# Hybrid functionals and ADMM

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What are hybrid functionals

Global Hybrid functions

mixing non-local Hartree-Fock exchange with semi-local DFT exchange

$$E_{XC} = \alpha E_X^{HFX}[\psi_i] + (1 - \alpha)E_X^{DFT}[\rho] + E_C^{DFT}[\rho]$$
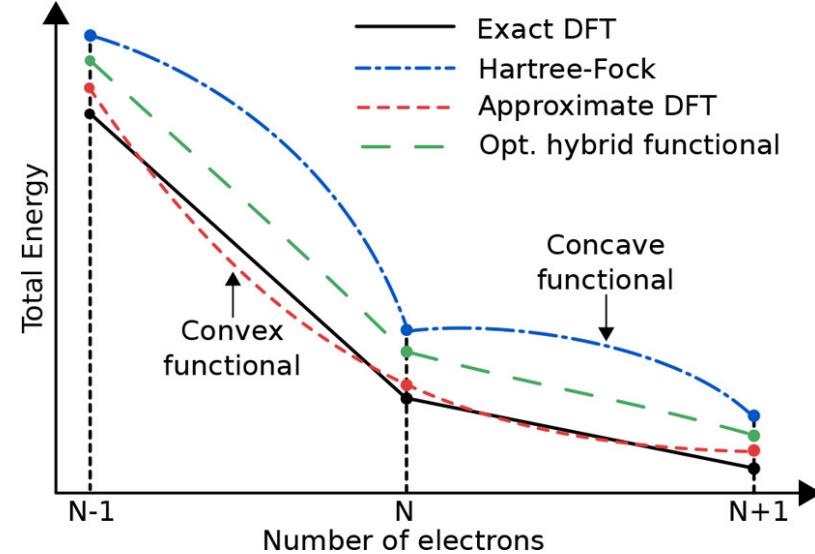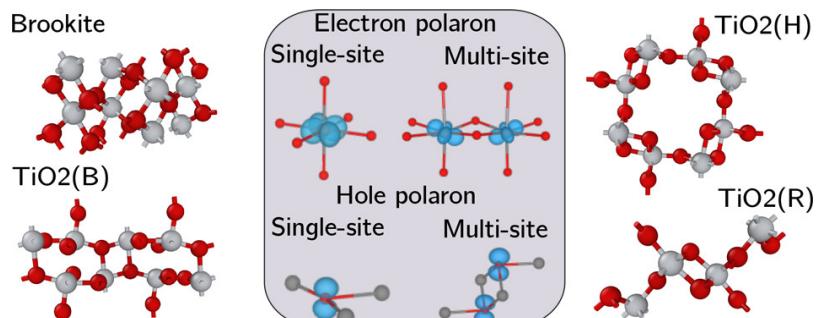
# Why do we need hybrids?

Practical motivations

- Improved description of thermochemistry (e.g. atomizations energies, heats of formation)

- Improved description of lattice constants, surface energies, ionization potentials and band gaps

- Qualitatively correct description of localized and correlated states

Theoretical motivations

- Adiabatic connection

- 1-e energy level
  discontinuity

Why do we need hybrids?

Functional	MAE (G2) / eV
SVWN	5.2
LSD (SVWN5)	3.6
PBE	0.73
BLYP	0.31
B3LYP	0.13
PBE0	0.21

Mean Absolute errors for atomization energies (eV)

Scuseria et al., J. Chem. Phys., 110, 5029 (1999)

Why do we need hybrids?

Statistic	LSDA	PBE	TPSS	HSE
ME	-1.14	-1.13	-0.98	-0.17
MAE	1.14	1.13	0.98	0.17
rms	1.24	1.25	1.12	0.34
Max (+)	-	-	-	0.32
Max (-)	-2.30	-2.88	-2.66	-0.72

Mean Absolute errors for Band Gaps (eV)

Scuseria et al., J. Chem. Phys., 123, 174101 (2005)

Hybrid Functionals with CP2K

- GGA: total energy functional of the electron density

$$E[\rho] = T_S[\rho] + J[\rho] + E_{XC}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r}$$

- hybrid: functional of density and two particle density matrix (orbitals)

$$E_{XC} = \alpha E_X^{HFX}[\psi_i] + (1 - \alpha)E_X^{DFT}[\rho] + E_C^{DFT}[\rho]$$

Guidon, Hutter and VandeVondele, J. Chem. Theory Comput., 6, 2348 (2010)

Hybrid Functionals with CP2K

- Hartree-Fock exchange
  energy

$$E_X^{HFX}[P] = -\frac{1}{2} \sum_{\lambda\sigma\mu\nu} P^{\mu\sigma} P^{\nu\sigma} (\mu\nu|\lambda\sigma)$$

$$P^{\mu\nu} = \sum_i C^{\mu i} C^{\nu i} = CC^T$$

$$(\mu\nu|\lambda\sigma) = \int\int \phi_\mu(\mathbf{r_1})\phi_\nu(\mathbf{r_1})g(|\mathbf{r_1}-\mathbf{r_2}|)\phi_\lambda(\mathbf{r_2})\phi_\sigma(\mathbf{r_2})\mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2}$$

Four-centre two-electron integrals (ERIs) in Mulliken motation: naively $O(N^4)$ scaling

Hybrid Functionals with CP2K

- permutation symmetry of the ERIs

$$(\mu\nu|\lambda\sigma) = (\nu\mu|\lambda\sigma) = (\nu\mu|\sigma\lambda) = (\mu\nu|\sigma\lambda)$$
$$= (\lambda\sigma|\mu\nu) = (\lambda\sigma|\nu\mu) = (\sigma\lambda|\nu\mu) = (\sigma\lambda|\mu\nu)$$

$$O(N^4) \rightarrow \tfrac{1}{8}O(N^4)$$

Guidon et al., J. Chem. Phys., 128, 214104 (2008)

Hybrid Functionals with CP2K

- Integral screening: Schwarz inequality

$$|(\mu\nu|\lambda\sigma)| \leq |(\mu\nu|\mu\nu)|^{1/2}|(\lambda\sigma)|\lambda\sigma)|^{1/2}$$

$\frac{1}{8}O(N^4) \rightarrow O(N^2)$

Ahlrichs et al., J. Comput. Chem., 10, 104 (1989)

(see EPS_SCHWARZ (https://manual.cp2k.org/trunk/CP2K_INPUT/FORCE_EVAL/DFT/XC/HF/SCREENING.html#list_EPS_SCHWARZ) keyword in &SCREENING (https://manual.cp2k.org/trunk/CP2K_INPUT/FORCE_EVAL/DFT/XC/HF/SCREENING.html) subsection)

Guidon et al., J. Chem. Phys., 128, 214104 (2008)

Hybrid Functionals with CP2K

- Density matrix
  screening

$$P_{\max} \times |(\mu\nu|\mu\nu)|^{1/2}|(\lambda\sigma|\lambda\sigma)|^{1/2} \leq \epsilon_{\text{Schwarz}}$$

where

$$P_{\max} = \max\{|P_{\mu\lambda}|, |P_{\mu\sigma}|, |P_{\nu\lambda}|, |P_{\nu\sigma}|\}$$

finally linear scaling

$$O(N^2) \rightarrow O(N)$$

(see SCREEN_ON_INITIAL_P (SCREEN_ON_INITIAL_P) keyword in &SCREENING
(https://manual.cp2k.org/trunk/CP2K_INPUT/FORCE_EVAL/DFT/XC/HF/SCREENING.html) subsection)

Guidon et al., J. Chem. Phys., 128, 214104 (2008)

P_{max}: largest density matrix element; usually, the density matrix from the previous SCF iteration is used for the screening in the next iteration, use pre-converged GGA density matrix; very useful for DFT molecular dynamics simulations using hybrid functionals

Interaction Potential

$$(\mu\nu|\lambda\sigma) = \int\int \phi_\mu(\mathbf{r_1})\phi_\nu(\mathbf{r_1})g\big(|\mathbf{r_1} - \mathbf{r_2}|\big)\phi_\lambda(\mathbf{r_2})\phi_\sigma(\mathbf{r_2})\mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2}$$

- Standard Coulomb potential gives a global hybrid

$$g(r) = \frac{1}{r}$$

(see POTENTIAL_TYPE
(https://manual.cp2k.org/trunk/CP2K_INPUT/FORCE_EVAL/DFT/XC/HF/INTERACTION_POTENTIAL.html#POTENTIAL_TYPE)
keyword in &INTERACTION_POTENTIAL
(https://manual.cp2k.org/trunk/CP2K_INPUT/FORCE_EVAL/DFT/XC/HF/INTERACTION_POTENTIAL.html) subsection)

Guidon et al., J. Chem. Phys., 128, 214104 (2008)

For gas-phase, this energy is easy to evaluate; for periodic boundary conditions, it suffers from the integratable singularity, different approaches have been developed to obtain good convergence with respect to the k-point sum.

Interaction Potential

$$(\mu\nu|\lambda\sigma) = \int\int \phi_\mu(\mathbf{r_1})\phi_\nu(\mathbf{r_1})g(|\mathbf{r_1}-\mathbf{r_2}|)\phi_\lambda(\mathbf{r_2})\phi_\sigma(\mathbf{r_2})\mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2}$$

- Range-separated Coulomb potential gives a range-separated hybrid

$$g(r) = \frac{\mathrm{erfc}(\omega r)}{r} + \frac{\mathrm{erf}(\omega r)}{r}$$

used in HSE06 etc.

(see POTENTIAL_TYPE (https://manual.cp2k.org/trunk/CP2K_INPUT/FORCE_EVAL/DFT/XC/HF/INTERACTION_POTENTIAL.html#POTENTIAL_TYPE) keyword in &INTERACTION_POTENTIAL (https://manual.cp2k.org/trunk/CP2K_INPUT/FORCE_EVAL/DFT/XC/HF/INTERACTION_POTENTIAL.html) subsection)

Guidon et al., J. Chem. Phys., 128, 214104 (2008)

If omega is not large enough very large cells might be needed for HSE calculations at the Γ point.

Costs are very different from plane-wave implementions - HSE is not typically cheaper than PBE0 - see next slide.

Interaction Potential

$$(\mu\nu|\lambda\sigma) = \int\int \phi_\mu(\mathbf{r_1})\phi_\nu(\mathbf{r_1})g(|\mathbf{r_1} - \mathbf{r_2}|)\phi_\lambda(\mathbf{r_2})\phi_\sigma(\mathbf{r_2})\mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2}$$

- truncated Coulomb potential gives a global hybrid

$$g(r_{12}) = \begin{cases} \frac{1}{r_{12}} & \text{if } r_{12} \leq R_c \\ 0 & \text{otherwise} \end{cases}$$

used in the snappily titles PBE0-TC family of functionals.

R_C is specified by the CUTOFF_RADIUS
(https://manual.cp2k.org/trunk/CP2K_INPUT/FORCE_EVAL/DFT/XC/HF/INTERACTION_POTENTIAL.html#list_CUTOFF_RA
keyword.

(see POTENTIAL_TYPE
(https://manual.cp2k.org/trunk/CP2K_INPUT/FORCE_EVAL/DFT/XC/HF/INTERACTION_POTENTIAL.html#POTENTIAL_TYP
keyword in &INTERACTION_POTENTIAL
(https://manual.cp2k.org/trunk/CP2K_INPUT/FORCE_EVAL/DFT/XC/HF/INTERACTION_POTENTIAL.html) subsection)

Guidon et al., J. Chem. Phys., 128, 214104 (2008)

Truncation is mainly for solid-state environments and avoids numerical problems with Γ point global hybrid calculations.

R_C must be smaller than half the smallest cell dimension.

Interaction Potential

$$(\mu\nu|\lambda\sigma) = \int\int \phi_\mu(\mathbf{r_1})\phi_\nu(\mathbf{r_1})g(|\mathbf{r_1} - \mathbf{r_2}|)\phi_\lambda(\mathbf{r_2})\phi_\sigma(\mathbf{r_2})\mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2}$$

- truncated Coulomb potential gives a global hybrid

$$g(r_{12}) = \begin{cases} \frac{1}{r_{12}} & \text{if } r_{12} \leq R_c \\ 0 & \text{otherwise} \end{cases}$$

We can add in a long range correction, to replace the exchange energy lost by truncation.

See the &PBE_HOLE_T_C_LR (https://manual.cp2k.org/trunk/CP2K_INPUT/FORCE_EVAL/DFT/XC/XC_FUNCTIONAL/PBE_HOLE_T_C_LR.html) subsection in the &XC_FUNCTIONAL (https://manual.cp2k.org/trunk/CP2K_INPUT/FORCE_EVAL/DFT/XC/XC_FUNCTIONAL.html) section.

This gives the even more snappily titled PBE0-TC-LRC family of functionals.

Guidon et al., J. Chem. Theory Comput., 5, 3010 (2008)

Auxiliary Density Matrix Methods (ADMM)

$$E[\rho] = T_S[\rho] + J[\rho] + E_{XC}[\rho, P] + \int v(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r}$$

$$E_{XC} = \alpha E_X^{HFX}[P] + (1 - \alpha)E_X^{DFT}[\rho] + E_C^{DFT}[\rho]$$

$$E_X^{HFX}[P] = -\frac{1}{2}\sum_{\lambda\sigma\mu\nu} P^{\mu\sigma}P^{\nu\sigma}(\mu\nu|\lambda\sigma)$$

introduce auxiliary density matrix $\hat{P} \approx P$

$$E_X^{HFX}[P] = E_X^{HFX}[\hat{P}] + E_X^{HFX}[P] - E_X^{HFX}[\hat{P}]$$

$$\approx E_X^{HFX}[\hat{P}] + E_X^{DFT}[P] - E_X^{DFT}[\hat{P}]$$

Guidon, Hutter and VandeVondele, J. Chem. Theory Comput., 6, 2348 (2010)

Auxiliary Density Matrix Methods (ADMM)

- total energy functional of both P and $\hat{P}$

$$E_{total} = E[P] + \hat{E}[\hat{P}]$$

- still Kohn-Sham theory with ADMM

$$K_{total} = \frac{\partial E[P]}{\partial P} + \frac{\partial \hat{E}[\hat{P}]}{\partial P}$$

$$= K + \frac{\partial \hat{E}[\hat{P}]}{\partial \hat{P}} \frac{\partial \hat{P}}{\partial P}$$

using a chain rule and

$$K_{total}C = SC\epsilon$$

as the equation to be solved self-consistently. (Simplest case given here, ADMM1)

Guidon, Hutter and VandeVondele, J. Chem. Theory Comput., 6, 2348 (2010)

Auxiliary Density Matrix Methods (ADMM)

- Construction of auxiliary density matrix

$$\hat{\psi}_i(\mathbf{r}) = \sum_{\mu} \hat{C}^{\mu i} \hat{\phi}_{\mu}(\mathbf{r})$$

$$\hat{P}^{\mu\nu} = \sum_{i} \hat{C}^{\mu i} \hat{C}^{\nu i} = \hat{C}\hat{C}^{T}$$

- we find the $\hat{C}$ that minimises the difference between occupied wavefunctions in the primary and secondary basis sets:

$$\sum_{i} \int \left(\psi_j(\mathbf{r}) - \hat{\psi}_j(\mathbf{r}) \right)^2 d\mathbf{r}$$

(see ADMM_PURIFICATION_METHOD=NONE keyword in &AUXILIARY_DENSITY_MATRIX_METHOD subsection)

Guidon, Hutter and VandeVondele, J. Chem. Theory Comput., 6, 2348 (2010)

Auxiliary Density Matrix Methods (ADMM)

- Construction of auxiliary density matrix enforcing indempotent auxiliary density matrix

$$\hat{\psi}_i(\mathbf{r}) = \sum_\mu \hat{C}^{\mu i}\, \hat{\phi}_\mu(\mathbf{r})$$

$$\hat{P}^{\mu\nu} = \sum_i \hat{C}^{\mu i}\, \hat{C}^{\nu i} = \hat{C}\hat{C}^T$$

- we find the $\hat{C}$ that minimises the difference between occupied wavefunctions in the primary and secondary basis sets subject to the constraint that the auxiliary wavefunctions are orthonormal:

$$\sum_i \int \left(\psi_j(\mathbf{r}) - \hat{\psi}_j(\mathbf{r})\right)^2 \mathrm{d}\mathbf{r} + \sum_{k,l} \Lambda_{kl}\left(\int \hat{\psi}_k(\mathbf{r})\hat{\psi}_l(\mathbf{r})\mathrm{d}\mathbf{r} - \delta_{kl}\right)$$

The Λ matrix contains the Lagrangian multipliers enforcing orthonormality.

(see ADMM_PURIFICATION_METHOD=MO_DIAG keyword in &AUXILIARY_DENSITY_MATRIX_METHOD subsection)

Guidon, Hutter and VandeVondele, J. Chem. Theory Comput., 6, 2348 (2010)

Auxiliary Density Matrix Methods (ADMM)

- Construction of auxiliary density matrix constraint on total charge

$$W_Q = \sum_i^{\text{occ}} \left\langle (i - \tilde{i})^2 \right\rangle + \lambda \left(\frac{N}{2} - \sum_i^{\text{occ}} \left\langle \tilde{i^2} \right\rangle \right)$$

(see EXCH_SCALING_MODEL keyword in &AUXILIARY_DENSITY_MATRIX_METHOD subsection)

Merlot et al., J. Chem. Phys., 141, 094101 (2014)

ADMM forces

$$\frac{dE}{d\mathbf{R}} = \frac{dE[P]}{d\mathbf{R}} + \frac{d\hat{E}[\hat{P}]}{d\mathbf{R}}$$

where $\hat{P}$ is defined via $\hat{C} = AC$. Then various chain rules ...

$$\frac{d\hat{E}[\hat{P}]}{d\mathbf{R}} + \frac{d\hat{E}[\hat{P}]}{d\hat{C}}\frac{\hat{C}}{d\mathbf{R}} = \hat{U}\frac{\hat{C}}{d\mathbf{R}}$$

$$\hat{U} = \frac{d\hat{E}[\hat{P}]}{d\hat{C}} = \frac{d\hat{E}[\hat{P}]}{d\hat{P}}\frac{d\hat{P}}{d\hat{C}} = \hat{K}\hat{C}$$

finally

$$\frac{d\hat{E}[\hat{P}]}{d\mathbf{R}} = \hat{U}_{ab}\left[\frac{dA}{d\mathbf{R}}C\Lambda^{-1/2}\right]_{ab} + \hat{U}_{ab}\left[AC\frac{d\Lambda^{-1/2}}{d\mathbf{R}}\right]_{ab}$$

Forces for MO_Diag and non-purified ADMM implemented. Linear algebra can get expensive for larger systems (reason for contracted auxiliary basis sets)

Auxiliary Density Matrix Methods (ADMM)

- several GGA exchange corrections using different functionals

$$E_X^{HFX}[P] = E_X^{HFX}[\hat{P}] + E_X^{HFX}[P] - E_X^{HFX}[\hat{P}]$$

$$\approx E_X^{HFX}[\hat{P}] + E_X^{DFT}[P] - E_X^{DFT}[\hat{P}]$$

DFT can be B88, PBE, OPTX, KT3X

(see EXCH_CORRECTION_FUNC keyword in &AUXILIARY_DENSITY_MATRIX_METHOD subsection)

ADMM basis sets

Initially available from H to Cl optimized against atomic calculations

Choice of auxiliary basis set for ADMM

- FIT3: three Gaussian exponents for each valence orbital
- cFIT3: a contraction of FIT3
- pFIT3: FIT3 + polarization functions
- cpFIT3: cFIT3 + polarization functions
- aug-FIT3, aug-cFIT3, aug-pFIT3, aug-cpFIT3: augmented with a "diffuse" function

(see $CP2K/cp2k/data/BASIS_ADMM)

Guidon, Hutter and VandeVondele, J. Chem. Theory Comput., 6, 2348 (2010)

ADMM basis sets

Uncontracted basis sets for transition metals:

- FIT10: 4s + 3p + 3d
- FIT11: 4s + 3p + 3d + 1f
- FIT12: 4s + 3p + 4d + 1f
- FIT13: 4s + 4p + 4d + 1f

Contracted basis sets (double-ζ quality)

- cFIT10 / cFIT11 / cFIT12 / cFIT13

Names of the ADMM basis sets for main group elements will differ slightly, and usually the first ADMM basis set will not contain polarisation function.

(see $CP2K/cp2k/data/BASIS_ADMM_MOLOPT)

Ling & Slater, unpublished

General remarks

- Always check the convergence of CUTOFF
- Always check the convergence of properties (e.g. lattice parameters, band gaps) with respect to supercell sizes
- Always start from pre-converged GGA (e.g. PBE) wavefunction and geometry
- Always check the convergence of primary and ADMM basis sets
    - start from a small basis and gradually increase the size
- ADMM has only been implemented for use with GPW
- Only ADMM1 will work with some other functionality (smearing, TDDFPT)

Example: Diamond band-gap

method	number of integrals	gap [eV]
PBE (PBS)		4.17
PBE (ABS)		4.37
PBE0 (PBS)	$40,787,850,778,591$	6.07
PBE0 (ABS)	$23,561,509,497$	6.25
PBE0 ADMM1	$24,816,897,009$	6.03
PBE0 ADMM2	$24,795,460,638$	6.02

Guidon, Hutter and VandeVondele, J. Chem. Theory Comput., 6, 2348 (2010)

Example: Silicon band-gap

Cutoff Radius [nm]	Band gap [eV]	# Integrals
0.2	1.16 [a]	77799946176 [a]
0.4	1.54 [a]	154325979000 [a]
0.6	1.71 [a]	265868148312 [a]
0.8	1.78 [a]	422457823080 [a]

PBE0-TC-LRC with cFIT3 ADMM basis, 3x3x3 supercell, 216 atoms

ADMM basis	Band gap [eV]	# Integrals
cFIT3	1.16 [a]	422457823080 [a]
FIT3	1.80 [a]	424426850352 [a]
pFIT3	1.98 [a]	1447428361680 [a]
Ref. (VASP)	1.93 [b]	

PBE0-TC-LRC with 8 Å cutoff radius, 3x3x3 supercell, 216 atoms

[a] Ling & Slater, unpublished; [b] Paier et al., J. Chem. Phys. 124, 154709 (2006)

Functionals

- PBE0-TC-LRC, Long Range Corrected truncated global hybrid

$$E_{XC}^{PBE0-TC-LRC} = aE_X^{HF,TC}(R_c) + aE_X^{PBE,LRC}(R_c) + (1-a)E_X^{PBE} + E_C^{PBE}$$

Guidon et al., J. Chem. Theory Comput., 5, 3010 (2008) Spencer & Alavi, Phys. Rev. B, 77, 193110 (2008)

- HSE, Range separated hybrid

$$E_{XC}^{HSE} = aE_X^{HF,SR}(\omega) + (1-a)E_X^{PBE,SR}(\omega) + E_X^{PBE,LR}(\omega) + E_C^{PBE}$$

Scuceria et al., J. Chem. Phys., 125, 224106 (2006)

"Empirical" parameters: a, R_c, and ω

(note the 0 in PBE0 stands for 0 empirical parameters...)

Input structure

Sketch of the key sections for running an ADMM calculation

```
&DFT
  …
  BASIS_SET_FILE_NAME ./BASIS_MOLOPT
  BASIS_SET_FILE_NAME ./BASIS_ADMM
  WFN_RESTART_FILE_NAME ${project}-RESTART.wfn
  ...
  &SCF
    ...
    SCF_GUESS RESTART
    ...
  &END SCF
  &AUXILIARY_DENSITY_MATRIX_METHOD
    METHOD BASIS_PROJECTION
    ADMM_PURIFICATION_METHOD MO_DIAG
  &END AUXILIARY_DENSITY_MATRIX_METHOD
  ...
  &XC
  ...
  &END XC
&END DFT
```

Note: The syntax for the AUX basis set changed (after 4.1?) before that it would be AUX_FIT_BASIS_SET ***

PBE0 vs HSE

Input structure (see examples in $CP2K/cp2k/tests/QS/regtest-admm-1/2/3/4)

```
&XC                                        &XC
  &XC_FUNCTIONAL                             &XC_FUNCTIONAL
    &PBE                                       &PBE
      SCALE_X 0.75                               SCALE_X 0.0
      SCALE_C 1.0                                SCALE_C 1.0
    &END PBE                                   &END PBE
    &PBE_HOLE_T_C_LR                           &XWPBE
      CUTOFF_RADIUS 2.0                          SCALE_X -0.25
      SCALE_X 0.25                               SCALE_X0 1.0
    &END PBE_HOLE_T_C_LR                        OMEGA 0.11
  &END XC_FUNCTIONAL                           &END XWPBE
  &HF                                        &END XC_FUNCTIONAL
    &SCREENING                               &HF
      EPS_SCHWARZ 1.0E-6                        &SCREENING
      SCREEN_ON_INITIAL_P FALSE                  EPS_SCHWARZ 1.0E-6
    &END SCREENING                               SCREEN_ON_INITIAL_P FALSE
    &INTERACTION_POTENTIAL                     &END SCREENING
      POTENTIAL_TYPE TRUNCATED                 &INTERACTION_POTENTIAL
      CUTOFF_RADIUS 2.0                          POTENTIAL_TYPE SHORTRANGE
      T_C_G_DATA ./t_c_g.dat                     OMEGA 0.11
```

Output

Step	Update method	Time	Convergence	Total energy	Change

```
        HFX_MEM_INFO| Est. max. program size before HFX [MiB]:              563

        *** WARNING in hfx_energy_potential.F:600 :: The Kohn Sham matrix is not  ***
        *** 100% occupied. This may result in incorrect Hartree-Fock results. Try ***
        *** to decrease EPS_PGF_ORB and EPS_FILTER_MATRIX in the QS section. For   ***
        *** more information see FAQ: https://www.cp2k.org/faq:hfx_eps_warning     ***

        HFX_MEM_INFO| Number of cart. primitive ERI's calculated:    218851035670
        HFX_MEM_INFO| Number of sph. ERI's calculated:               152193561473
        HFX_MEM_INFO| Number of sph. ERI's stored in-core:            22711518963
        HFX_MEM_INFO| Number of sph. ERI's stored on disk:                       0
        HFX_MEM_INFO| Number of sph. ERI's calculated on the fly:                0
        HFX_MEM_INFO| Total memory consumption ERI's RAM [MiB]:              21290
        HFX_MEM_INFO| Whereof max-vals [MiB]:                                 1516
        HFX_MEM_INFO| Total compression factor ERI's RAM:                     8.14
        HFX_MEM_INFO| Total memory consumption ERI's disk [MiB]:                 0
        HFX_MEM_INFO| Total compression factor ERI's disk:                    0.00
        HFX_MEM_INFO| Size of density/Fock matrix [MiB]:                       764
        HFX_MEM_INFO| Size of buffers [MiB]:                                   118
```

`Number of sph. ERI's calculated on the fly`: should ideally be zero.
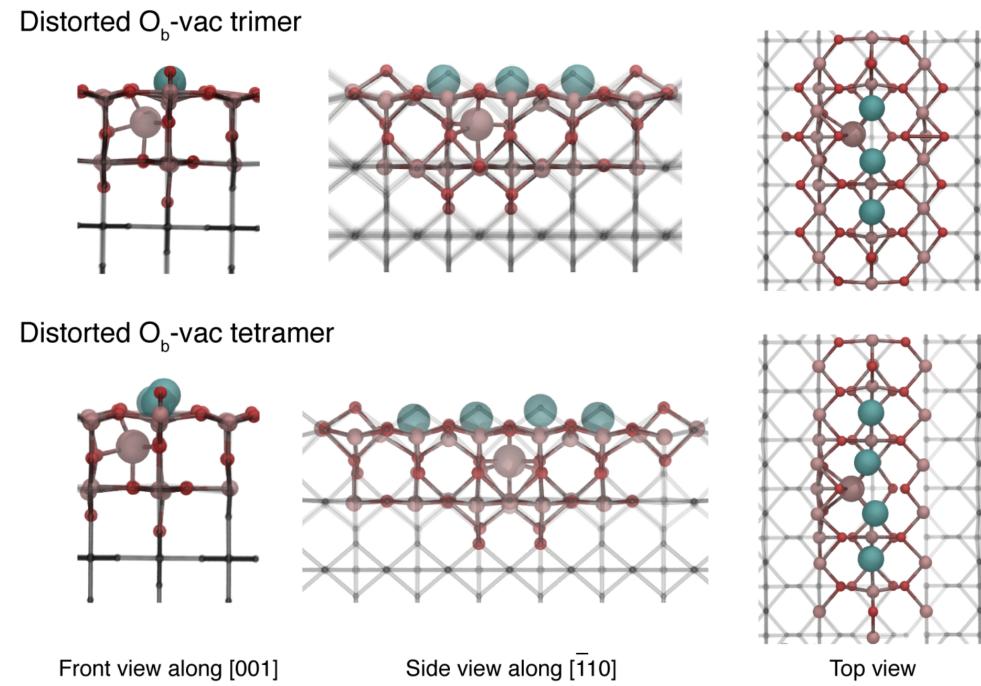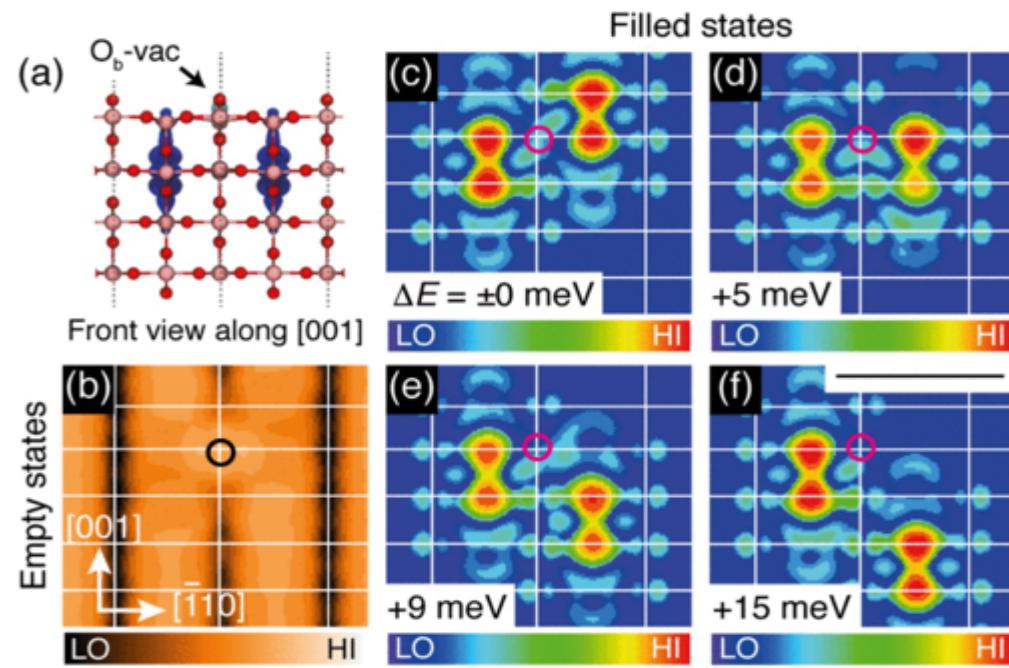
We want to keep ERIs in memory during the SCF loop.
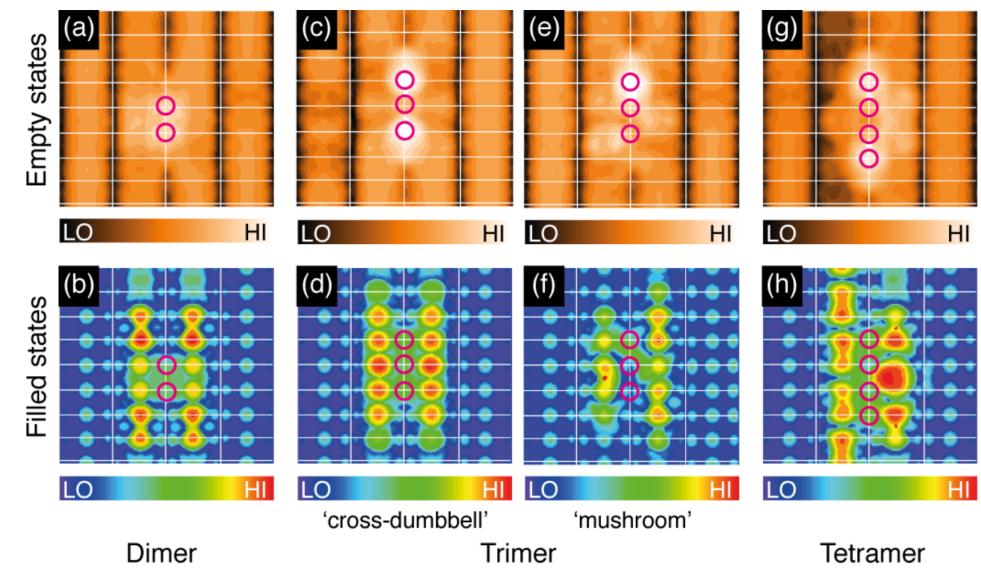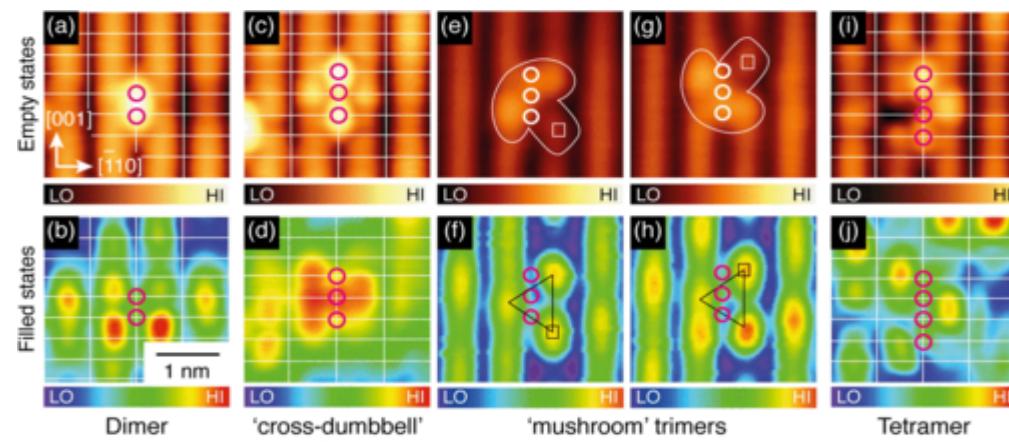
Extra remarks

- Libint library is used to calculate ERIs and their analytic derivatives, see $CP2K/cp2k/INSTALL for more details on installation and linking with CP2K

- Hybrid DFT calculations of large systems are memory demanding, try to increase MAX_MEMORY or run the job with more MPI processes. Note MAX_MEMORY is the memory per MPI process for ERIs, you must leave space for operating system and rest of the CP2K calculation.

- For extremely large hybrid DFT calculations, try hybrid MPI/OpenMP binary (i.e. cp2k.psmp)

Examples
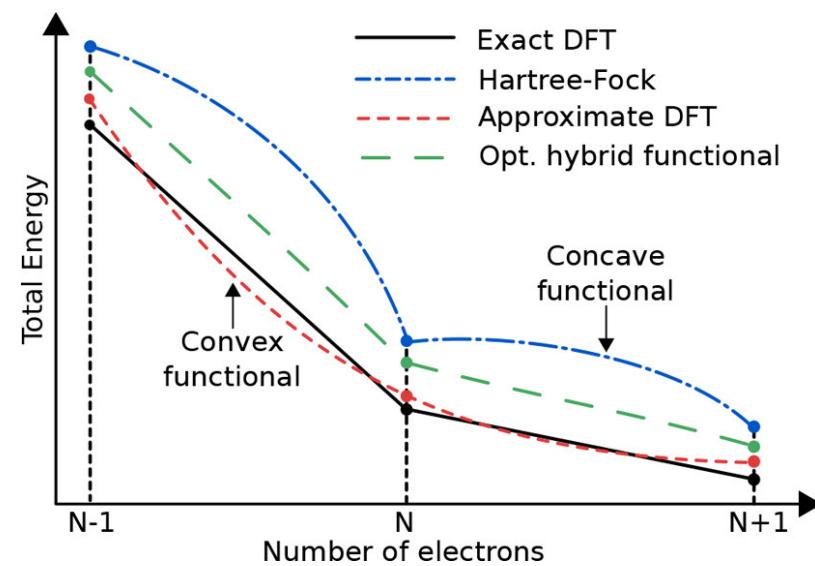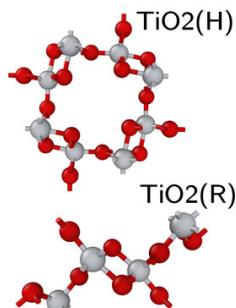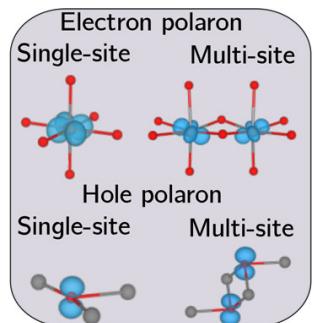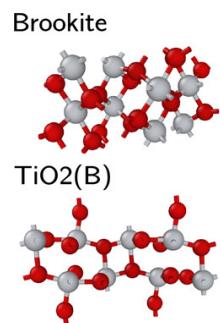
TiO$_2$ is everyone's favourite material - hybrid calculations with ~1000 atoms and good basis sets using CP2K

Yim et al, Phys. Rev. Lett. 117, 116402 (2016)

Yim et al, Phys. Rev. Lett. 117, 116402 (2016)

TiO2-Polarons

Brookite

TiO2(B)

Electron polaron
Single-site   Multi-site

Hole polaron
Single-site   Multi-site

TiO2(H)

TiO2(R)

Total Energy

Exact DFT
Hartree-Fock
Approximate DFT
Opt. hybrid functional

Concave
functional

Convex
functional

N-1   N   N+1
Number of electrons
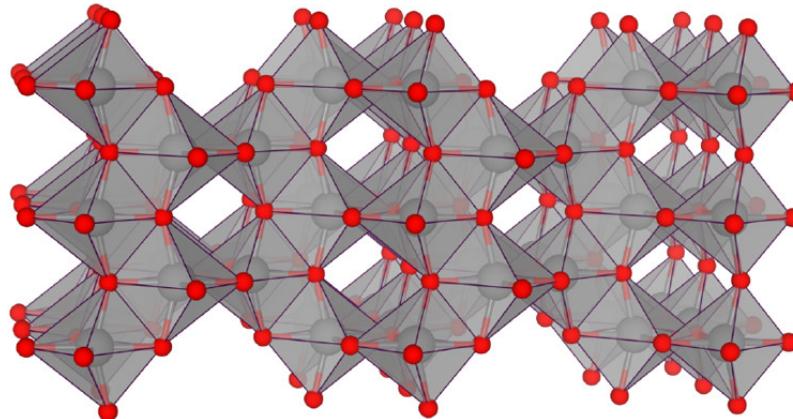
A. R. Elmaslmane et al, J. Chem. Theory Comput., 2018, 14, 3740

TiO2-Polarons

Rutile
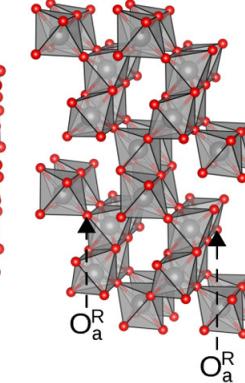
Anatase

Brookite

O_a^{Br} O_b^{Br}

TiO$_2$(R)

O_a^R

O_a^R

TiO$_2$(H)

O_a^H O_a^H

TiO$_2$(B)

Ti$_a^B$ —   — O_a^B

Ti$_b^B$ —   — O_b^B

O_d^B O_c^B

A. R. Elmaslmane et al, J. Chem. Theory Comput., 2018, 14, 3740

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A. R. Elmaslmane et al, J. Chem. Theory Comput., 2018, 14, 3740

TiO2-Polarons

Anatase

Rutile

Electron

Hole

A. R. Elmaslmane et al, J. Chem. Theory Comput., 2018, 14, 3740

TiO2-Polarons

A. R. Elmaslmane et al, J. Chem. Theory Comput., 2018, 14, 3740
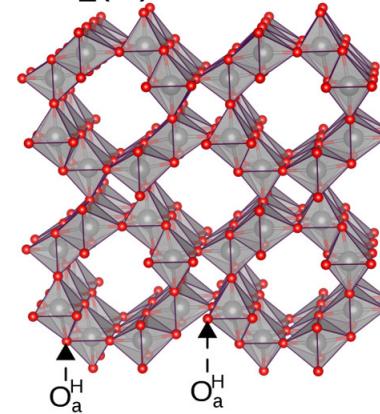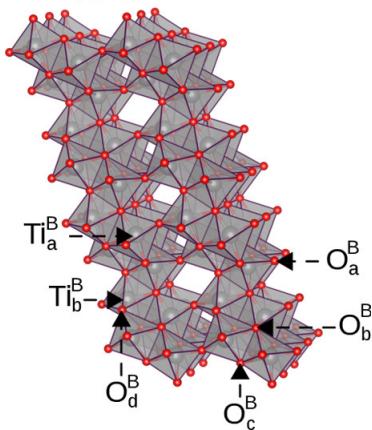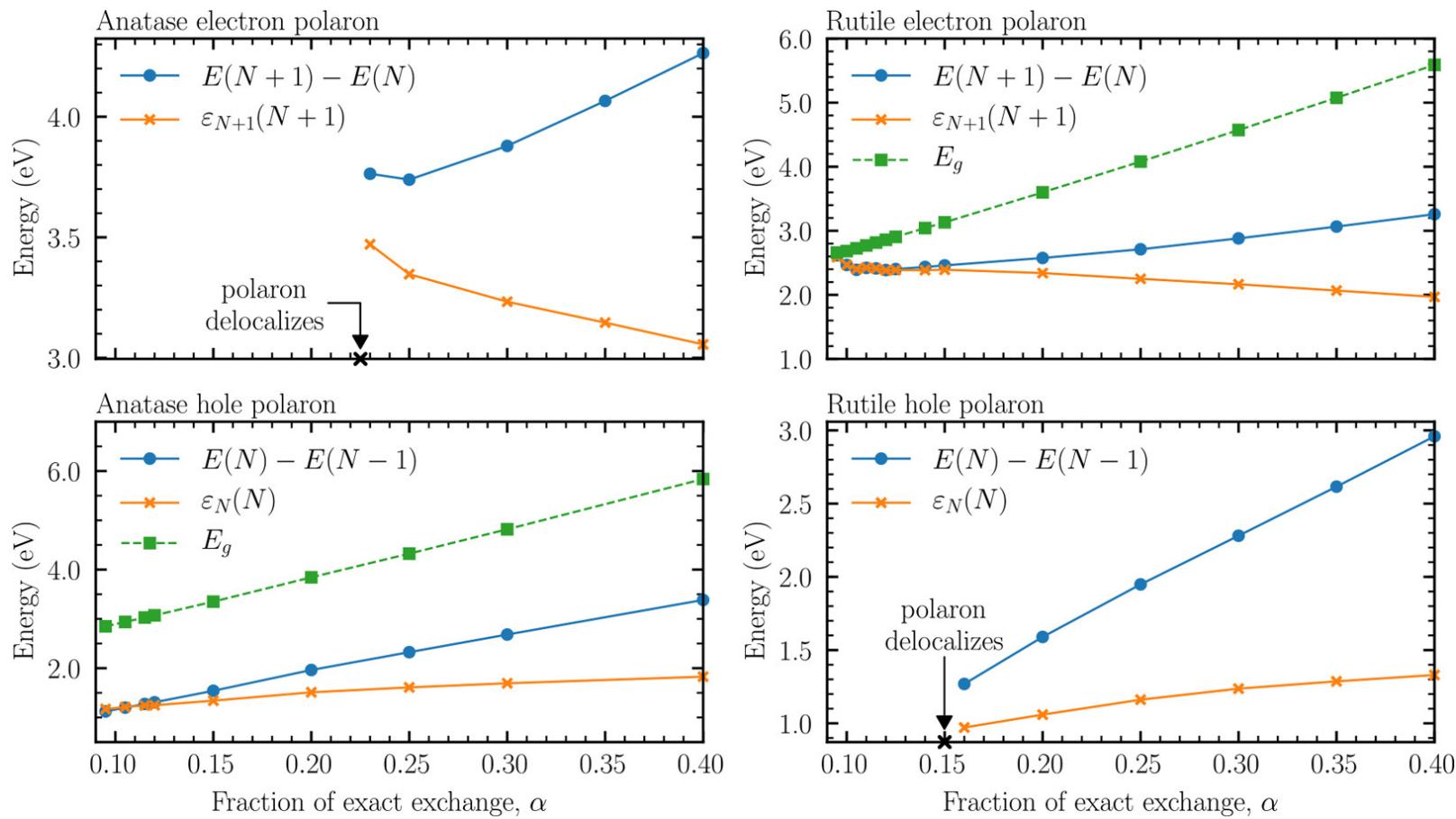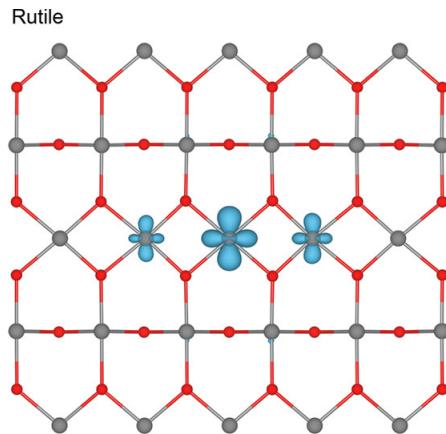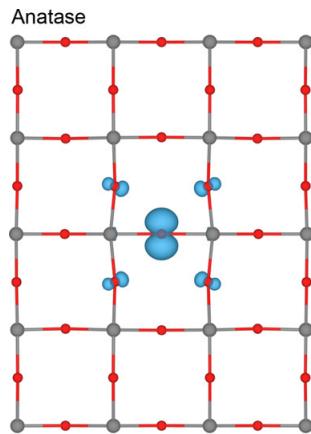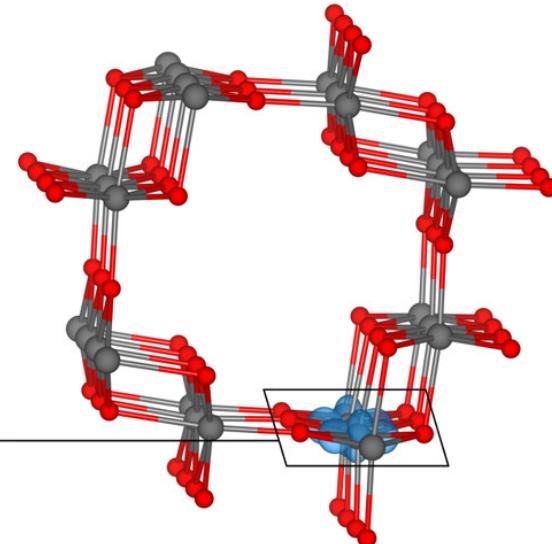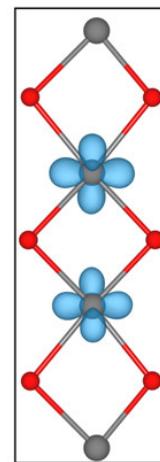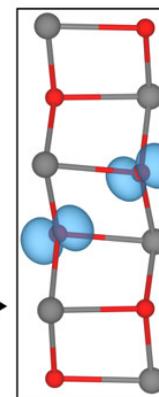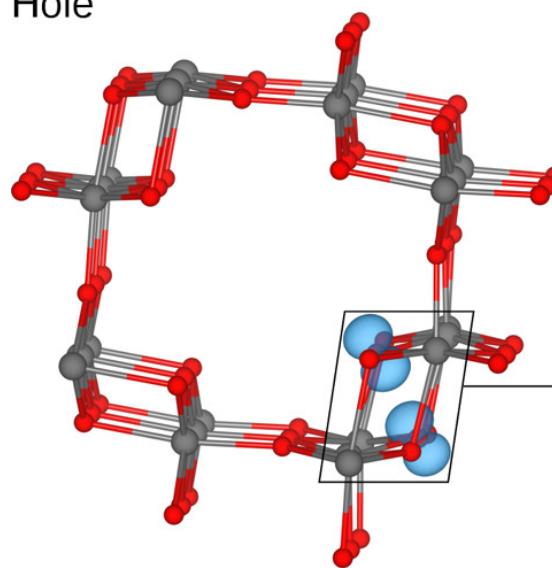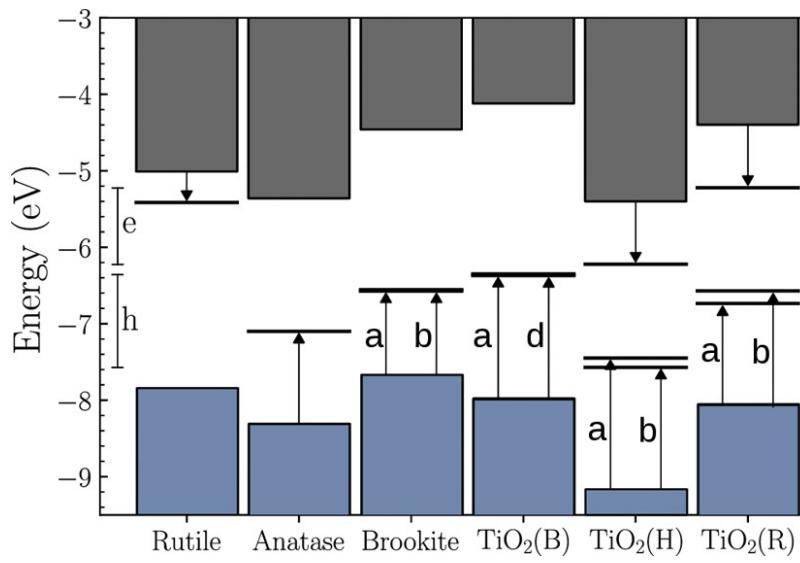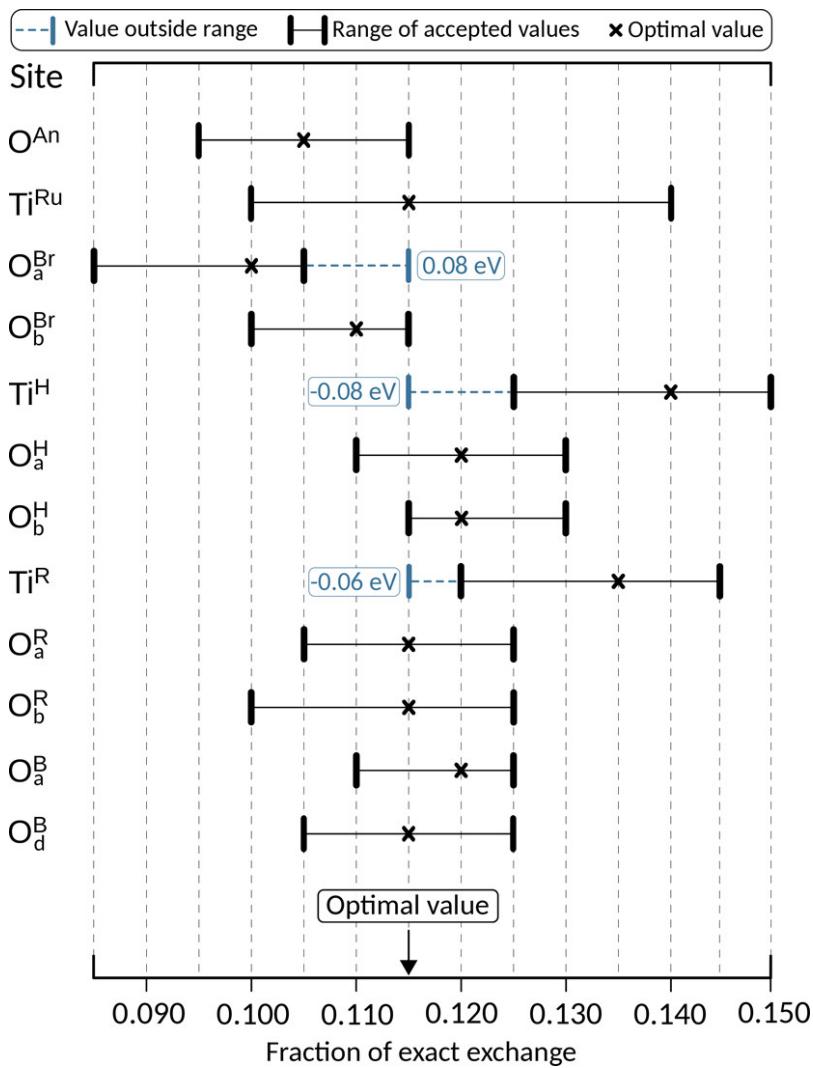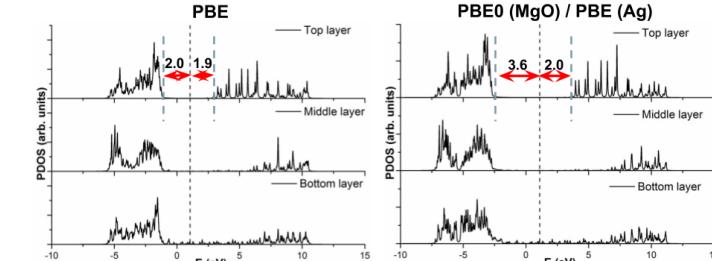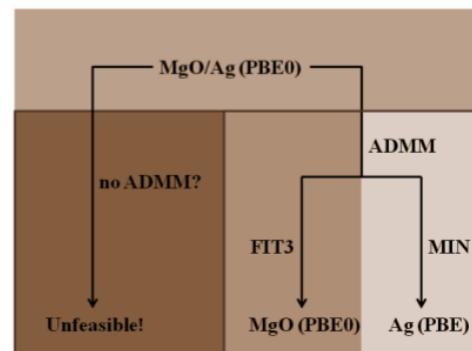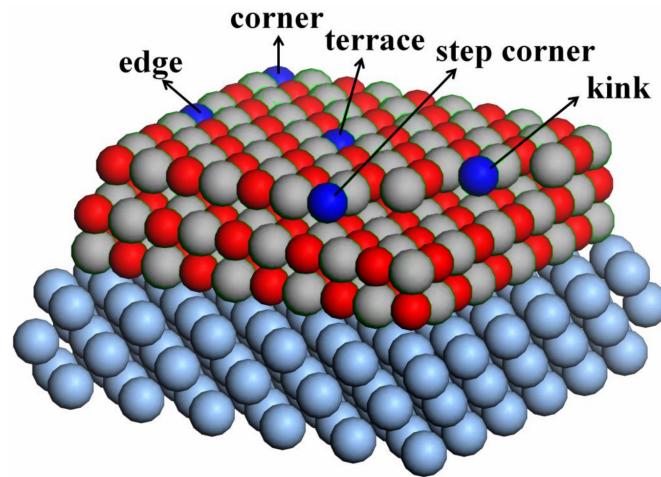
Fun and games

ADMM is not just an approximation to full hybrid DFT, but can be used in other ways

- embedding: smaller basis sets / no basis sets on some atoms

Ling et al. "Effects of oxide roughness at metal oxide interface: MgO on Ag (001)." J. Phys. Chem. C 117.10 (2013): 5075-5083.

Up Jacob's Ladder

Beyond hybrid functionals

Hybrid functions use information from the occupied orbitals - if we use information from the unoccupied orbitals we can construct more advanced functionals - double hybrids, RPA.

Hybrid / ADMM Exercises [here (https://www.cp2k.org/exercises:2017_uzh_cp2k-tutorial:hybrid)](https://www.cp2k.org/exercises:2017_uzh_cp2k-tutorial:hybrid)

Note: The syntax for the AUX basis set changed, use 'BASIS_SET AUX_FIT cFIT3' instead of 'AUX_FIT_BASIS_SET ***' in the example.

Post Hartree Fock wavefunction correlation

CP2K also implements several post-Hartree Fock correlation methods, [MP2 (https://www.cp2k.org/_media/exercises:2017_uzh_cp2k-tutorial:tutorial_rybkin.pdf)](https://www.cp2k.org/_media/exercises:2017_uzh_cp2k-tutorial:tutorial_rybkin.pdf), RPA, [GW (https://www.cp2k.org/_media/exercises:2017_uzh_cp2k-tutorial:tutorial_wilhelm.pdf)](https://www.cp2k.org/_media/exercises:2017_uzh_cp2k-tutorial:tutorial_wilhelm.pdf)

MP2 exercises [here (https://www.cp2k.org/exercises:2017_uzh_cp2k-tutorial:wfc)](https://www.cp2k.org/exercises:2017_uzh_cp2k-tutorial:wfc)

GW exercises [here (https://www.cp2k.org/exercises:2017_uzh_cp2k-tutorial:gw)](https://www.cp2k.org/exercises:2017_uzh_cp2k-tutorial:gw)

Thanks

- Sanliang Ling, University of Nottingham (these slides are basically his reformatted)
- Sanliang's notes also have details of using dispersion corrected functionals here (https://www.cp2k.org/_media/events:2018_summer_school:cp2k-uk-stfc-june-2018-sanliang-ling.pdf)
- CP2K developers