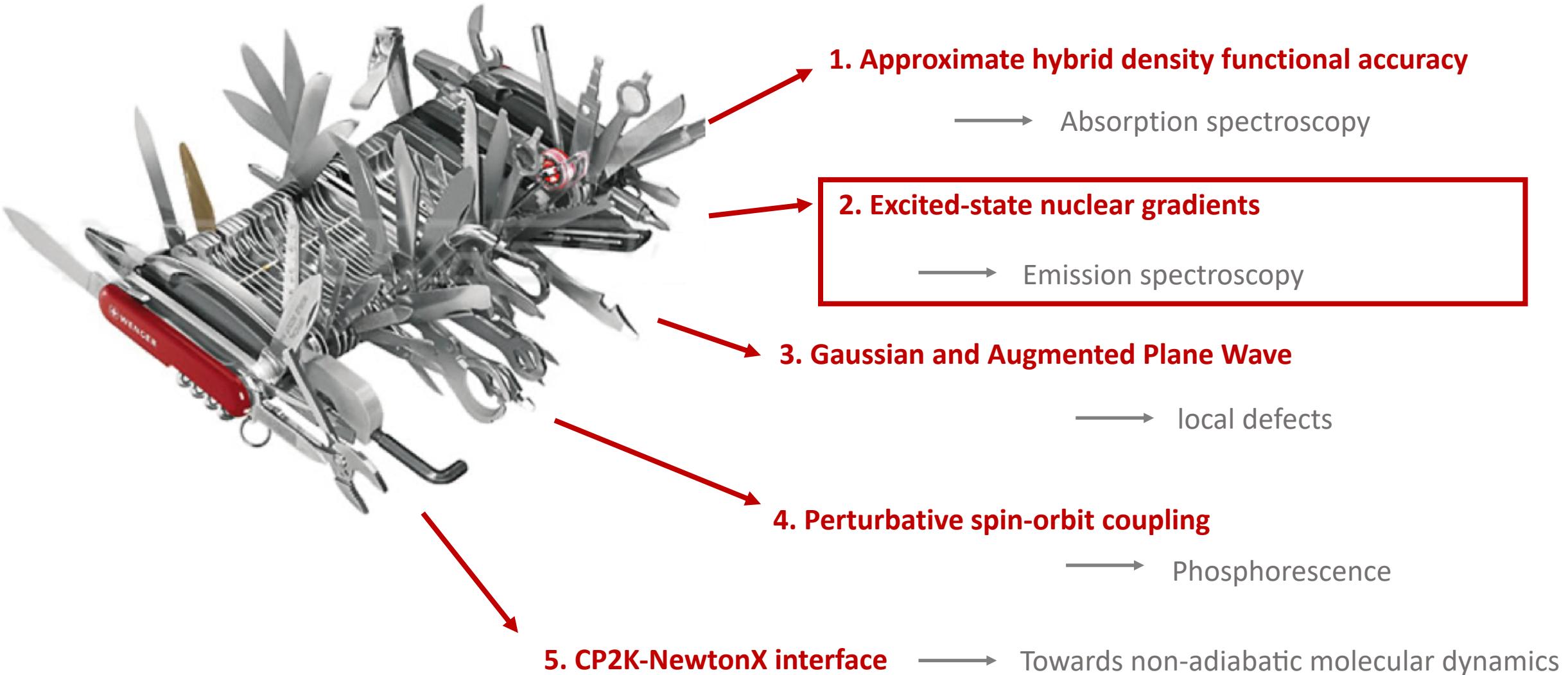
### How to cite this record

Anna-Sophia Hehn, Beliz Sertcan, Fabian Belleflamme, Sergey K. Chulkov, Matthew B. Watkins, Jürg Hutter, *Excited-state properties for extended systems: efficient hybrid density functional methods*, Materials Cloud Archive **2022.81** (2022), <https://doi.org/10.24435/materialscloud:gw-kq>

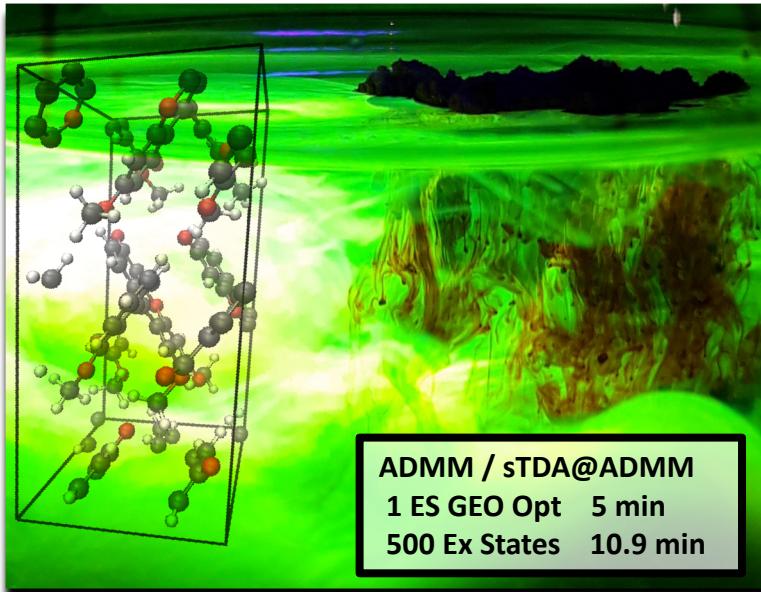
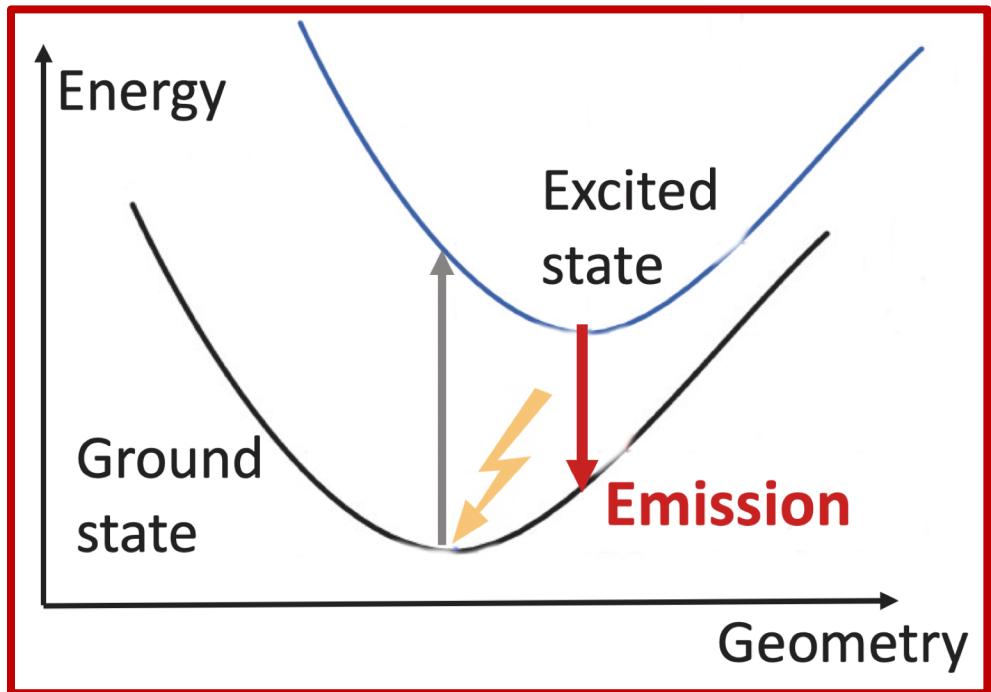
### Description

Time-dependent density functional theory has become state-of-the-art for describing photophysical and photochemical processes in extended materials due to its affordable cost. The inclusion of exact exchange was shown to be essential for the correct description of the long-range asymptotics of electronic interactions and thus a well-balanced description of valence, Rydberg and charge-transfer excitations. Several approaches for an efficient treatment of exact exchange have been established for the ground state, while implementations for excited-state properties are rare. Furthermore, the high computational costs required for excited-state properties in comparison to ground-state computations often hinder large-scale applications on periodic systems with hybrid functional accuracy. We therefore propose two approximate schemes for improving computational efficiency for the treatment of exact exchange. Within the auxiliary density matrix method (ADMM), exact exchange is estimated using a relatively small auxiliary basis and the introduced basis-set incompleteness error is compensated by an exchange density functional correction term. Benchmark results for a test set of 35 molecules demonstrate that the mean absolute error introduced by

# Tailoring the Swiss Army Knife for efficient absorption and emission spectroscopy



# Optimizing the excited state to compute emission spectra



River Chicago  
in Chicago  
on St Patrick's Day

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

$$\frac{d\Omega(\zeta, \mathbf{C}, \mathbf{X})}{d\zeta} = \frac{\partial\Omega}{\partial\zeta} + \frac{\partial\Omega}{\partial\mathbf{X}} \frac{\partial\mathbf{X}}{\partial\zeta} + \frac{\partial\Omega}{\partial\mathbf{C}} \frac{\partial\mathbf{C}}{\partial\zeta}$$

## 1. Excitation energies

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

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

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



# Sternheimer formulation for excited-state gradients

Lagrange formalism to avoid 1st order response:

## 1. Excitation energies

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

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

## 2. Z vector equation

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

## 3. Excited-state gradient

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

Furche, Ahlrichs, *J Chem Phys*, 121, 12772 (2002);  
 Hutter, *J Chem Phys*, 118, 3928 (2003);  
 AH, Sertcan, Belleflamme, Chulkov, Watkins, Hutter,  
*J. Chem. Theory Comput.* 18, 4186 (2022).

## 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

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

## Treatment of the virtual space

$$\begin{aligned} G[\mathbf{X}, \mathbf{C}, \Omega, \bar{\mathbf{W}}^x] \\ = \sum_{\kappa k\sigma} X_{\kappa k\sigma}^T \sum_{\lambda l} [F_{\kappa\lambda\sigma} \delta_{kl} - F_{kl\sigma} S_{\kappa\lambda}] X_{\lambda l\sigma} \\ + \sum_{\kappa\lambda\sigma} D_{\kappa\lambda\sigma}^x K_{\kappa\lambda\sigma} [\mathbf{D}^x] - \sum_{\kappa\lambda k l\sigma} \Omega (X_{\kappa k\sigma}^T S_{\kappa\lambda} X_{\lambda l\sigma} - \delta_{kl}) \\ - \sum_{kl\sigma} (\bar{W}_{kl\sigma}^x)^T \sum_{\kappa\lambda} \frac{1}{2} (C_{\kappa k\sigma}^T S_{\kappa\lambda} X_{\lambda l\sigma} + X_{\kappa k\sigma}^T S_{\kappa\lambda} C_{\lambda l\sigma}) \end{aligned}$$

Orthogonality of  $\mathbf{X}$  and  $\mathbf{C}$  can be ensured via  $\mathbf{Q}$ !

# Input for excited-state gradients and emission spectroscopy

## Exemplary Input for TDDFT forces:

```
&GLOBAL
  PROJECT S20Acetone
  RUN_TYPE ENERGY_FORCE / GEO_OPT
&END GLOBAL
```

```
&PROPERTIES
  &TDDFPT
    NSTATES 10
    MAX_ITER 100
    CONVERGENCE [eV] 1.0e-7
    RKS_TRIPLETS F
    ADMM_KERNEL_CORRECTION_SYMMETRIC T
  &END TDDFPT
  &END PROPERTIES
```

```
&DFT
  &EXCITED_STATES T
    STATE 1
  &END EXCITED_STATES
&END DFT
....
```

## Exemplary Output for TDDFT forces:

```
!----- Excited State Energy -----!
Excitation Energy [Hartree] 0.1719188002
Total Energy [Hartree] -36.3332484083
!----- Excited State Forces -----!
```

Iteration	Method	Restart	Stepsize	Convergence	Time
1	PCG	F	0.00E+00	0.0231470476	0.02
2	PCG	F	0.30E+00	0.0003972862	1.56
3	PCG	F	0.60E+00	0.0000361012	3.11
4	PCG	F	0.62E+00	0.0000031865	4.65
5	PCG	F	0.63E+00	0.0000002183	6.19
6	PCG	F	0.73E+00	0.0000000147	7.73
7	PCG	F	0.70E+00	0.0000000014	9.27
8	PCG	F	0.72E+00	0.0000000001	10.82
9	PCG	F	0.71E+00	0.0000000000	12.35

```
ENERGY| Total FORCE_EVAL ( QS ) energy [a.u.]: -36.333248408276823
```

For gradients: **ADMM\_KERNEL\_CORRECTION\_SYMMETRIC** in TDDFT section!

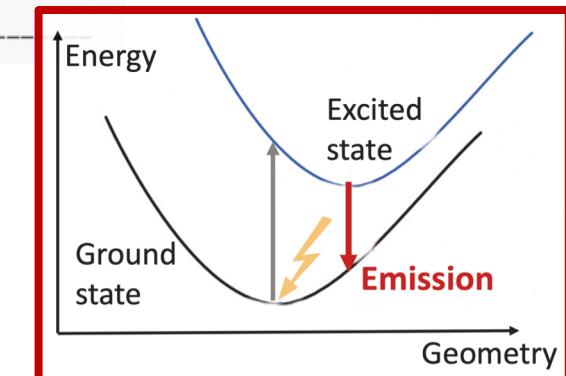
$$\check{M}^\zeta = \check{U}^\zeta \check{M} \check{U}^T + \check{U} \check{M}^\zeta \check{U}^T + \check{U} \check{M} (\check{U}^T)^\zeta$$

1. Excitation energies

$$AX_n = \Omega_n SX_n$$

2. Z vector equation

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



## Exemplary Input for TDDFT forces:

```

&GLOBAL
  PROJECT S20Acetone
  RUN
&END

&PROPERTIES
  &TDDFPT
    CONVERGENCE [eV] 1.0e-7
    KERNEL FULL
    NSTATES 5
    RKS_TRIPLETS F
  &LINRES
    EPS 1.0E-10
    EPS_FILTER 1.0E-15
    MAX_ITER 20
    PRECONDITIONER FULL_SINGLE_INVERSE
  &END LINRES
  &XC
    &XC_FUNCTIONAL NONE
  &END XC_FUNCTIONAL
  &END XC
  &END TDDFPT
&END PROPERTIES

```

## Convergence problems with TDDFT forces:

## Exemplary Output for TDDFT forces:

```

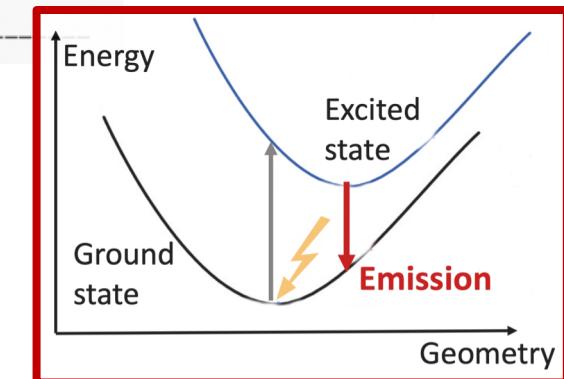
!----- Excited State Energy -----!
Excitation Energy [Hartree]          0.1719188002
Total Energy [Hartree]             -36.3332484083
!----- Excited State Forces -----!
Method   Restart   Stepsize   Convergence   Time
PCG      F         0.00E+00   0.0231470476   0.02
PCG      F         0.30E+00   0.0003972862   1.56
PCG      F         0.60E+00   0.0000361012   3.11
PCG      F         0.62E+00   0.00000031865  4.65
PCG      F         0.63E+00   0.0000002183   6.19
PCG      F         0.73E+00   0.0000000147   7.73
PCG      F         0.70E+00   0.0000000014   9.27
PCG      F         0.72E+00   0.0000000001   10.82
PCG      F         0.71E+00   0.0000000000   12.35
!----- al FORCE_EVAL ( QS ) energy [a.u.]: -----!
                                         -36.333248408276823

```

Change LINRES section for Z vector equation

1. Excitation energies  
 $\mathbf{AX}_n = \Omega_n \mathbf{SX}_n$

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





# Input for excited-state gradients and emission spectroscopy



## Exemplary Input for TDDFT forces:

```
&GLOBAL
  PROJECT S20Acetone
  RUN_TYPE ENERGY_FORCE
&END GLOBAL

&PROPERTIES
  &TDDFPT
    NSTATES 10
    MAX_ITER 100
    CONVERGENCE [eV] 1.0e-7
    RKS_TRIPLETS F
    ADMM_KERNEL_CORRECTION_SYMMETRIC T
  &END TDDFPT
&END PROPERTIES

&DFT
  &EXCITED_STATES T
    STATE 1
  &END EXCITED_STATES
&END DFT
....
```

## Printing TDDFT forces:

```
&MOTION
  &GEO_OPT
  &PRINT
    &STRUCTURE_DATA
      DISTANCE 3 4
      ANGLE 2 1 3
      ....
    &END STRUCTURE_DATA
  &END PRINT
  &END GEO_OPT
  &END MOTION

  &FORCE_EVAL
    &PRINT
      &FORCES
    &END FORCES
  &END PRINT
  &END FORCE_EVAL
```

```
*****
***                                GEOMETRY OPTIMIZATION COMPLETED
*****
***** REQUESTED STRUCTURE DATA *****

Distance vector r(i,j) between the atom i and j in ANGSTROM

r(3,4)      = -0.000002   -1.498276   -0.000000   |r| = 1.498276
r(1,2)      = -0.000000   -0.000000   1.452633   |r| = 1.452633
r(1,3)      = 0.000001    0.749138   -1.136396   |r| = 1.361104

Angle a(i,j,k) between the atomic distance vectors r(j,i) and r(j,k) in DEGREE

a(2,1,3)      = 146.606

Reevaluating energy at the minimum

***** REQUESTED STRUCTURE DATA *****

Distance vector r(i,j) between the atom i and j in ANGSTROM

r(3,4)      = -0.000002   -1.498276   -0.000000   |r| = 1.498276
r(1,2)      = -0.000000   -0.000000   1.452633   |r| = 1.452633
r(1,3)      = 0.000001    0.749138   -1.136396   |r| = 1.361104

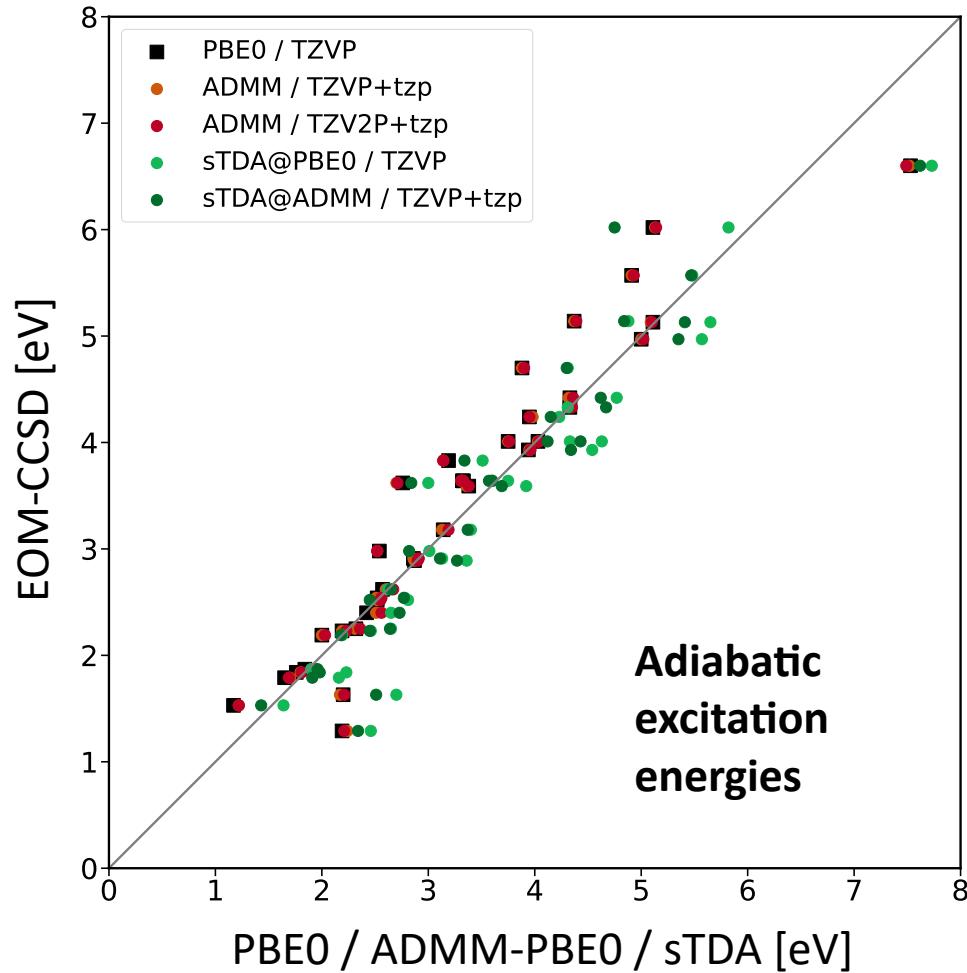
Angle a(i,j,k) between the atomic distance vectors r(j,i) and r(j,k) in DEGREE

a(2,1,3)      = 146.606

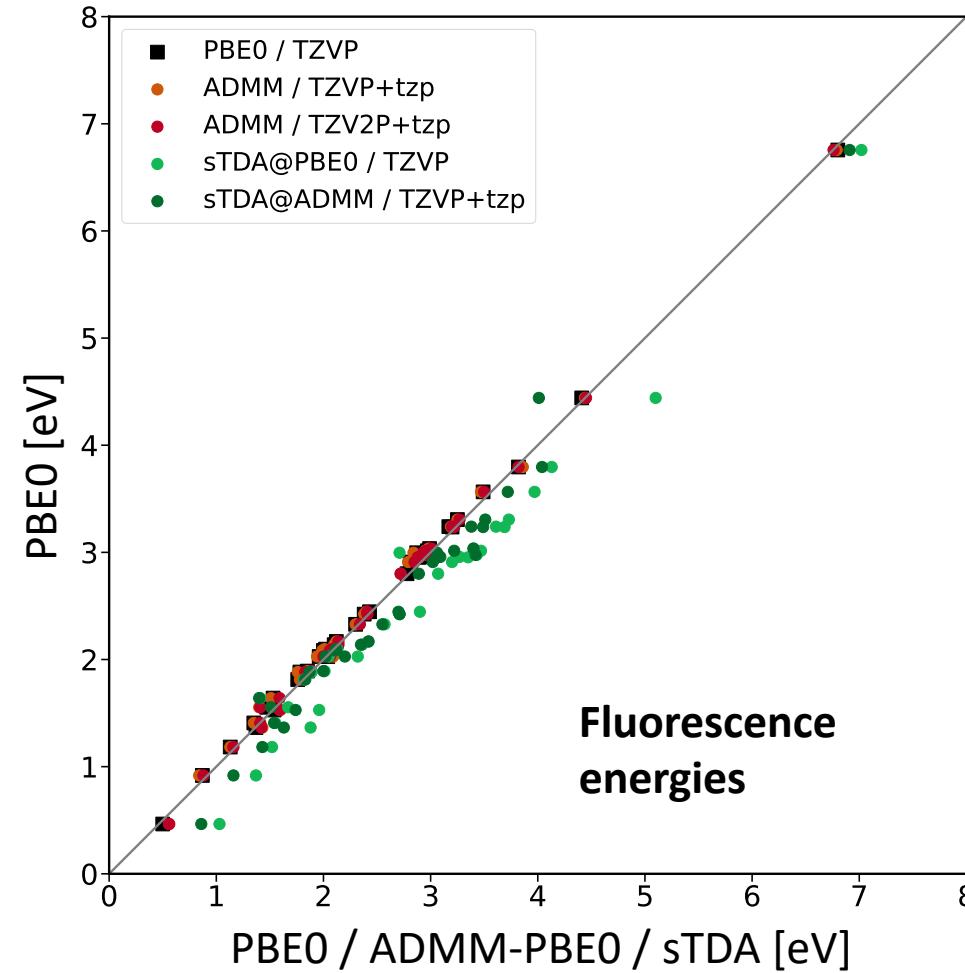
Number of electrons: 20
Number of occupied orbitals: 10
Number of molecular orbitals: 10
Number of orbital functions: 72

***** ATOMIC FORCES in [a.u.] *****

# Atom   Kind   Element       X           Y           Z
  1       1       o            0.17332783  0.00184309 -0.19299556
  2       2       h           -0.01797113 -0.00003132 -0.01654525
  3       2       h           -0.15521341  0.00081876  0.20864035
SUM OF ATOMIC FORCES          0.00014328  0.00263052 -0.00090047  0.00278406
```



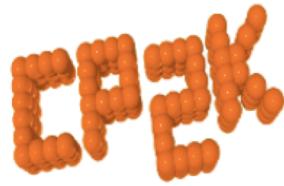
Adiabatic  
excitation  
energies



Fluorescence  
energies

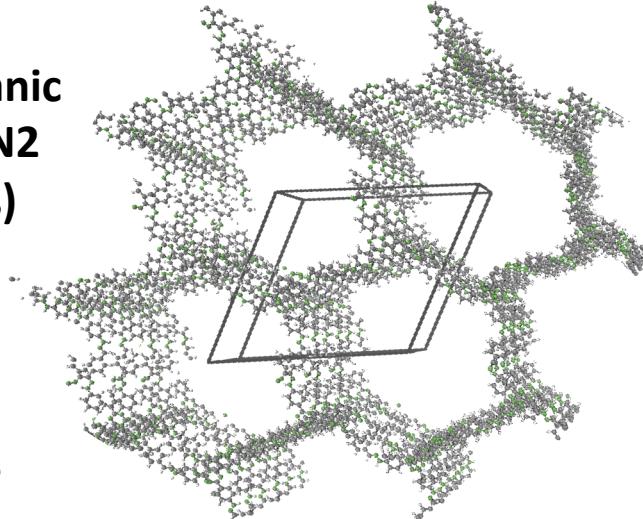
ADMM-PBEO wrt PBEO < 0.3 pm ; 0.02 – 0.07 eV  
sTDA wrt EOM-CCSD < 1.1 pm ; 0.2 – 0.5 eV

Hehn et al., J. Chem. Theory Comput. 18, 4186 (2022).

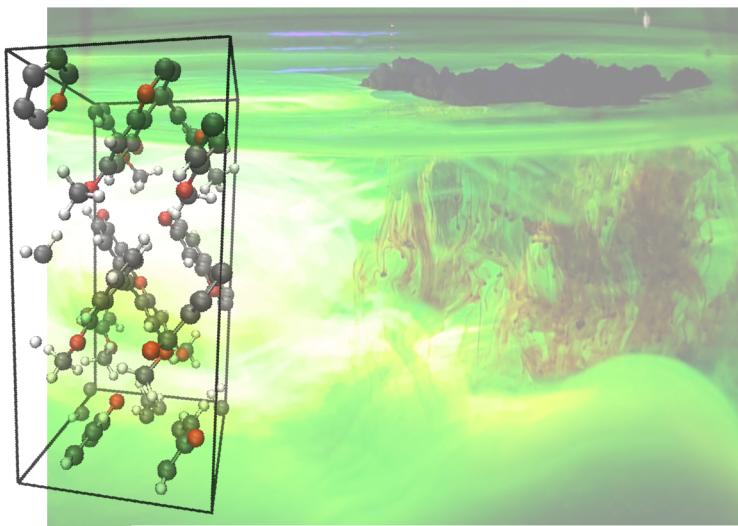


# Efficient algorithms for excited states of framework materials

Covalent Organic  
Framework 20611N2  
(262 atoms)



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



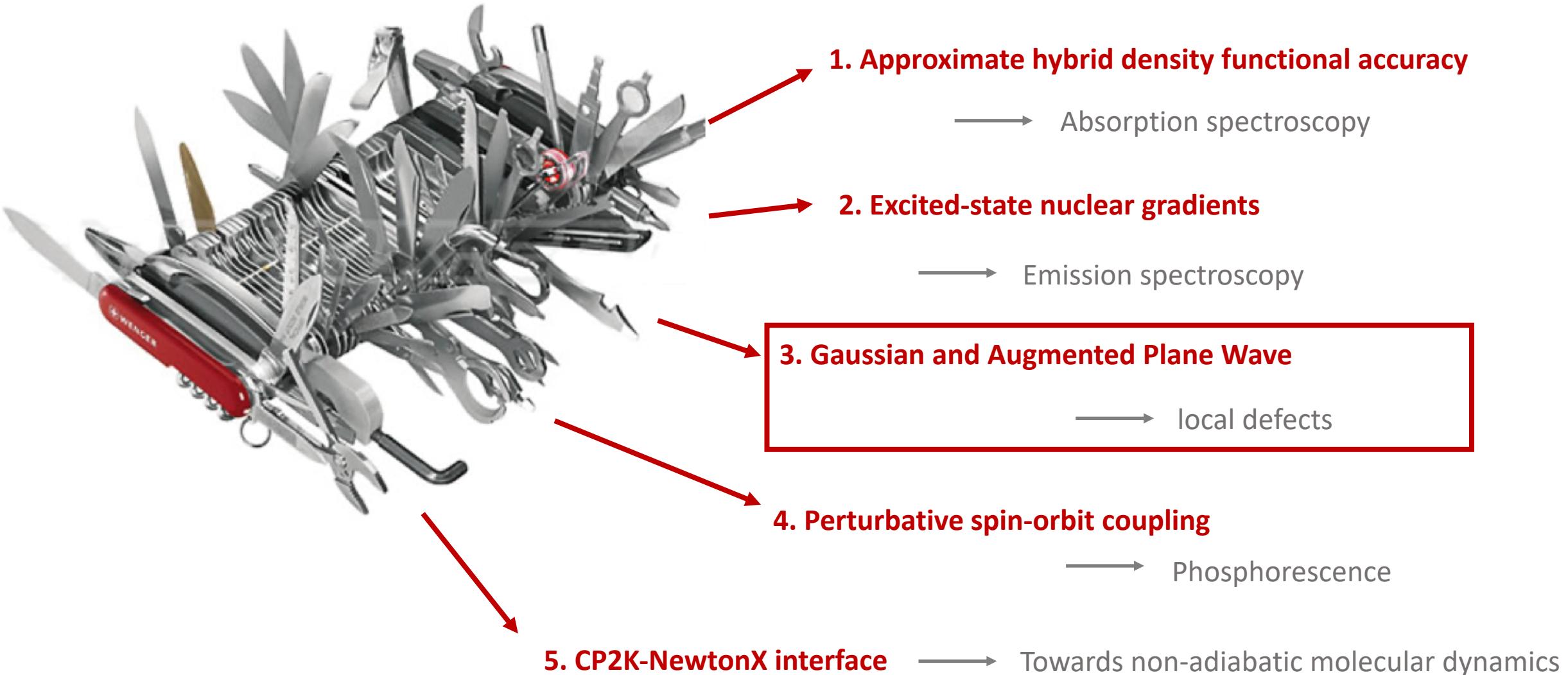
Feng et al. *Chem. Commun.*  
56, 2511, 2020.

Costs for 36 nodes with 36 MPI tasks / node

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

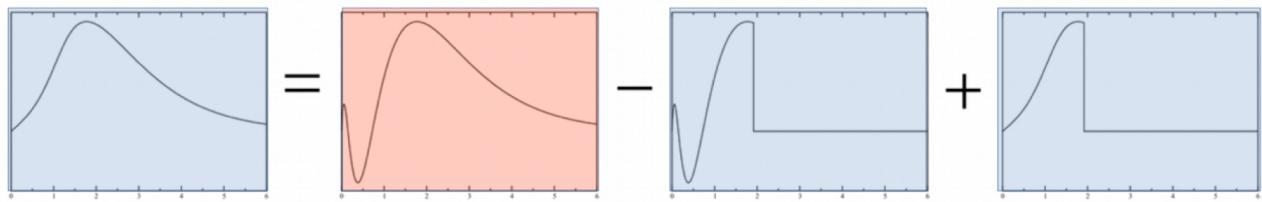
→ gain in efficiency by one order of magnitude

# Tailoring the Swiss Army Knife for efficient absorption and emission spectroscopy





# Gaussian and augmented plane-wave (GAPW) for excited-state TDDFT gradients



**Equivalence of hard and soft densities**

$$n(\mathbf{r}) - \sum_A n_A^1(\mathbf{r}) = \tilde{n}(\mathbf{r}) - \sum_A \tilde{n}_A^1(\mathbf{r})$$

**Atomic hard and soft density**

$$n(\mathbf{r}) = \sum_A n_A^1(\mathbf{r})$$

$$\tilde{n}(\mathbf{r}) = \sum_A \tilde{n}_A^1(\mathbf{r})$$

**ATOMIC**

**Global soft density**

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r})$$

$$n_A^1(\mathbf{r}) = \tilde{n}_A^1(\mathbf{r})$$

**INTERATOMIC**

$$\tilde{n}^x - \sum_A \tilde{n}_A^{x_1} = n^x - \sum_A n_A^{x_1}$$

$$Q_L^A = Nq^L[n_A^{x_1} - \tilde{n}_A^{x_1}]$$

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

$$\tilde{n} + \mathbf{n}^C - \sum_A \tilde{n}_A^1 = n + \mathbf{n}^C - \sum_A n_A^1$$

$$\breve{Q}_L^A = N\breve{q}^L[n_A^1 - \tilde{n}_A^1 + \mathbf{n}^C]$$

## 2. Z vector equation

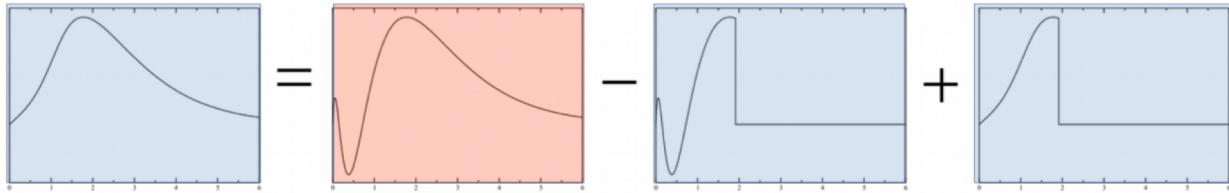
$$\frac{\partial L}{\partial \mathbf{C}} \rightarrow \mathbf{B}\bar{\mathbf{Z}} = -\bar{\mathbf{R}}$$

Mixed  
expressions

## 3. Excited-state gradient

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

# Gaussian and augmented plane-wave (GAPW) for excited-state TDDFT gradients



**Equivalence of hard and soft densities**

$$n(\mathbf{r}) - \sum_A n_A^1(\mathbf{r}) = \tilde{n}(\mathbf{r}) - \sum_A \tilde{n}_A^1(\mathbf{r})$$

**Atomic hard and soft density**

$$n(\mathbf{r}) = \sum_A n_A^1(\mathbf{r})$$

$$\tilde{n}(\mathbf{r}) = \sum_A \tilde{n}_A^1(\mathbf{r})$$

**ATOMIC**

**Global soft density**

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r})$$

$$n_A^1(\mathbf{r}) = \tilde{n}_A^1(\mathbf{r})$$

**INTERATOMIC**

**Input for GAPW TDDFT gradients:**

&DFT

&QS

**METHOD GAPW**

EPS\_DEFAULT 1.0E-14

LMAXNO 4

GAPW\_1C\_BASIS EXT\_SMALL

&END QS

&MGRID

**CUTOFF 400**

REL\_CUTOFF 60

&END MGRID

&END DFT

....

&KIND Li

BASIS\_SET def2-TZVPP

POTENTIAL ALL

RADIAL\_GRID 50

LEBEDEV\_GRID 50

HARD\_EXP\_RADIUS 1.52

&END KIND

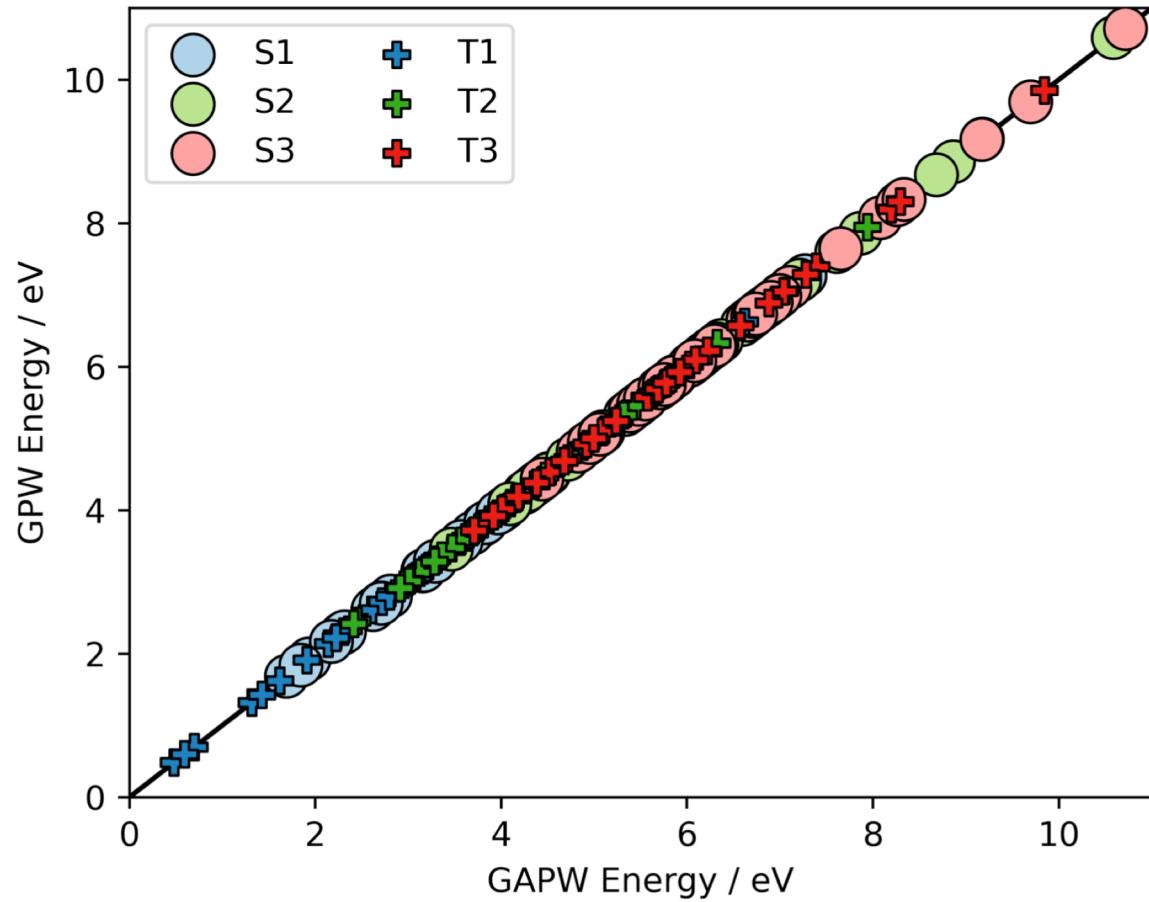
augmented atomic basis

smaller grid

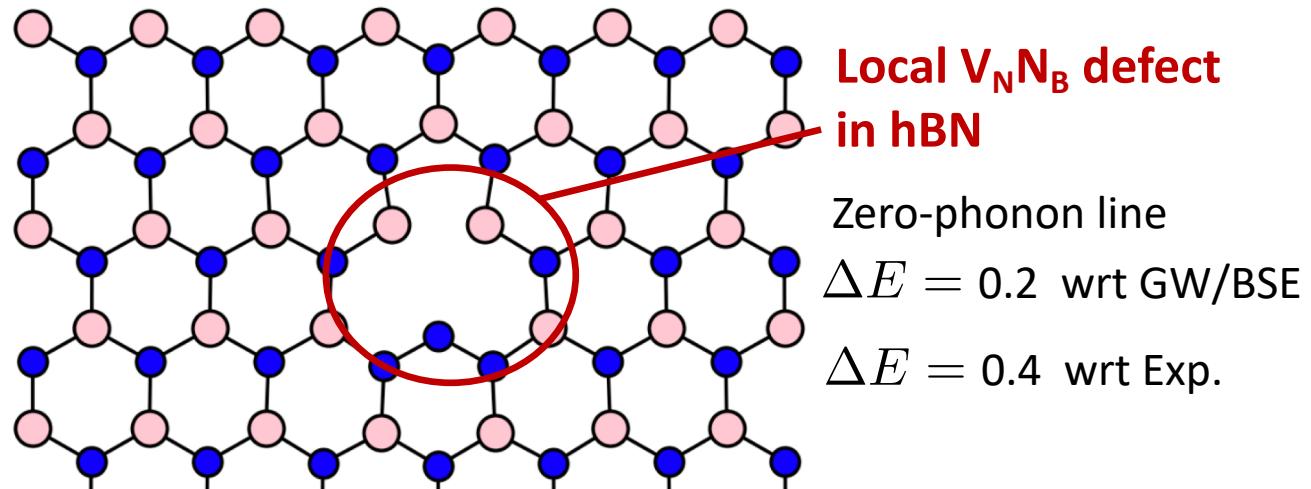
adjusted atomic grids and radii

# Gaussian and augmented plane-wave (GAPW) for excited-state TDDFT gradients

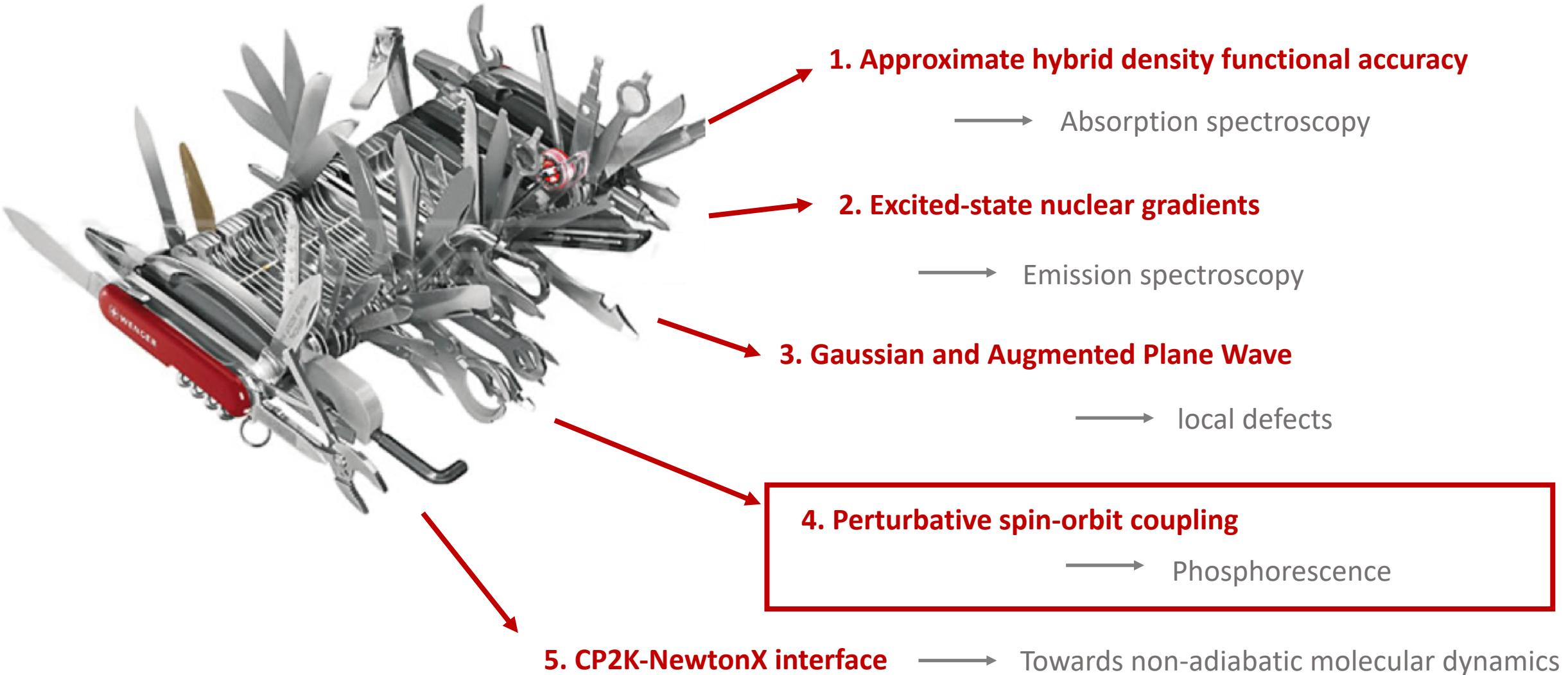
Comparison wrt GAUSSIAN



	GS		Singlet ES		Triplet ES	
	E [a.u./atom]	F [eV/Å]	E [eV]	F [eV/Å]	E [eV]	F [eV/Å]
Max	7.1x10 <sup>-5</sup>	0.029	0.010	0.030	0.002	0.047
MAE	1.8x10 <sup>-5</sup>	0.003	0.002	0.003	0.001	0.004

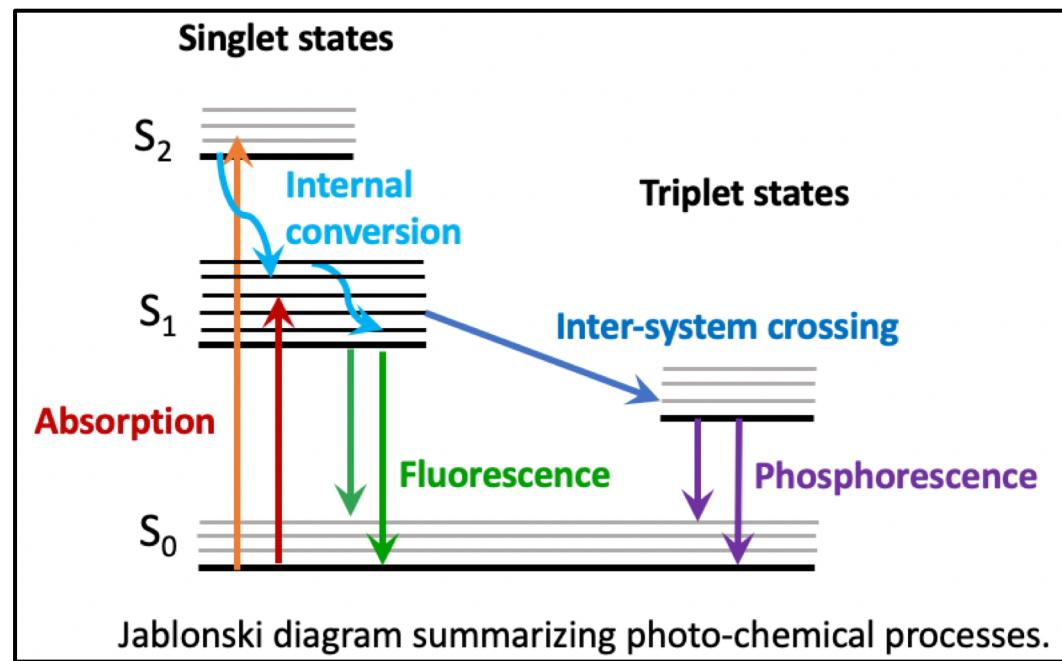


# Tailoring the Swiss Army Knife for efficient absorption and emission spectroscopy

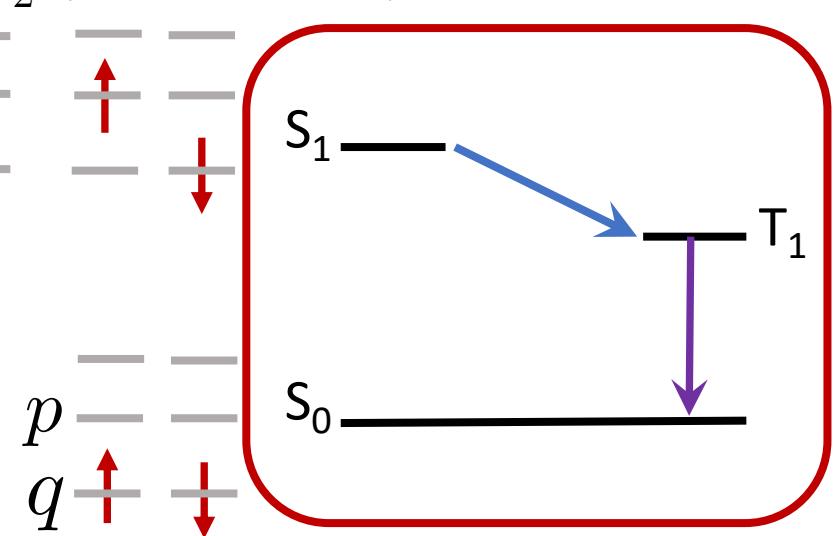


# Towards non-adiabatic molecular dynamics on spin-diabatic surfaces: perturbative spin-orbit coupling

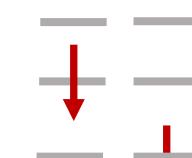
Simulation of phosphorescence (and towards the description of inter-system crossing)



$$S_{pq}^1 = \frac{1}{\sqrt{2}} (a_{p\alpha}^\dagger a_{q\alpha} + a_{p\beta}^\dagger a_{q\beta})$$

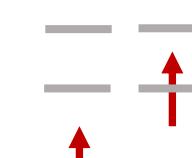


$$T_{pq}^{1,-1} = a_{p\beta}^\dagger a_{q\alpha}$$



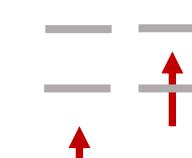
$m_s = -1$

$$T_{pq}^{1,0} = \frac{1}{\sqrt{2}} (a_{p\alpha}^\dagger a_{q\alpha} - a_{p\beta}^\dagger a_{q\beta})$$



$m_s = 0$

$$T_{pq}^{1,1} = -a_{p\alpha}^\dagger a_{q\beta}$$



$m_s = 1$

Perturbative energy correction results in splitting of excited states.



# Towards non-adiabatic molecular dynamics on spin-diabatic surfaces: perturbative spin-orbit coupling



## Perturbative correction

$$H_{SM,SM'} = \delta_{SS'}\delta_{MM'}\Omega^{SM} + \langle \Psi^{SM} | V_{\text{SO}} | \Psi^{S'M'} \rangle$$

relying on **auxiliary set of many-electron wave functions**

$$\begin{aligned} |\Psi_s\rangle &= \frac{1}{\sqrt{2}} \sum_i \left[ (\hat{r}_{i\alpha}^s)^\dagger \hat{a}_{i\alpha} + (\hat{r}_{i\beta}^s)^\dagger \hat{a}_{i\beta} \right] |\Psi_0\rangle & |\Psi_t^{-1}\rangle &= \sum_i \left[ (\hat{r}_{i\beta}^t)^\dagger \hat{a}_{i\alpha} \right] |\Psi_0\rangle \\ |\Psi_t^0\rangle &= \frac{1}{\sqrt{2}} \sum_i \left[ (\hat{r}_{i\alpha}^t)^\dagger \hat{a}_{i\alpha} - (\hat{r}_{i\beta}^t)^\dagger \hat{a}_{i\beta} \right] |\Psi_0\rangle & |\Psi_t^{+1}\rangle &= \sum_i \left[ (\hat{r}_{i\alpha}^t)^\dagger \hat{a}_{i\beta} \right] |\Psi_0\rangle \end{aligned}$$

restricted to **all-electron atomic model ZORA**

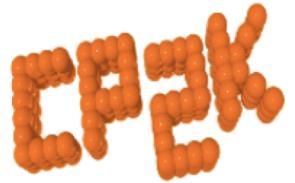
$$V_{\text{SO}}^{\text{ZORA}} = \frac{c^2}{(2c^2 - V)^2} \boldsymbol{\sigma}(\nabla \mathbf{V} \times \mathbf{p})$$

or

**SOC-including pseudopotential**

$$V_{\text{SO}}^{\text{PP}} = \sum_l \Delta V_l^{\text{PP}} \mathbf{L} \cdot \mathbf{S}$$

$$\Delta V_l^{\text{PP}}(\mathbf{r}, \mathbf{r}') = \sum_{i,j=1}^3 \sum_{l=-m}^m Y_{lm}(\hat{\mathbf{r}}) p_i^l(r) k_{ij}^l p_j^l(r') Y_{lm}^*(\hat{\mathbf{r}}')$$



# Towards non-adiabatic molecular dynamics on spin-diabatic surfaces: perturbative spin-orbit coupling



## Perturbative correction

$$H_{SM,SM'} = \delta_{SS'}\delta_{MM'}\Omega'$$

relying on **auxiliary set of many-electron wavefunctions**

$$|\Psi_s\rangle = \frac{1}{\sqrt{2}} \sum_i [(\hat{r}_{i\alpha}^s)^\dagger \hat{a}_{i\alpha} + (\hat{r}_{i\beta}^s)^\dagger \hat{a}_{i\beta}]$$

$$|\Psi_t^0\rangle = \frac{1}{\sqrt{2}} \sum_i [(\hat{r}_{i\alpha}^t)^\dagger \hat{a}_{i\alpha} - (\hat{r}_{i\beta}^t)^\dagger \hat{a}_{i\beta}]$$

restricted to **all-electron atomic model ZORA**

$$V_{SO}^{ZORA} = \frac{c^2}{(2c^2 - V)^2} \boldsymbol{\sigma}(\nabla \mathbf{V}) \times \mathbf{V}$$

de Carvalho *et al.*, *J. Chem. Phys.* 140,

Hartwigsen, Goedecker, Hutter, *Phys. Rev. B* 58, 3641 (1998).

```
&PROPERTIES
&TDDFPT
  KERNEL FULL
  NSTATES 3
  RKS_TRIPLETS F
  &DIPOLE_MOMENTS
    DIPOLE_FORM LENGTH
  &END DIPOLE_MOMENTS
  &PRINT
    &SOC_PRINT
      SPLITTING
      SOME
    &END SOC_PRINT
  &END PRINT
  &SOC
  &END SOC
  &XC
    &XC_FUNCTIONAL PBE
  &END XC_FUNCTIONAL
  &END XC
  &END TDDFPT
&END PROPERTIES
&FORCE_EVAL
  &DFT
    BASIS_SET_FILE_NAME BASIS_MOLOPT
    POTENTIAL_FILE_NAME GTH_SOC_POTENTIALS
  &END DFT
  &END FORCE_EVAL
&SUBSYS
  &KIND Ne
    BASIS_SET DZVP-MOLOPT-SR-GTH
    POTENTIAL GTH-PBE
  &END KIND
  &END SUBSYS
```

## Perturbative correction

$$H_{SM,SM'} = \delta_{SS'}\delta_{MM'}\Omega'$$

relying on **auxiliary set of many-electron wavefunctions**

$$|\Psi_s\rangle = \frac{1}{\sqrt{2}} \sum_i [(\hat{r}_{i\alpha}^s)^\dagger \hat{a}_{i\alpha} + (\hat{r}_{i\beta}^s)^\dagger \hat{a}_{i\beta}]$$

### &PROPERTIES

#### &TDDFPT

KERNEL FULL

NSTATES 3

RKS\_TRIPLETS F

#### &DIPOLE\_MOMENTS

DIPOLE\_FORM LENGTH

#### &END DIPOLE\_MOMENTS

#### &PRINT

#### &SOC\_PRINT

### &FORCE\_EVAL

#### &DFT

BASIS\_SET FILE\_NAME BASIS MOLOPT

**POTENTIAL\_FILE\_NAME GTH\_SOC\_POTENTIALS**

#### &END DFT

#### &END FORCE\_EVAL

### &SUBSYS

#### &KIND Ne

BASIS\_SET DZVP-MOLOPT-SR-GTH

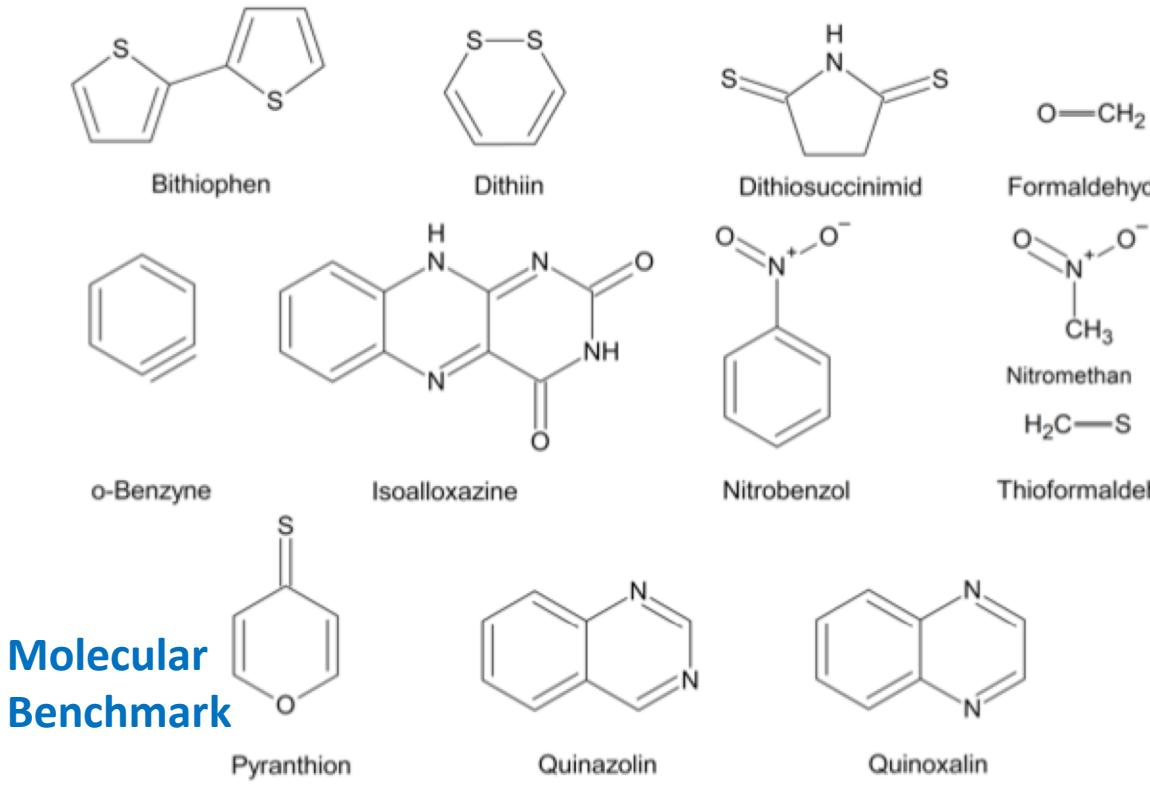
POTENTIAL GTH-PBE

#### &END KIND

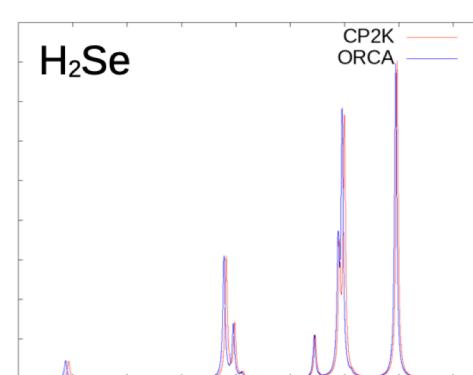
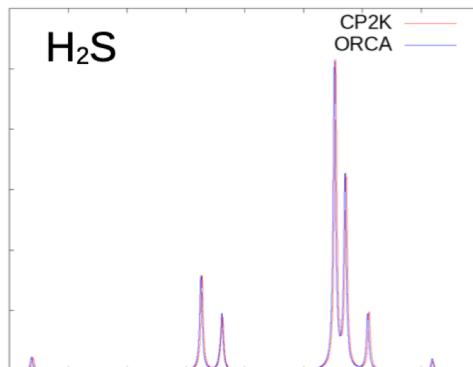
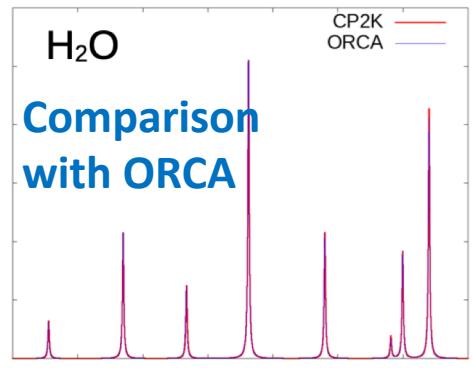
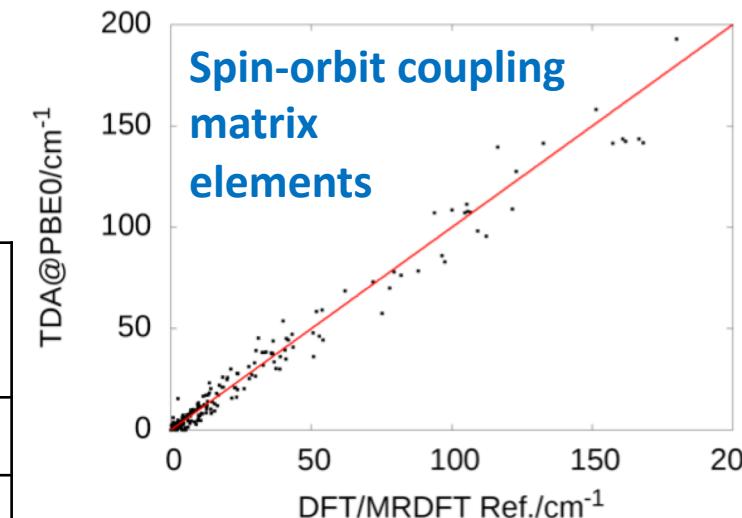
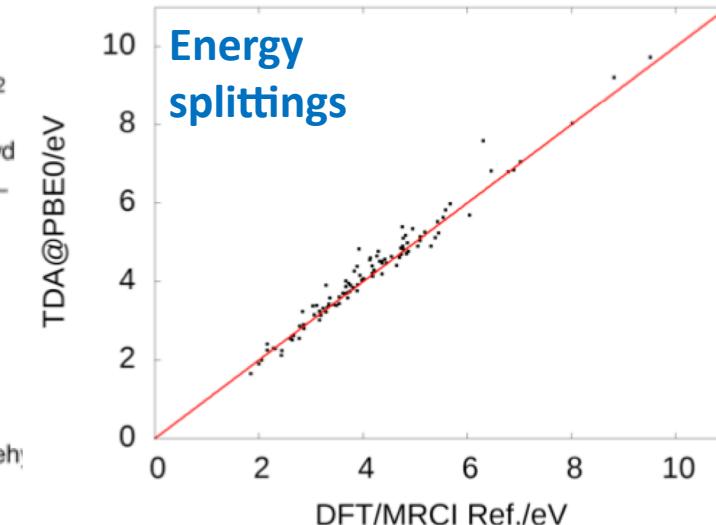
#### &END SUBSYS

```
#####
# Potential database file for CP2K/Quickstep with spin-orbit coupling parameters
#
#####
# Pseudopotentials of Goedecker, Teter and Hutter (GTH)
# -----
#
# History:   - Creation (26.06.2023, Matthias Krack)
#             - Last update (30.06.2023, MK)
#
# Literature: - S. Goedecker, M. Teter, and J. Hutter,
#               Phys. Rev. B 54, 1703 (1996)
#               - C. Hartwigsen, S. Goedecker, and J. Hutter,
#                 Phys. Rev. B 58, 3641 (1998)
#               - M. Krack,
#                 Theor. Chem. Acc. 114, 145 (2005)
```

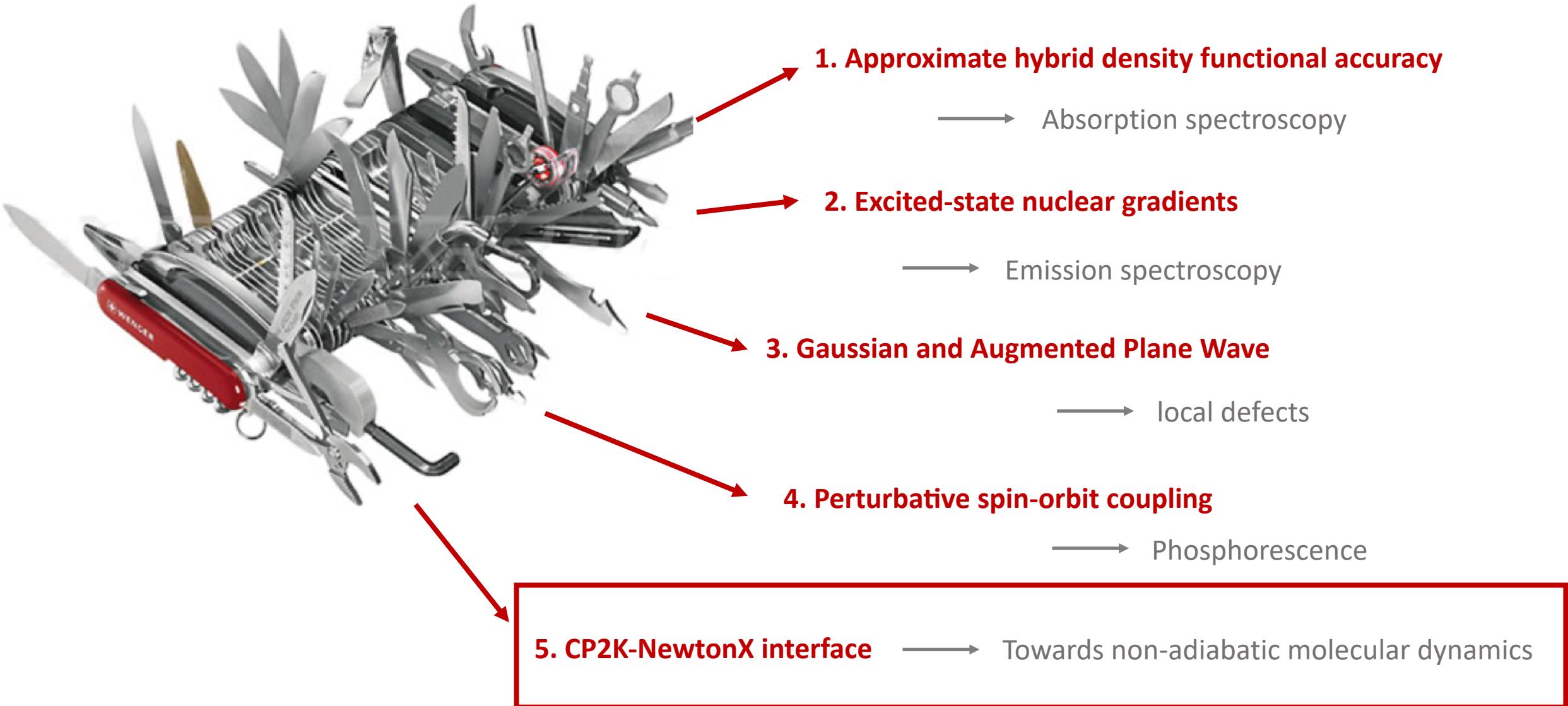
# Towards non-adiabatic molecular dynamics on spin-diabatic surfaces: perturbative spin-orbit coupling



	RMSD (E) / eV	RMSD (SOME) / cm <sup>-1</sup>
TDA@PBE0 wrt DFT/MRCI Ref.	0.28	5.9
wrt TDA@PBE0 Ref.	0.10	3.7



# Tailoring the Swiss Army Knife for efficient absorption and emission spectroscopy



# Towards efficient NAMD / Surface hopping based on time-derivative couplings

Within the Born-Oppenheimer approximation, we are describing excited states based on **adiabatic eigenfunctions** and adiabatic **potential energy surfaces**

$$\Psi(\mathbf{R}(t)) = \sum_M c^M(t) \Psi^M(\mathbf{R}(t))$$

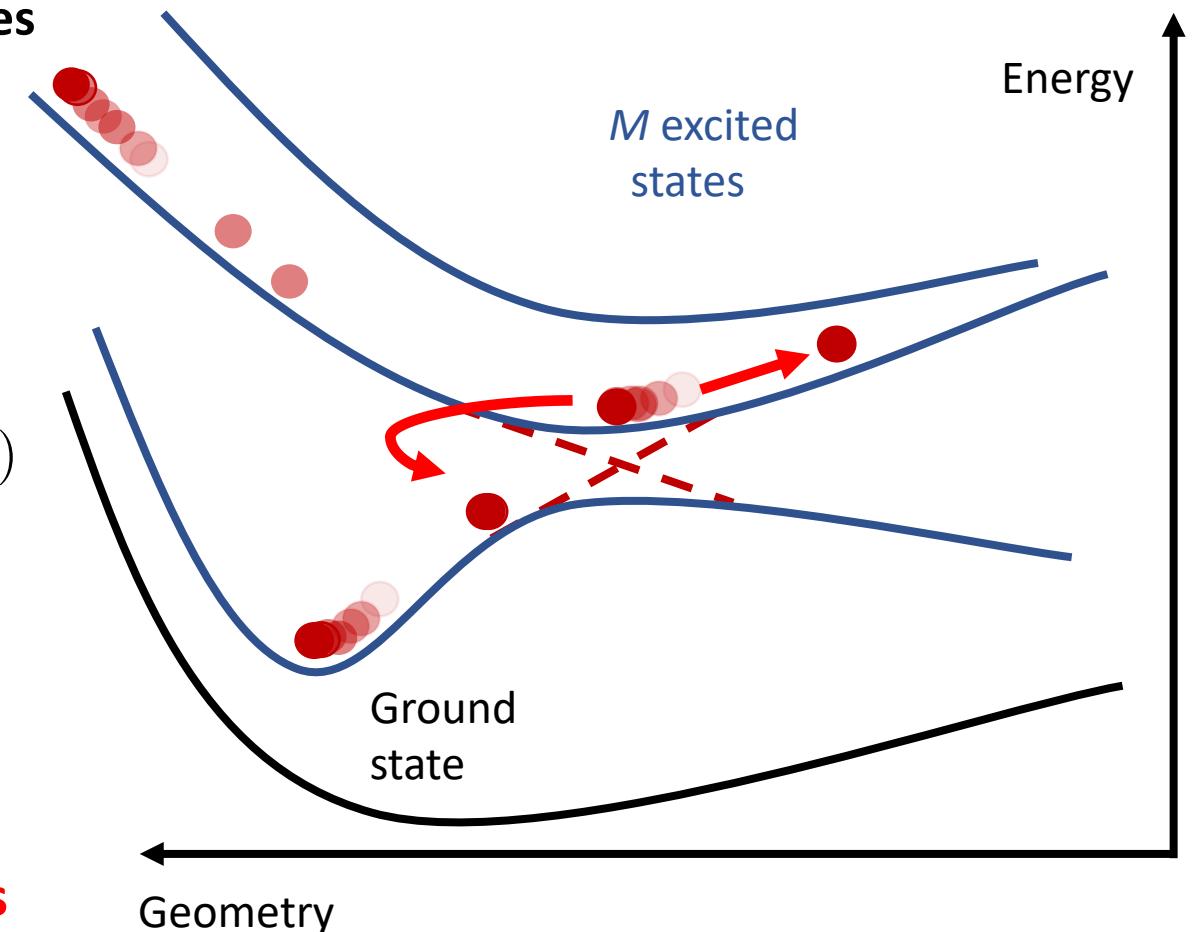
Time-dependent Schrödinger equation

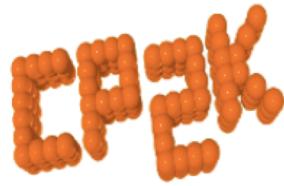
$$i \frac{dc^M(t)}{dt} = \sum_N c^N(t) (\delta_{MN} E_N(\mathbf{R}(t)) - i\sigma_{MN}(t))$$

Non-adiabatic time derivative couplings

$$\sigma_{MN}(t) = \left\langle \Psi^M(\mathbf{R}(t)) \left| \frac{\partial}{\partial t} \Psi^N(\mathbf{R}(t)) \right. \right\rangle$$

Stochastic hopping process with classical particles





# Towards efficient NAMD / Surface hopping based on time-derivative couplings



Stochastic algorithm of the fewest-switches prescription

$$P_{M \rightarrow N} = \max \left[ 0, \frac{-2\Delta t}{|C^M|^2} \operatorname{Re}(C^M C^{N*}) \sigma_{MN} \right]$$

Kinetic energy rescaling after a surface hop for energy conservation

## 1) Local diabatization

$$\mathbf{C}(\Delta t) = \mathbf{T}^\dagger \exp^{-i\mathbf{Z}\Delta t} \mathbf{C}(0)$$

adiabatic-to-diabatic transformation matrix depending on  
 $S_{pq}(\mathbf{R}(t), \mathbf{R}(t + \Delta t))$

## 2) Explicit evaluation

$$\sigma_{MN} = \langle \Psi^M(\mathbf{R}(t)) | \nabla | \Psi^N(\mathbf{R}(t)) \rangle \mathbf{v}$$

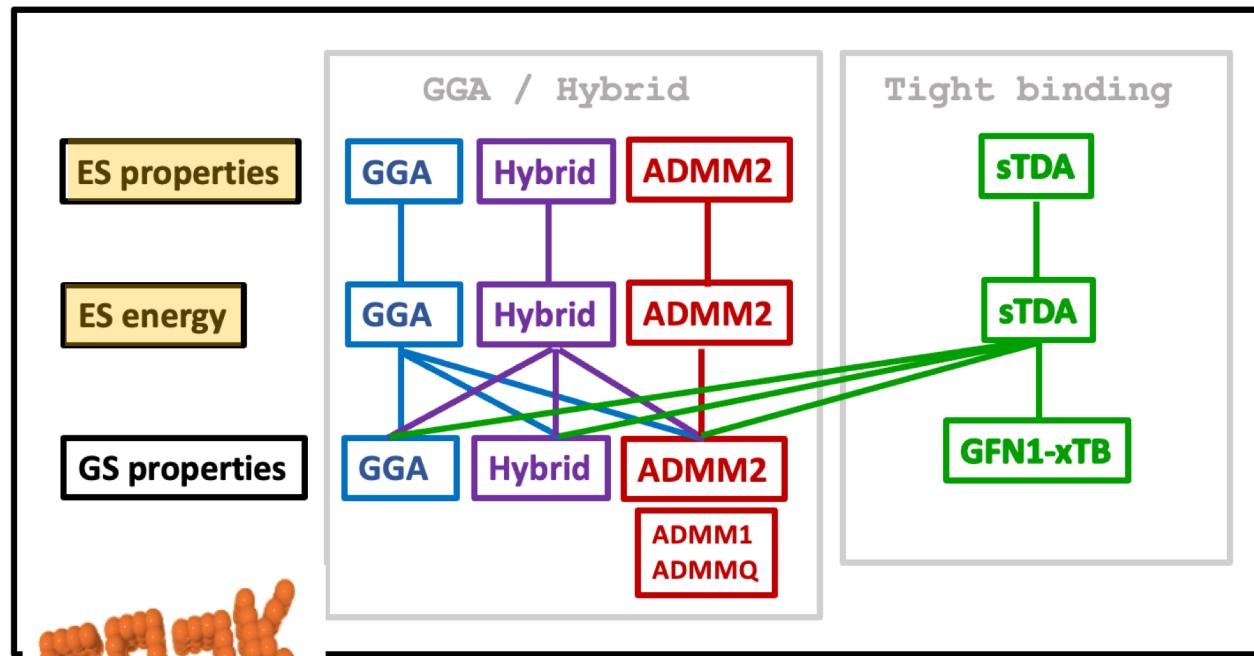
## 3) Numerical time derivatives

$$\sigma_{MN} = \frac{1}{4\Delta t} [3S_{MN}(t) - 3S_{NM}(t) - S_{MN}(t - \Delta t) + S_{NM}(t - \Delta t)]$$

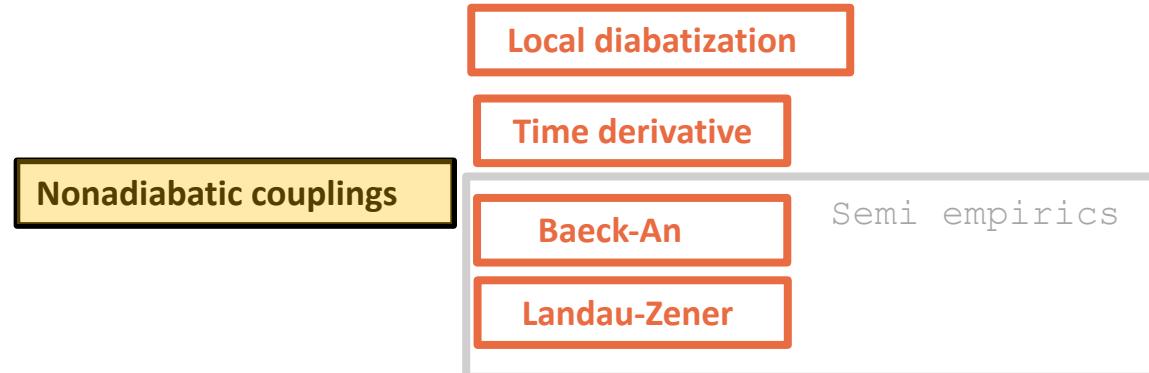
Implies uniform kinetic energy rescaling

Tapavicza, Tavernelli, Rothlisberger, *Phys. Rev. Lett.* 98, 023001 (2007);  
Pittner, Lischka, Barbatti, *Chem. Phys.* 356, 147 (2009).

## Efficient TDDFPT module implying PBC



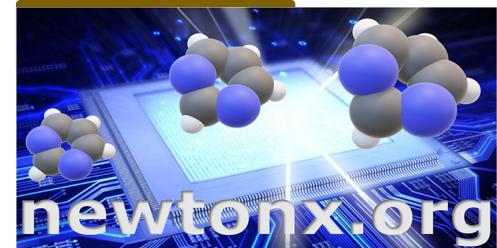
combined with state-of-the-art NAMD



Fewest switches surface hopping

+Decoherence corrections

+Thermostats



implying periodic boundary conditions

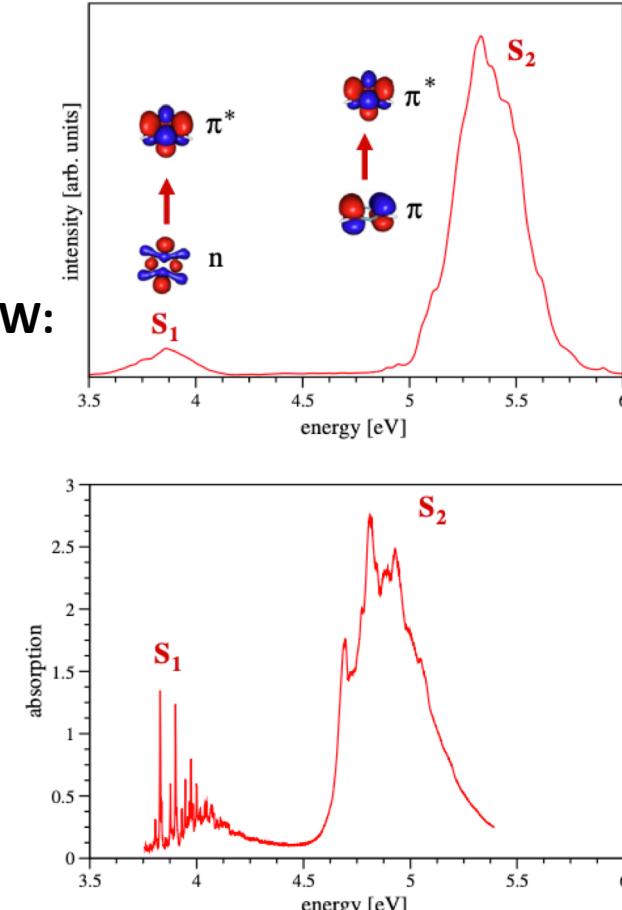
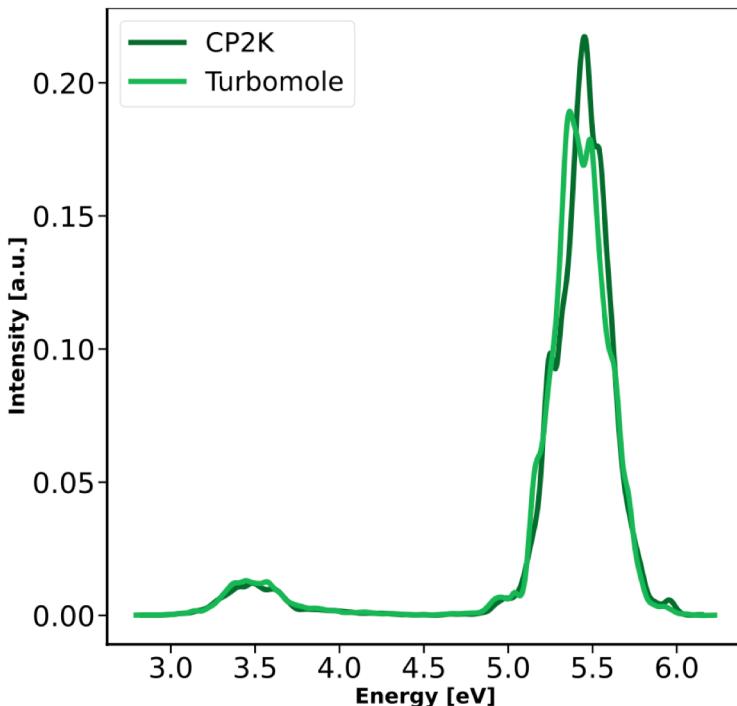
## Available features within CP2K-NewtonX

- On-the-fly velocity Verlet MD
- **Fewest switches surface hopping**
- **Various non-adiabatic couplings**
  - Analytical coupling vectors
  - Time-derivative couplings (DD or OD)
  - Semi-empirical couplings (Baeck-An, Landau-Zener)
  - Local diabatization
- Decoherence corrections
- Thermostats, QM/MM, Spectra, Initial conditions ...



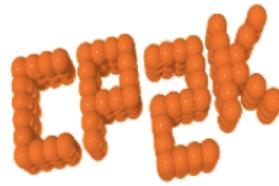
Barbatti *et al.*, WIREs: Comp. Mol. Sci. 4, 26 (2014).

## Exploiting extension from GPW to GAPW:



Absorption spectrum of pyrazine (PBE / 6-311G\*\*).

Werner *et al.*, Chem. Phys. 349, 319 (2008).



# Towards efficient non-adiabatic molecular dynamics

CP2K

Search docs

## GETTING STARTED

Spack

## METHODS

⊕ Density Functional Theory

⊕ Post Hartree-Fock

⊕ Semi-Empiricals

⊕ Machine Learning

⊕ Embedding

⊕ QM/MM

⊖ Sampling

/ Sampling

## Sampling

- Molecular Dynamics
- Metadynamics
- Path Integrals
- Surface Hopping with NEWTON-X
- i-PI
- Monte Carlo
- Langevin Dynamics
- Ehrenfest Dynamics

Previous

By performing a TDDFPT computation, excitation energies  $\Omega^M(\mathbf{R}(t))$ , excited-state eigenvectors  $\mathbf{X}^M(\mathbf{R}(t))$  and corresponding excited-state gradients  $\nabla\Omega^M(\mathbf{R}(t))$  are provided by CP2K. On the so-defined potential energy surfaces, the nuclei are propagated classically relying on the surface hopping code of NEWTONX,

$$\mathbf{R}(t + \Delta t) = \mathbf{R}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2}\mathbf{a}(t)\Delta t^2,$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \frac{1}{2}(\mathbf{a}(t) + \mathbf{a}(t + \Delta t))\Delta t,$$

$$\mathbf{a}(t) = -\frac{1}{m}\nabla\Omega^M(\mathbf{R}(t)).$$

The coefficients  $c^M(t)$  of the total wave function  $\Psi(\mathbf{R}(t))$  over all excited states  $M$  are obtained implying hopping probabilities  $P_{M \rightarrow N}$  of Tully's surface hopping,

$$\Psi(\mathbf{R}(t)) = \sum_M c^M(t)\Psi^M(\mathbf{R}(t))$$

$$i\frac{dc^M(t)}{dt} = \sum_N c^N(t) (\delta_{MN}E_N(\mathbf{R}(t)) - i\sigma_{MN}(t)),$$

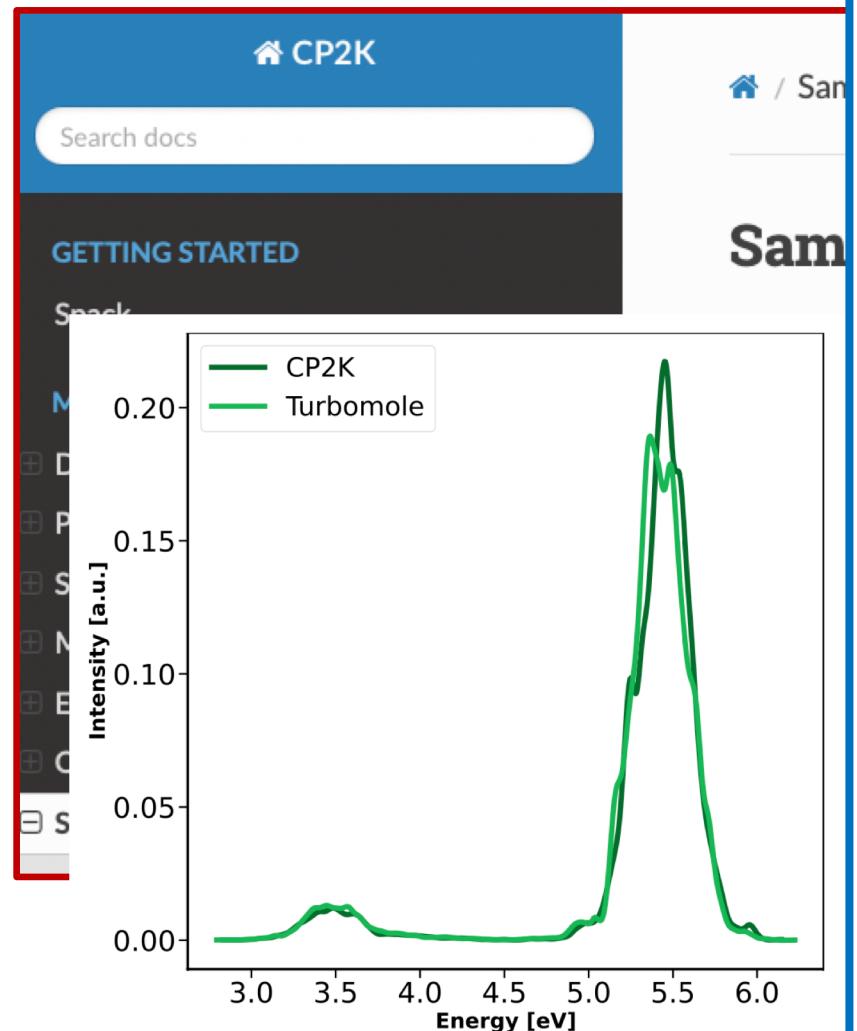
$$P_{M \rightarrow N} = \max \left[ 0, \frac{-2\Delta t}{|c^M|^2} \operatorname{Re}(c^M c^{N*}) \sigma_{MN} \right].$$

The therefore required non-adiabatic time derivative couplings  $\sigma_{MN}$  can be obtained relying on semi-empirical models (Baeck-An; please cite [Barbatti et al., Open Research Europe 1, 49 \(2021\)](#).) or as numerical time derivative couplings (orbital time derivative (OD); please cite [Ryabinkin et al., J. Phys. Chem. Lett. 6, 4200 \(2015\)](#); [Barbatti et al., Molecules 21, 1603 \(2016\)](#).), with the corresponding molecular orbital overlap matrix  $\mathbf{S}^{t-\Delta t, t}$  being provided by CP2K,

$$\sigma_{MN}^{\text{OD}} = \sum_{ia} X_{ia}^M \frac{\partial}{\partial t} X_{ia}^N + \sum_{iab} X_{ia}^M X_{ib}^N S_{ab}^{t-\Delta t, t} - \sum_{ija} P_{ij} X_{ia}^M X_{ja}^N S_{ji}^{t-\Delta t, t}$$

$$S_{pq}^{t-\Delta t, t} = \frac{\langle \phi_i(\mathbf{R}(t - \Delta t)) | \phi_j(\mathbf{R}(t)) \rangle}{\Delta t}.$$

$a, b, \dots$  denote virtual molecular orbitals.



### Exemplary Input-file CP2K

```
&GLOBAL  
  RUN_TYPE VIBRATIONAL_ANALYSIS
```

```
&END GLOBAL
```

```
&FORCE_EVAL  
  &FORCES  
  &END FORCES  
&END FORCE_EVAL
```

```
&COORD  
  @include coord.cp2k  
&END COORD
```

```
&VIBRATIONAL_ANALYSIS  
  DX 0.001  
  &PRINT  
    &NAMD_PRINT  
    &END NAMD_PRINT  
  &END PRINT  
&END VIBRATIONAL_ANALYSIS
```

### Exemplary Input-file NewtonX

```
&dat  
  nact = 2  
  iprog = 10  
  numat = 3  
  npoints = 500  
  file_geom = geom  
  file_nmodes = normal_modes_for_h2o-VIBRATIONS-1.eig  
  anh_f = 1  
  rescale = n  
  temp = 0  
  ics_flg = n  
  chk_e = 1  
  nis = 1  
  nfs = 11  
  kvert = 1  
  de = 100  
  prog = 14  
  iseed = 0  
  lvprt = 1  
 /
```

Work in progress...

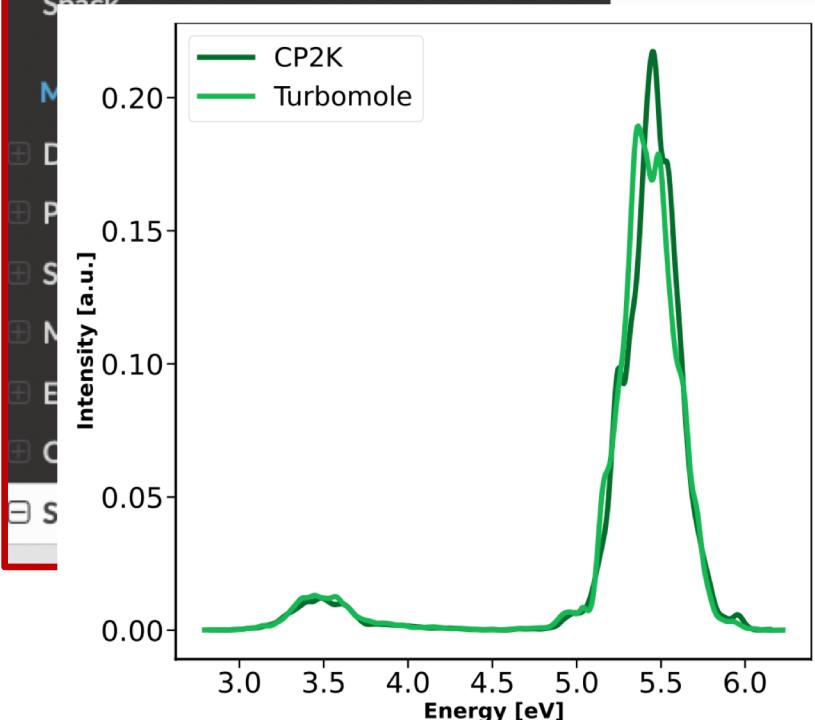
CP2K

Search docs

GETTING STARTED

Sampling

# Sampling



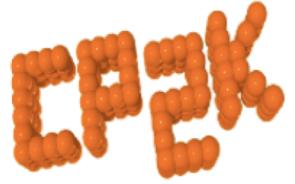
## NewtonX tutorials

<https://newtonx.org/documentation-tutorials/>

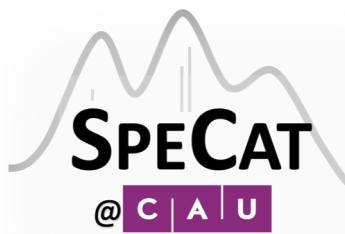
[https://vdv.dcf.mybluehost.me/nx/wp-content/uploads/2020/02/tutorial-2\\_2.pdf](https://vdv.dcf.mybluehost.me/nx/wp-content/uploads/2020/02/tutorial-2_2.pdf)

## Exemplary output

```
Initial condition = 1
Geometry in COLUMBUS and NX input format:
o 8.0 5.00630777 5.00000001 4.46399957 15.99491464
h 1.0 6.37684065 5.00000128 5.50815661 1.00782504
h 1.0 3.52303474 5.00000149 5.58297278 1.00782504
Velocity in NX input format:
-0.000089112 0.000000000 -0.000020915
0.000417197 0.000000002 0.000694479
0.000997296 0.000000013 -0.000362483
Epot of initial state (eV): 0.0865 Epot of final state (eV): 19.0799
Vertical excitation (eV): 18.9935 Is Ev in the required range? YES
Ekin of initial state (eV): 0.0479 Etot of initial state (eV): 0.1343
Oscillator strength: 0.1221
State: 10
```



## Acknowledgements



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Augustin Bussy



Beliz

Matt Watkins  
Sergey Chulkov



Jan Wilhelm

Dorothea Golze



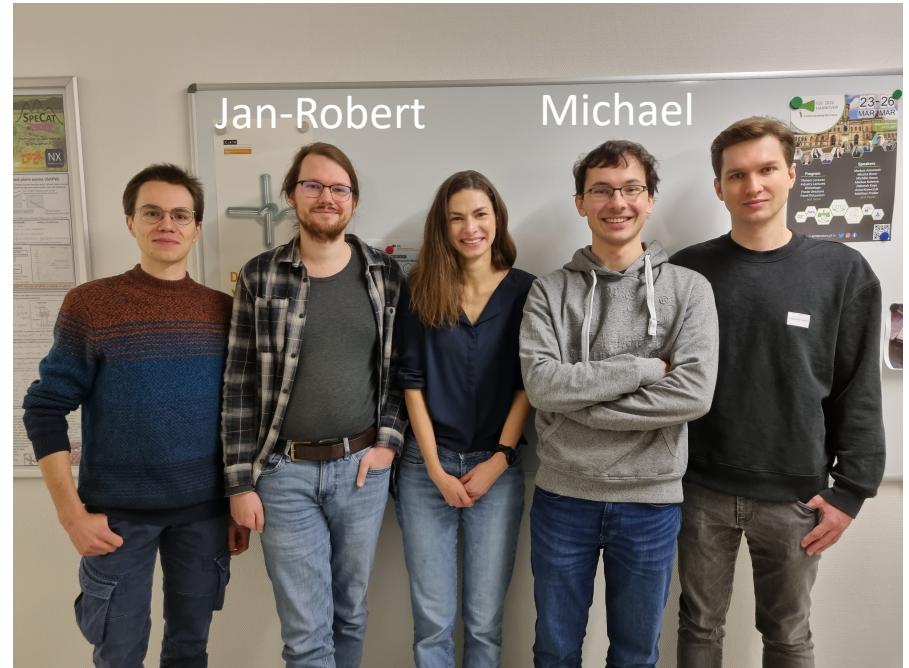
Fabian

Giovanni Granucci  
Maurizio Persico

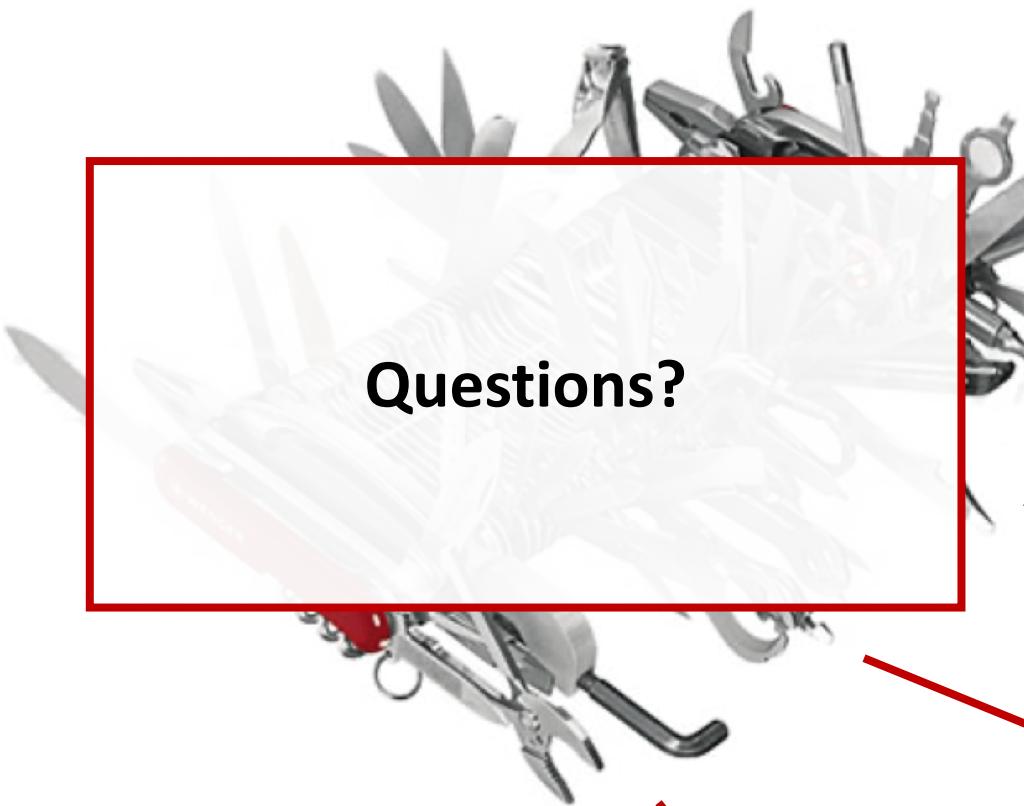
Mario Barbatti



Jan-Robert Vogt  
Michael Schulz



Thank you for your kind attention!



Questions?

1. Approximate hybrid density functional accuracy → Absorption spectroscopy
2. Excited-state nuclear gradients → Emission spectroscopy
3. Gaussian and Augmented Plane Wave → local defects
4. Perturbative spin-orbit coupling → Phosphorescence
5. CP2K-NewtonX interface → Towards non-adiabatic molecular dynamics

