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- **Introduction: what is CDFT and why use it?**

- **Theoretical basis of CDFT in brief**

- **CDFT implementation in CP2K**
  - Algorithmic framework
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- **Summary**

# Introduction

- **CDFT allows creation of charge and spin localized states**

- **Why are such states needed?**
  - Charge transfer phenomena
  - Electronic couplings (key role in charge transfer kinetics)
  - Treating self-interaction error due to spurious electron delocalization
  - Parametrizing model Hamiltonians (e.g. Heisenberg spin Hamiltonian)
  - And more... [1]

- **CDFT in CP2K [2] requires version 5.1 or newer**

1. Kaduk, B.; Kowalczyk, T.; van Voorhis, T., *Chem. Rev.,* **2012**, 112, 321−370.
2. Holmberg, N.; Laasonen, K., *J. Chem. Theory Comput.,* **2017**, 13, 587−601.

# Generation of constrained states

- **Enforce density localization in atom-centered regions with constraint potential(s) [3,4]**

Lagrange multiplier (potential strength)

$$E_{\mathrm{CDFT}}[\boldsymbol{\lambda}, \rho] = \max_{\boldsymbol{\lambda}} \min_{\rho} \left( E_{\mathrm{KS}}[\rho] + \sum_c \lambda_c \left\{ \sum_{i=\uparrow,\downarrow} \int w_c^i(\boldsymbol{r}) \rho^i(\boldsymbol{r}) d\boldsymbol{r} - N_c \right\} \right)$$

Weight function

Target value

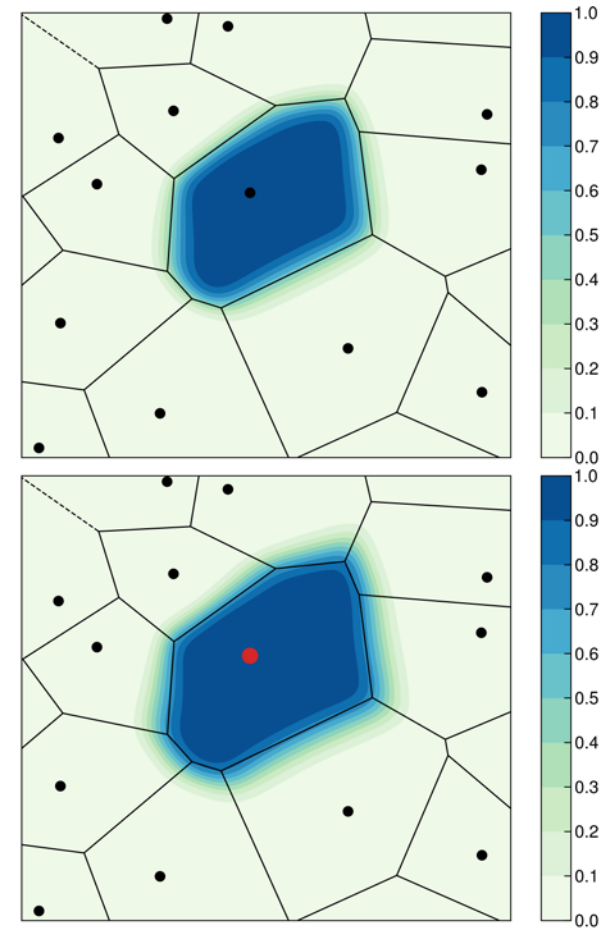- **Weight function defines the type of constraint**

  o Total density constraint $(\rho^\uparrow + \rho^\downarrow)$: $w^\uparrow = w^\downarrow = w$

  o Magnetization density constraint $(\rho^\uparrow - \rho^\downarrow)$: $w^\uparrow = -w^\downarrow = w$

  o Spin specific constraint $(\rho^\uparrow)$: $w^\uparrow = w,\ \ w^\downarrow = 0$

3.   Wu, Q.; van Voorhis, T., *Phys. Rev. A: At., Mol., Opt. Phys.,* **2005**, 72, 024502.
4.   Wu, Q.; van Voorhis, T., *J. Chem. Theory Comput.,* **2006**, 2, 765−774.

# CDFT weight function



- **Constructed as sum of normalized atomic weight functions**

$$w_c^i(\boldsymbol{r}) = \sum_{i \in \mathcal{C}} c_i P_i(\boldsymbol{r}) \Big/ \sum_i^N P_i(\boldsymbol{r})$$

- **CP2K uses Becke partitioning**
  - Smoothed Voronoi-like scheme
  - Atomic sizes can be taken into account (recommended)
    - *E.g. oxygen has positive charge in water without adjustment*

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Engineering**

# Optimization of the CDFT energy (1/2)

- **Constraints are satisfied when**

$$c(\lambda) = \left[ \sum_{i=\uparrow,\downarrow} \int w_1^i(\boldsymbol{r}) \rho^i(\boldsymbol{r}) d\boldsymbol{r} - N_1 \atop \vdots \right] = 0$$

- **In practice, $\lambda$ iteratively optimized until $\max|c(\lambda)| \leq \epsilon$**
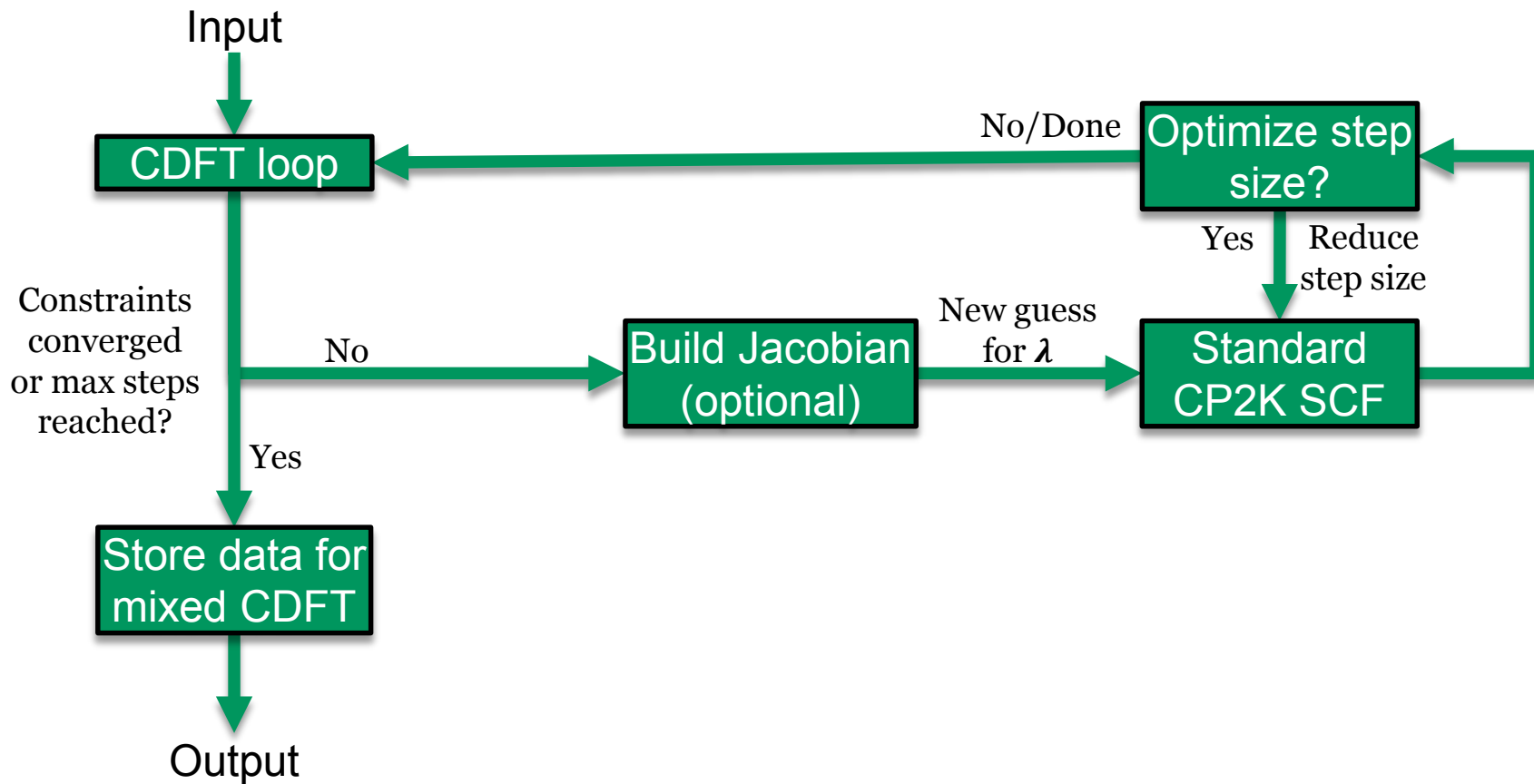  - Uses root-finding algorithms, e.g., Newton's method

  $$\lambda_{n+1} = \lambda_n - \alpha J_n^{-1} c(\lambda_n)$$

  Step size $\in [-1, 0)$

Jacobian matrix, approximated by finite differences

$$J_{ij} = \frac{\partial c_i}{\partial \lambda_j} \approx \frac{c_i(\lambda + \delta_j) - c_i(\lambda)}{\delta_j}$$

# Optimization of the CDFT energy (2/2)

# Defining constraints (1/2)

```
&QS
  ...
  &CDFT
    TYPE_OF_CONSTRAINT BECKE
    &OUTER_SCF ON
      TYPE BECKE_CONSTRAINT
      EXTRAPOLATION_ORDER 2
      MAX_SCF 10
      ! Convergence threshold
      EPS_SCF 1.0E-3
      ! Optimizer selection: now Newton's method with backtracking line search
      OPTIMIZER NEWTON_LS
      ! Optimizer step size
      STEP_SIZE -1.0
      ! Line search settings
      MAX_LS 5
      CONTINUE_LS
      FACTOR_LS 0.5
      ! Finite difference settings for calculation of Jacobian matrix
      JACOBIAN_STEP 1.0E-2
      JACOBIAN_FREQ 1 1
      JACOBIAN_TYPE FD1
      JACOBIAN_RESTART FALSE
    &END OUTER_SCF
  &END CDFT
```

Full example files at https://www.cp2k.org/howto:cdft

# Defining constraints (2/2)

```
&QS
  ...
  &CDFT
    ...
  &END CDFT
  &BECKE_CONSTRAINT
    ! Take atomic radii into account?
    ADJUST_SIZE       FALSE
    ATOMIC_RADII      0.63 0.32
    ! Compute Becke charges?
    ATOMIC_CHARGES TRUE
    ! Constraint strength and target values
    ! Give one value per constraint
    STRENGTH          ${BECKE_STR}
    TARGET            ${BECKE_TARGET}
    ! Cutoff scheme
    CUTOFF_TYPE       ELEMENT
    ELEMENT_CUTOFF    7.0
    ! Perform Becke partitioning only within the space
    ! spanned by constraint atom centered spherical Gaussians
    ! (reduces cost for solvated systems)
    CAVITY_CONFINE    TRUE
    CAVITY_SHAPE      VDW
    EPS_CAVITY        1.0E-7
    IN_MEMORY         TRUE
    SHOULD_SKIP       TRUE
```

Use e.g. covalent radii

```
    ! Constraint definitions
    ! Each repetition defines a constraint
    &ATOM_GROUP
      ATOMS 1
      COEFF 1
      CONSTRAINT_TYPE CHARGE
    &END ATOM_GROUP
    ! No constraint but calculate charges
    &DUMMY_ATOMS
      ATOMS 2
    &END DUMMY_ATOMS
    ! Print info about CDFT calculation
    &PROGRAM_RUN_INFO ON
      &EACH
        QS_SCF 1
      &END EACH
      COMMON_ITERATION_LEVELS 2
      ADD_LAST NUMERIC
      FILENAME ./${NAME}
    &END PROGRAM_RUN_INFO
  &END BECKE_CONSTRAINT
&END QS
```

# Example: $Zn_2^+$ (1/2)

- **When $R_{Zn-Zn}$ grows, charge should localize onto one Zn atom**
  - Standard GGA/hybrid functionals place +0.5 charge on both atoms

- **Force charge localization on first atom**

```
! Set initial constraint strength to 0 (restarting from DFT)
STRENGTH 0.0
! Constraint target is the number of valence electrons - 1
TARGET   11.0
&ATOM_GROUP
  ATOMS 1
  COEFF 1
  CONSTRAINT_TYPE CHARGE
&END ATOM_GROUP
```

# Example: $Zn_2^+$ (2/2)

- **The default output file contains the CDFT SCF iterations**
  - Each iteration corresponds to standard CP2K energy optimization
  - Uses optimized solution from line search as restart if available

- **The following files are created with (quasi-)Newton optimizers**
  - *.LineSearch.out: Electronic structure SCF and optimization of step size
  - *.cdftLog: Summary of CDFT parameters and computed partial charges
  - *.JacobianInfo.out: Calculation of Jacobian matrix with perturbed $\lambda$
  - *.inverseJacobian: Restart file for inverse Jacobian matrix

Standard CP2K SCF with fixed values of constraint strength and step size

Restarted from converged density obtained during line search

CDFT SCF iteration information

Constraint information

```
-------------------------------- OT --------------------------------

 Step     Update method      Time    Convergence         Total energy      Change
 ------------------------------------------------------------------------------
 qs_ot_get_orbitals_ref  0: ||P-I||= 0.10493E-10, ortho_irac = POLY
 qs_ot_ref_poly  1: quick exit!
 qs_ot_get_orbitals_ref  0: ||P-I||= 0.11959E-12, ortho_irac = POLY
 qs_ot_ref_poly  1: quick exit!
     1 OT DIIS    0.15E+00    2.5     0.00000022      -120.6126709217 -1.21E+02

 *** SCF run converged in     1 steps ***


 Electronic density on regular grids:         -22.9999999253        0.0000000747
 Core density on regular grids:                24.0000000000       -0.0000000000
 Total charge density on r-space grids:         1.0000000746
 Total charge density g-space grids:            1.0000000746


 Overlap energy of the core charge distribution:          0.00000000000000
 Self energy of the core charge distribution:          -159.30058829583706
 Core Hamiltonian energy:                                 50.63132167014943
 Hartree energy:                                           5.66516329750697
 Exchange-correlation energy:                            -17.60803221234604
 Dispersion energy:                                       -0.00058223840320


 Total energy:                                          -120.61267092172808


 outer SCF iter =     1 RMS gradient =   0.22E-06 energy =      -120.6126709217
 outer SCF loop converged in   1 iterations or     1 steps
```
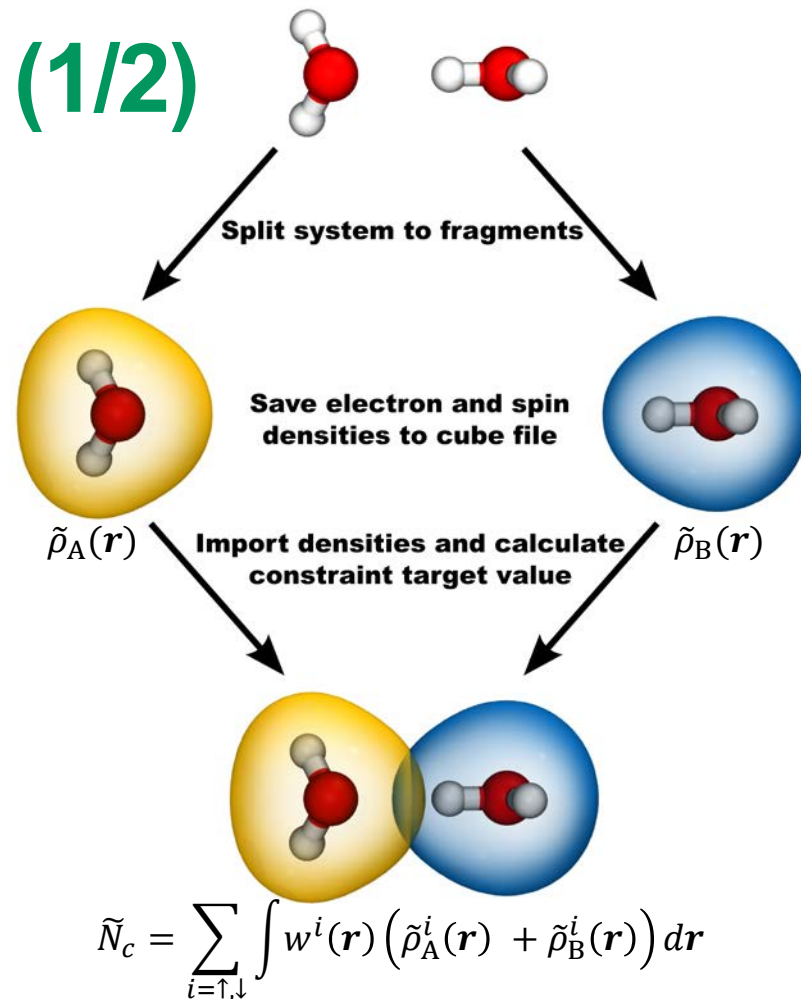
```
 CDFT SCF iter =      5 RMS gradient =   0.13E-03 energy =      -120.6126709217
 CDFT SCF loop converged in   5 iterations or    37 steps
```

```
 -------------------- Becke constraint information --------------------
 Atomic group                 :                                     1
 Type of constraint           :              Charge density constraint
 Target value of constraint   :                       11.000000000000
 Current value of constraint  :                       11.000126158558
 Deviation from target        :                             1.262E-04
 Strength of constraint       :                          0.371415167271
 --------------------------------------------------------------------
```

# Fragment constraints (1/2)

- **Number of valence electrons per molecule not necessarily well defined**
  - Case for overlapping, strongly interacting molecules
  - How to set constraint target value?

- **Use a fragment based constraint**
  - Only single-point calculations

- **Cube read/write accelerated with MPI I/O since r18131**



Split system to fragments

Save electron and spin densities to cube file

$\tilde{\rho}_A(r)$

Import densities and calculate constraint target value

$\tilde{\rho}_B(r)$

$$\tilde{N}_c = \sum_{i=\uparrow,\downarrow} \int w^i(r) \left( \tilde{\rho}_A^i(r) + \tilde{\rho}_B^i(r) \right) dr$$

# Fragment constraints (2/2)

- **Charge transfer energies of strongly interacting complexes**

$$-\Delta E_{\mathrm{CT}} = E_{\mathrm{CDFT}} - E_{\mathrm{DFT}}$$

Energy of system with charge transfer prevented

- **Magnitude of charge transferred, $|\Delta q|$, overestimated by non-fragment constraints**

BW:     Becke
BW+A:   Becke with atomic size adjustments
FBB+A:  Fragment Becke with atomic size adjustments

| System | $-\Delta E_{\mathrm{CT}}$ | | | | $|\Delta q|$ | | | $|\Delta N_c|$ |
|---|---|---|---|---|---|---|---|---|
| | Ref. | BW | BW+A | FBB+A | BW | BW+A | FBB+A | |
| $H_2O - H_2O$ | 1.7 | 45.9 | 1.1 | 2.1 | 0.29 | 0.03 | 0.04 | 0.01 |
| $C_2H_2 - ClF$ | 2.0 | 0.0 | 41.1 | 3.9 | 0.01 | 0.48 | 0.15 | 0.33 |
| $C_2H_4 - F_2$ | 0.6 | 5.1 | 12.0 | 2.1 | 0.13 | 0.18 | 0.10 | 0.09 |
| $H_2O - ClF$ | 2.9 | 2.4 | 73.8 | 4.0 | 0.10 | 0.47 | 0.12 | 0.36 |
| $HCN - ClF$ | 1.3 | 0.3 | 21.9 | 1.8 | 0.03 | 0.31 | 0.08 | 0.23 |
| $NH_3 - BH_3$ | 18.5 | 81.1 | 175.8 | 25.5 | 0.73 | 1.14 | 0.40 | 0.74 |
| $NH_3 - Cl_2$ | 4.2 | 0.1 | 67.4 | 5.6 | 0.02 | 0.53 | 0.18 | 0.35 |
| $NH_3 - ClF$ | 11.6 | 0.1 | 104.5 | 13.2 | 0.03 | 0.76 | 0.29 | 0.47 |
| $NH_3 - F_2$ | 1.1 | 10.7 | 20.6 | 3.5 | 0.18 | 0.23 | 0.13 | 0.10 |
| $NH_3 - SO_2$ | 3.0 | 0.2 | 55.9 | 2.8 | 0.03 | 0.42 | 0.11 | 0.31 |
| $NMe_3 - BH_3$ | 20.0 | 63.0 | 153.3 | 27.0 | 0.74 | 1.20 | 0.47 | 0.73 |
| $NMe_3 - SO_2$ | 20.8 | 0.0 | 132.6 | 18.9 | 0.00 | 1.07 | 0.43 | 0.64 |
| MUE (mHa) | | 17.2 | 64.4 | 2.3 | | | | |
| MSE (mHa) | | 10.1 | 64.4 | 1.9 | | | | |
| MAX (mHa) | | 62.6 | 157.2 | 7.0 | | | | |

# Combining multiple CDFT states

- **Additional properties can be computed from the interactions between CDFT states**
  - Charge transfer kinetics (Marcus theory)

$$k_{ab} = \frac{2\pi}{\hbar} \frac{\langle|\boldsymbol{H}_{ab}|^2\rangle_T}{\sqrt{4\pi kT\xi}} \exp\left(-\frac{(\xi + \Delta A)^2}{4\pi kT\xi}\right)$$

  Electronic coupling
  Solvent reorganization energy
  Reaction free energy

  - Configuration interaction within the basis of CDFT states

- **Approximate electronic coupling with CDFT Kohn-Sham determinants after orthogonalization [5]**

$$\boldsymbol{H}_{ij} \approx \left\langle \boldsymbol{\Phi}_{CDFT}^{i} \middle| \hat{H}_{KS} \middle| \boldsymbol{\Phi}_{CDFT}^{j} \right\rangle = \frac{E_{CDFT}^{i} + E_{CDFT}^{j}}{2} \boldsymbol{S}_{ij} - \sum_{c} \left\langle \boldsymbol{\Phi}_{CDFT}^{i} \middle| \frac{\lambda_c^i w_c^i(\boldsymbol{r}) + \lambda_c^j w_c^j(\boldsymbol{r})}{2} \middle| \boldsymbol{\Phi}_{CDFT}^{j} \right\rangle$$

5. Wu, Q.; van Voorhis, T., *J. Chem. Phys.*, **2006**, 125, 164105.

# The mixed CDFT module

```
&MULTIPLE_FORCE_EVALS
  FORCE_EVAL_ORDER 2 3
  MULTIPLE_SUBSYS  FALSE
&END
&FORCE_EVAL
  METHOD MIXED
  &MIXED
    MIXING_TYPE MIXED_CDFT
    NGROUPS  1
    &MIXED_CDFT
      ! Calculate mixed CDFT properties every COUPLING step
      COUPLING     1
      ! Settings determining how forces are mixed
      FORCE_STATES 1 2
      LAMBDA       1.0
      ! Orthogonalize CDFT states with Lowdin's method
      LOWDIN       TRUE
      ! Configuration interaction?
      CI           FALSE
      &PRINT
        &PROGRAM_RUN_INFO ON
        &END
      &END PRINT
    &END MIXED_CDFT
  &END MIXED
  @include subsys.inc
&END FORCE_EVAL
```

```
# Zn+ Zn
&FORCE_EVAL
  @SET WFN_FILE      ${WFN_FILE_1}
  @SET RESTART       ${RESTART_1}
  @SET NAME          ${PROJECT_NAME}-state1
  @SET BECKE_TARGET  ${BECKE_TARGET_1}
  @SET BECKE_STR     ${BECKE_STR_1}
  METHOD QS
  @include ${DFT_FILE}
&END FORCE_EVAL
# Zn Zn+
&FORCE_EVAL
  @SET WFN_FILE      ${WFN_FILE_2}
  @SET RESTART       ${RESTART_2}
  @SET NAME          ${PROJECT_NAME}-state2
  @SET BECKE_TARGET  ${BECKE_TARGET_2}
  @SET BECKE_STR     ${BECKE_STR_2}
  METHOD QS
  @include ${DFT_FILE}
&END FORCE_EVAL
```

Additional settings available and explained in the manual

# Electronic coupling in $Zn_2^+$

$$\langle Zn^+Zn|\hat{H}|ZnZn^+\rangle$$

```
MIXED_CDFT| Activating mixed CDFT calculation
MIXED_CDFT| Number of CDFT states:                                      2
MIXED_CDFT| CDFT states calculation mode: serial
MIXED_CDFT| Becke constraint is built before the SCF procedure of the first
            CDFT state and subsequently copied to other states
MIXED_CDFT| Calculating electronic coupling between states:             T
MIXED_CDFT| Calculating electronic coupling reliability metric:         F
MIXED_CDFT| Configuration interaction (CDFT-CI) was requested:          F
MIXED_CDFT| Block diagonalizing the mixed CDFT Hamiltonian:             F
MIXED_CDFT| Dynamic load balancing enabled:                             F
MIXED_CDFT| Matrix inversions calculated with LU decomposition.


------------------------ CDFT coupling information ----------------------
Information at step (fs):                                            0.00

#############################################
###### CDFT states I =  1 and J =   2 ######
#############################################
Atomic group:                                                          1
Strength of constraint I:                                   0.371415167271
Strength of constraint J:                                  -0.378315361740
Final value of constraint I:                               11.000125488935
Final value of constraint J:                               11.999828674539

Overlap between states I and J:                             0.030261294466
Charge transfer energy (J-I) (Hartree):                     0.000739539045

Diabatic electronic coupling (rotation, mHartree):          5.674875246867
Diabatic electronic coupling (Lowdin, mHartree):            5.674714192287
-------------------------------------------------------------------------
NO FORCE_EVAL section calculated the dipole

ENERGY| Total FORCE_EVAL ( MIXED ) energy (a.u.):         -120.612670921735003
```
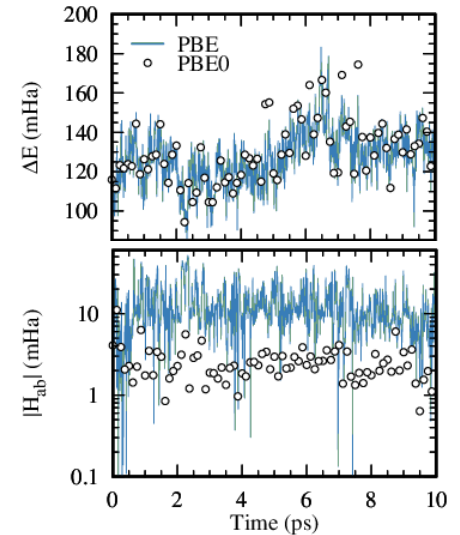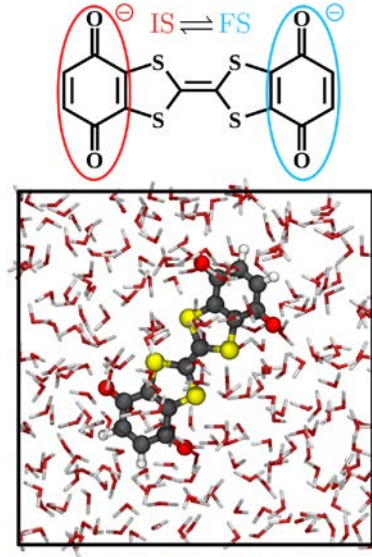
Different
orthogonalization
algorithms

# Electronic coupling in $Zn_2^+$

$$\langle Zn^+Zn | \widehat{H} | ZnZn^+ \rangle$$

```
MIXED_CDFT| Activating mixed CDFT calculation
MIXED_CDFT| Number of CDFT states:                                    2
MIXED_CDFT| CDFT states calculation mode: serial
MIXED_CDFT| Becke constraint is built before the SCF procedure of the first
            CDFT state and subsequently copied to other states
MIXED_CDFT| Calculating electronic coupling between states:           T
MIXED_CDFT| Calculating electronic coupling reliability metric:       F
MIXED_CDFT| Configuration interaction (CDFT-CI) was requested:        F
MIXED_CDFT| Block diagonalizing the mixed CDFT Hamiltonian:           F
MIXED_CDFT| Dynamic load balancing enabled:                           F
MIXED_CDFT| Matrix inversions calculated with LU decomposition.


---------------------- CDFT coupling information ----------------------
Information at step (fs):                                        0.00

#############################################
###### CDFT states I =  1 and J =   2 ######
#############################################
Atomic group:                                                        1
Strength of constraint I:                                0.371415167271
Strength of constraint J:                               -0.378315361740
Final value of constraint I:                            11.000125488935
Final value of constraint J:                            11.999828674539

Overlap between states I and J:                          0.030261294466
Charge transfer energy (J-I) (Hartree):                  0.000739539045

Diabatic electronic coupling (rotation, mHartree):       5.674875246867
Diabatic electronic coupling (Lowdin, mHartree):         5.674714192287
---------------------------------------------------------------
NO FORCE_EVAL section calculated the dipole

ENERGY| Total FORCE_EVAL ( MIXED ) energy (a.u.):      -120.612670921735003
```

Agrees with 5.49 mHartree estimate from more expensive wavefunction based method CASSCF/MRCI+Q

Different orthogonalization algorithms

# CDFT in solvated systems

- **Computational efficiency of GPW/OT allows study of solvated charge transfer processes at full DFT level**

- **Evaluating intramolecular charge transfer kinetics in QTTFQ⁻**

  - 258 water, 12 ps (0.5 fs timestep)

  - 48 s/timestep @ 384 MPI cores (~120k core hours)

# List of CDFT capabilities in CP2K

- **GPW and GAPW (no fragment constraint)**
- **Full DFT or QM/MM**
- **Primarily for OT, diagonalization is supported but difficult to converge**
- **Energies and forces for an unlimited number of constraints (any type)**
- **Mixed CDFT module supports**
  - Electronic couplings with various orthogonalization methods
  - Configuration interaction
  - Removal of linearly-dependent MOs via SVD decomposition
  - Electronic coupling reliability metrics

# Summary

- **CDFT is a tool to study charge transfer phenomena**

- **Available in latest release version**

- **Tutorial at [https://www.cp2k.org/howto:cdft](https://www.cp2k.org/howto:cdft) that complements regtests**
  - Summaries of CDFT theory and the CP2K implementation
  - Walk throughs of example calculations

- **Help provided on Google groups if you encounter issues with CDFT features**

Questions?