

# Hybrid Functionals, ADMM, Basis Set Optimisation, etc

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# Why do we need to go beyond pure GGA?

- Improved description of the thermochemistry (e.g. atomisation energy, heats of formation, etc) of molecular systems
- Improved description of the lattice constants, surface energies, ionisation potentials
- Correction for electron self-interaction error (better predictions of band gaps of semiconductors and insulators)
- Correction for missing van der Waals interactions

# What is available in CP2K?

- Correction for electron self-interaction error
  - nonlocal hybrid density functionals with Hartree-Fock exact exchange
  - GGA+U (on-site Coulomb interaction)
- Correction for missing van der Waals interactions
  - Stefan Grimme's DFT+D2/D3
  - nonlocal van der Waals functionals
  - use functionals from Libxc

# Hybrid DFT Calculations with CP2K

- ADMM: Auxiliary Density Matrix Methods for Hartree-Fock Exchange Calculations
- Total energy as a functional of the electron density

$$E[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

- Exchange-correlation energy with a hybrid functional

$$E_{xc}[\rho] = \alpha E_x^{\text{HFX}}[\{\psi_i\}] + (1 - \alpha) E_x^{\text{DFT}}[\rho] + E_c^{\text{DFT}}[\rho]$$

# ADMM in CP2K

- Hartree-Fock exchange energy

$$E_x^{\text{HFX}}[P] = -\frac{1}{2} \sum_{\lambda\sigma\mu\nu} P^{\mu\sigma} P^{\nu\lambda} (\mu\nu|\lambda\sigma) \longrightarrow \text{scales as } N^4$$

$$P^{\mu\nu} = \sum_i C^{ui} C^{vi} \Leftrightarrow P = CC^T$$

$$(\mu\nu|\lambda\sigma) = \int \int \phi_\mu(\mathbf{r}_1) \phi_\nu(\mathbf{r}_1) g(|\mathbf{r}_2 - \mathbf{r}_1|) \phi_\lambda(\mathbf{r}_2) \phi_\sigma(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

- Introducing auxiliary density matrix  $\hat{P} \approx P$

$$\begin{aligned} E_x^{\text{HFX}}[P] &= E_x^{\text{HFX}}[\hat{P}] + (E_x^{\text{HFX}}[P] - E_x^{\text{HFX}}[\hat{P}]) \\ &\approx E_x^{\text{HFX}}[\hat{P}] + (E_x^{\text{DFT}}[P] - E_x^{\text{DFT}}[\hat{P}]) \end{aligned}$$

- How to construct auxiliary basis set?
  - smaller in size (i.e. less number of basis functions)
  - more rapidly decaying (i.e. bigger Gaussian exponents)

# ADMM in CP2K

## Choice of auxiliary basis set for ADMM

- FIT3: three Gaussian exponents for each valence orbital
- cFIT3: a contraction of FIT3 (i.e. fixed linear combinations of Gaussian functions)
- pFIT3: FIT3 + polarization functions (i.e. higher angular momentum functions)
- cpFIT3: cFIT3 + polarization functions
- aug-FIT3, aug-cFIT3, aug-pFIT3, aug-cpFIT3: augmented with a “diffuse” function (i.e. smaller Gaussian exponents)

# ADMM in CP2K

<b>1A</b>																	<b>8A</b>	
1 <b>H</b> 1s <sup>1</sup>	<b>2A</b>												<b>3A</b>	<b>4A</b>	<b>5A</b>	<b>6A</b>	<b>7A</b>	2 <b>He</b> 1s <sup>2</sup>
3 <b>Li</b> 1s <sup>2</sup> 2s <sup>1</sup>	4 <b>Be</b> 1s <sup>2</sup> 2s <sup>2</sup>											5 <b>B</b> 1s <sup>2</sup> 2s <sup>2</sup> p <sup>1</sup>	6 <b>C</b> 1s <sup>2</sup> 2s <sup>2</sup> p <sup>2</sup>	7 <b>N</b> 1s <sup>2</sup> 2s <sup>2</sup> p <sup>3</sup>	8 <b>O</b> 1s <sup>2</sup> 2s <sup>2</sup> p <sup>4</sup>	9 <b>F</b> 1s <sup>2</sup> 2s <sup>2</sup> p <sup>5</sup>	10 <b>Ne</b> 1s <sup>2</sup> 2s <sup>2</sup> p <sup>6</sup>	
11 <b>Na</b> [Ne]3s <sup>1</sup>	12 <b>Mg</b> [Ne]3s <sup>2</sup>											13 <b>Al</b> [Ne]3s <sup>2</sup> p <sup>1</sup>	14 <b>Si</b> [Ne]3s <sup>2</sup> p <sup>2</sup>	15 <b>P</b> [Ne]3s <sup>2</sup> p <sup>3</sup>	16 <b>S</b> [Ne]3s <sup>2</sup> p <sup>4</sup>	17 <b>Cl</b> [Ne]3s <sup>2</sup> p <sup>5</sup>	18 <b>Ar</b> [Ne]3s <sup>2</sup> p <sup>6</sup>	
		<b>3B</b>	<b>4B</b>	<b>5B</b>	<b>6B</b>	<b>7B</b>	<b>8B</b>		<b>1B</b>	<b>2B</b>								
19 <b>K</b> [Ar]4s <sup>1</sup>	20 <b>Ca</b> [Ar]4s <sup>2</sup>	21 <b>Sc</b> [Ar]3d <sup>1</sup> 4s <sup>2</sup>	22 <b>Ti</b> [Ar]3d <sup>2</sup> 4s <sup>2</sup>	23 <b>V</b> [Ar]3d <sup>3</sup> 4s <sup>2</sup>	24 <b>Cr</b> [Ar]3d <sup>5</sup> 4s <sup>1</sup>	25 <b>Mn</b> [Ar]3d <sup>5</sup> 4s <sup>2</sup>	26 <b>Fe</b> [Ar]3d <sup>6</sup> 4s <sup>2</sup>	27 <b>Co</b> [Ar]3d <sup>7</sup> 4s <sup>2</sup>	28 <b>Ni</b> [Ar]3d <sup>8</sup> 4s <sup>2</sup>	29 <b>Cu</b> [Ar]3d <sup>10</sup> 4s <sup>1</sup>	30 <b>Zn</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup>	31 <b>Ga</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup> p <sup>1</sup>	32 <b>Ge</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup> p <sup>2</sup>	33 <b>As</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup> p <sup>3</sup>	34 <b>Se</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup> p <sup>4</sup>	35 <b>Br</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup> p <sup>5</sup>	36 <b>Kr</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup> p <sup>6</sup>	
37 <b>Rb</b> [Kr]5s <sup>1</sup>	38 <b>Sr</b> [Kr]5s <sup>2</sup>	39 <b>Y</b> [Kr]4d <sup>1</sup> 5s <sup>2</sup>	40 <b>Zr</b> [Kr]4d <sup>2</sup> 5s <sup>2</sup>	41 <b>Nb</b> [Kr]4d <sup>4</sup> 5s <sup>1</sup>	42 <b>Mo</b> [Kr]4d <sup>5</sup> 5s <sup>1</sup>	43 <b>Tc</b> [Kr]4d <sup>5</sup> 5s <sup>2</sup>	44 <b>Ru</b> [Kr]4d <sup>7</sup> 5s <sup>1</sup>	45 <b>Rh</b> [Kr]4d <sup>8</sup> 5s <sup>1</sup>	46 <b>Pd</b> [Kr]4d <sup>10</sup>	47 <b>Ag</b> [Kr]4d <sup>10</sup> 5s <sup>1</sup>	48 <b>Cd</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup>	49 <b>In</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup> p <sup>1</sup>	50 <b>Sn</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup> p <sup>2</sup>	51 <b>Sb</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup> p <sup>3</sup>	52 <b>Te</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup> p <sup>4</sup>	53 <b>I</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup> p <sup>5</sup>	54 <b>Xe</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup> p <sup>6</sup>	
55 <b>Cs</b> [Xe]6s <sup>1</sup>	56 <b>Ba</b> [Xe]6s <sup>2</sup>	57-71 Lanthanides		72 <b>Hf</b> [Xe]4f <sup>14</sup> 5d <sup>2</sup> 6s <sup>2</sup>	73 <b>Ta</b> [Xe]4f <sup>14</sup> 5d <sup>3</sup> 6s <sup>2</sup>	74 <b>W</b> [Xe]4f <sup>14</sup> 5d <sup>4</sup> 6s <sup>2</sup>	75 <b>Re</b> [Xe]4f <sup>14</sup> 5d <sup>5</sup> 6s <sup>2</sup>	76 <b>Os</b> [Xe]4f <sup>14</sup> 5d <sup>6</sup> 6s <sup>2</sup>	77 <b>Ir</b> [Xe]4f <sup>14</sup> 5d <sup>7</sup> 6s <sup>2</sup>	78 <b>Pt</b> [Xe]4f <sup>14</sup> 5d <sup>9</sup> 6s <sup>1</sup>	79 <b>Au</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup>	80 <b>Hg</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>	81 <b>Tl</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> p <sup>1</sup>	82 <b>Pb</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> p <sup>2</sup>	83 <b>Bi</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> p <sup>3</sup>	84 <b>Po</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> p <sup>4</sup>	85 <b>At</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> p <sup>5</sup>	86 <b>Rn</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> p <sup>6</sup>
87 <b>Fr</b> [Rn]7s <sup>1</sup>	88 <b>Ra</b> [Rn]7s <sup>2</sup>	89-103 Actinides		104 <b>Rf</b> [Rn]5f <sup>14</sup> 6d <sup>2</sup> 7s <sup>2</sup>	105 <b>Db</b> [Rn]5f <sup>14</sup> 6d <sup>3</sup> 7s <sup>2</sup>	106 <b>Sg</b> [Rn]5f <sup>14</sup> 6d <sup>4</sup> 7s <sup>2</sup>	107 <b>Bh</b> [Rn]5f <sup>14</sup> 6d <sup>5</sup> 7s <sup>2</sup>	108 <b>Hs</b> [Rn]5f <sup>14</sup> 6d <sup>6</sup> 7s <sup>2</sup>	109 <b>Mt</b> [Rn]5f <sup>14</sup> 6d <sup>7</sup> 7s <sup>2</sup>	110 <b>Ds</b> [Rn]5f <sup>14</sup> 6d <sup>9</sup> 7s <sup>1</sup>	111 <b>Rg</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>1</sup>	112 <b>Cn</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup>	113 <b>Uut</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> p <sup>1</sup>	114 <b>F1</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> p <sup>2</sup>	115 <b>Uup</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> p <sup>3</sup>	116 <b>Lv</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> p <sup>4</sup>	117 <b>Uus</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> p <sup>5</sup>	118 <b>Uuo</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> p <sup>6</sup>

Limited availability of ADMM basis sets

# Basis Fitting with OPTIMIZE\_BASIS

**Choosing a reference (complete) basis**

**Performing accurate molecular calculations with ref. basis**

**Choosing a form of the basis to be fitted**

**Minimizing the objective function**

$$\Omega(\{\alpha_i, c_j\}) = \sum_B \sum_M (\rho^{B,M}(\{\alpha_i, c_j\}) + \gamma \ln \kappa^{B,M}(\{\alpha_i, c_j\}))$$



# Basis Fitting with OPTIMIZE\_BASIS

- Reference (Complete) basis
  - check **GTH-def2-QZVP** and **aug-GTH-def2-QZVP** included in `$CP2K/cp2k/tests/QS/BASIS_ADMM`
  - generate uncontracted basis sets with the **ATOMIC** code (see Marcella's slides and examples in `$CP2K/cp2k/tests/ATOM`)
- Molecular calculations
  - consider different chemical environments of an element
  - chosen element using ref. basis, other elements using moderate basis (e.g. TZVP-MOLOPT-GTH)
  - avoid homonuclear diatomic molecules
  - use equilibrium geometry (i.e. GEO\_OPT)

# Input Structure: OPTIMIZE\_BASIS

```

&GLOBAL
  PROJECT optbas
  PROGRAM_NAME OPTIMIZE_BASIS
  PRINT_LEVEL HIGH
&END GLOBAL
&OPTIMIZE_BASIS
  BASIS_TEMPLATE_FILE BASIS_SET_TEMPLATE
  BASIS_WORK_FILE WORK_BASIS_STRUCTURE
  BASIS_OUTPUT_FILE Ti_FIT_temp
#  USE_CONDITION_NUMBER Y
#  CONDITION_WEIGHT 0.0005
  WRITE_FREQUENCY 10
  &OPTIMIZATION
    MAX_FUN 50000
  &END OPTIMIZATION
  ...
  &TRAINING_FILES
    DIRECTORY ../ticl4
    INPUT_FILE_NAME ticl4.inp
  &END TRAINING_FILES
  ...
  &FIT_KIND Ti
    BASIS_SET FIT10
    INITIAL_DEGREES_OF_FREEDOM EXPONENTS
    &CONSTRAIN_EXPONENTS
      BOUNDARIES 0.1 20
      USE_EXP -1 -1
    &END CONSTRAIN_EXPONENTS
  &END FIT_KIND
&END OPTIMIZE_BASIS

```



Ti FIT10		
10		
1 0 0 1 1		
	0.10001966	1.00000000
1 0 0 1 1		
	1.06186104	1.00000000
1 0 0 1 1		
	0.40963197	1.00000000
1 0 0 1 1		
	4.39901876	1.00000000
1 1 1 1 1		
	0.52985233	1.00000000
1 1 1 1 1		
	1.57394040	1.00000000
1 1 1 1 1		
	11.83843422	1.00000000
1 2 2 1 1		
	0.25675246	1.00000000
1 2 2 1 1		
	1.02358115	1.00000000
1 2 2 1 1		
	4.21355677	1.00000000

(see \$CP2K/cp2k/tests/QS/regtest-optbas)

# ADMM in CP2K

1A		2A												3A	4A	5A	6A	7A	8A	
1 H $1s^1$																				2 He $1s^2$
3 Li $1s^2 2s^1$	4 Be $1s^2 2s^2$												5 B $1s^2 2s^2 2p^1$	6 C $1s^2 2s^2 2p^2$	7 N $1s^2 2s^2 2p^3$	8 O $1s^2 2s^2 2p^4$	9 F $1s^2 2s^2 2p^5$	10 Ne $1s^2 2s^2 2p^6$		
11 Na $[Ne]3s^1$	12 Mg $[Ne]3s^2$												13 Al $[Ne]3s^2 3p^1$	14 Si $[Ne]3s^2 3p^2$	15 P $[Ne]3s^2 3p^3$	16 S $[Ne]3s^2 3p^4$	17 Cl $[Ne]3s^2 3p^5$	18 Ar $[Ne]3s^2 3p^6$		
19 K $[Ar]4s^1$	20 Ca $[Ar]4s^2$	21 Sc $[Ar]3d^1 4s^2$	22 Ti $[Ar]3d^2 4s^2$	23 V $[Ar]3d^3 4s^2$	24 Cr $[Ar]3d^5 4s^1$	25 Mn $[Ar]3d^5 4s^2$	26 Fe $[Ar]3d^6 4s^2$	27 Co $[Ar]3d^7 4s^2$	28 Ni $[Ar]3d^8 4s^2$	29 Cu $[Ar]3d^{10} 4s^1$	30 Zn $[Ar]3d^{10} 4s^2$	31 Ga $[Ar]3d^{10} 4s^2 4p^1$	32 Ge $[Ar]3d^{10} 4s^2 4p^2$	33 As $[Ar]3d^{10} 4s^2 4p^3$	34 Se $[Ar]3d^{10} 4s^2 4p^4$	35 Br $[Ar]3d^{10} 4s^2 4p^5$	36 Kr $[Ar]3d^{10} 4s^2 4p^6$			
37 Rb $[Kr]5s^1$	38 Sr $[Kr]5s^2$	39 Y $[Kr]4d^1 5s^2$	40 Zr $[Kr]4d^2 5s^2$	41 Nb $[Kr]4d^4 5s^1$	42 Mo $[Kr]4d^5 5s^1$	43 Tc $[Kr]4d^5 5s^2$	44 Ru $[Kr]4d^7 5s^1$	45 Rh $[Kr]4d^8 5s^1$	46 Pd $[Kr]4d^{10}$	47 Ag $[Kr]4d^{10} 5s^1$	48 Cd $[Kr]4d^{10} 5s^2$	49 In $[Kr]4d^{10} 5s^2 5p^1$	50 Sn $[Kr]4d^{10} 5s^2 5p^2$	51 Sb $[Kr]4d^{10} 5s^2 5p^3$	52 Te $[Kr]4d^{10} 5s^2 5p^4$	53 I $[Kr]4d^{10} 5s^2 5p^5$	54 Xe $[Kr]4d^{10} 5s^2 5p^6$			
55 Cs $[Xe]6s^1$	56 Ba $[Xe]6s^2$	57-71 Lanthanides	72 Hf $[Xe]4f^{14} 5d^2 6s^2$	73 Ta $[Xe]4f^{14} 5d^3 6s^2$	74 W $[Xe]4f^{14} 5d^4 6s^2$	75 Re $[Xe]4f^{14} 5d^5 6s^2$	76 Os $[Xe]4f^{14} 5d^6 6s^2$	77 Ir $[Xe]4f^{14} 5d^7 6s^2$	78 Pt $[Xe]4f^{14} 5d^9 6s^1$	79 Au $[Xe]4f^{14} 5d^{10} 6s^1$	80 Hg $[Xe]4f^{14} 5d^{10} 6s^2$	81 Tl $[Xe]4f^{14} 5d^{10} 6s^2 6p^1$	82 Pb $[Xe]4f^{14} 5d^{10} 6s^2 6p^2$	83 Bi $[Xe]4f^{14} 5d^{10} 6s^2 6p^3$	84 Po $[Xe]4f^{14} 5d^{10} 6s^2 6p^4$	85 At $[Xe]4f^{14} 5d^{10} 6s^2 6p^5$	86 Rn $[Xe]4f^{14} 5d^{10} 6s^2 6p^6$			
87 Fr $[Rn]7s^1$	88 Ra $[Rn]7s^2$	89-103 Actinides	104 Rf $[Rn]5f^{14} 6d^2 7s^2$	105 Db $[Rn]5f^{14} 6d^3 7s^2$	106 Sg $[Rn]5f^{14} 6d^4 7s^2$	107 Bh $[Rn]5f^{14} 6d^5 7s^2$	108 Hs $[Rn]5f^{14} 6d^6 7s^2$	109 Mt $[Rn]5f^{14} 6d^7 7s^2$	110 Ds $[Rn]5f^{14} 6d^9 7s^1$	111 Rg $[Rn]5f^{14} 6d^{10} 7s^1$	112 Cn $[Rn]5f^{14} 6d^{10} 7s^2$	113 Uut $[Rn]5f^{14} 6d^{10} 7s^2 7p^1$	114 Fl $[Rn]5f^{14} 6d^{10} 7s^2 7p^2$	115 Uup $[Rn]5f^{14} 6d^{10} 7s^2 7p^3$	116 Lv $[Rn]5f^{14} 6d^{10} 7s^2 7p^4$	117 Uus $[Rn]5f^{14} 6d^{10} 7s^2 7p^5$	118 Uuo $[Rn]5f^{14} 6d^{10} 7s^2 7p^6$			

**New ADMM basis sets available upon request!**  
 (Email: [S.Ling@ucl.ac.uk](mailto:S.Ling@ucl.ac.uk))

# Input Structure: ADMM

&DFT

...

BASIS\_SET\_FILE\_NAME ./BASIS\_MOLOPT

BASIS\_SET\_FILE\_NAME ./BASIS\_ADMM

(files can be found in \$CP2K/cp2k/tests/QS)

...

&AUXILIARY\_DENSITY\_MATRIX\_METHOD

METHOD BASIS\_PROJECTION

ADMM\_PURIFICATION\_METHOD **MO\_DIAG**

&END AUXILIARY\_DENSITY\_MATRIX\_METHOD

...

&XC

...

&END XC

&END DFT

&SUBSYS

&KIND Si

BASIS\_SET DZVP-MOLOPT-SR-GTH

AUX\_FIT\_BASIS\_SET **cFIT3**

POTENTIAL GTH-PBE-q4

&END KIND

&END SUBSYS

# Which functional to use?

- **PBE0-TC-LRC**

$$E_{xc}^{PBE0-TC-LRC} = aE_x^{HF,TC}(R_C) + aE_x^{PBE,LRC}(R_C) \\ + (1-a)E_x^{PBE} + E_c^{PBE}$$

J. Chem. Theory Comput., 5, 3010 (2009)

- **HSE06**

$$E_{xc}^{HSE06} = aE_x^{HF,SR}(\omega) + (1-a)E_x^{PBE,SR}(\omega) \\ + E_x^{PBE,LR}(\omega) + E_c^{PBE}$$

J. Chem. Phys., 125, 224106 (2006)

# Input Structure: PBE0 vs. HSE06

&XC

```

&XC_FUNCTIONAL
  &PBE
    SCALE_X 0.75
    SCALE_C 1.0
  &END PBE
  &PBE_HOLE_T_C_LR
    CUTOFF_RADIUS 6.0
    SCALE_X 0.25
  &END PBE_HOLE_T_C_LR
&END XC_FUNCTIONAL
&HF
  &SCREENING
    EPS_SCHWARZ 1.0E-6
    SCREEN_ON_INITIAL_P FALSE
  &END SCREENING
  &INTERACTION_POTENTIAL
    POTENTIAL_TYPE TRUNCATED
    CUTOFF_RADIUS 6.0
    T_C_G_DATA ./t_c_g.dat
  &END INTERACTION_POTENTIAL
  &MEMORY
    MAX_MEMORY 2400
    EPS_STORAGE_SCALING 0.1
  &END MEMORY
  FRACTION 0.25
&END HF
&END XC

```

**PBE0-TC-LRC**

&XC

```

&XC_FUNCTIONAL
  &PBE
    SCALE_X 0.0
    SCALE_C 1.0
  &END PBE
  &XWPBE
    SCALE_X -0.25
    SCALE_X0 1.0
    OMEGA 0.11
  &END XWPBE
&END XC_FUNCTIONAL
&HF
  &SCREENING
    EPS_SCHWARZ 1.0E-6
    SCREEN_ON_INITIAL_P FALSE
  &END SCREENING
  &INTERACTION_POTENTIAL
    POTENTIAL_TYPE SHORTRANGE
    OMEGA 0.11
  &END INTERACTION_POTENTIAL
  &MEMORY
    MAX_MEMORY 2400
    EPS_STORAGE_SCALING 0.1
  &END MEMORY
  FRACTION 0.25
&END HF
&END XC

```

**HSE06**

# 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

**3x3x3 supercell**

# Example: Bulk Silicon

Cutoff radius (Å)	Band gap (eV)
2	1.16 <sup>a</sup>
4	1.54 <sup>a</sup>
6	1.71 <sup>a</sup>
8	1.78 <sup>a</sup>

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

Cutoff radius

$$R_C \leq \frac{L}{2}$$

ADMM basis	Band gap (eV)
cFIT3	1.78 <sup>a</sup>
FIT3	1.80 <sup>a</sup>
pFIT3	1.98 <sup>a</sup>
Ref. (VASP/PBE0)	1.93 <sup>b</sup> (indirect)

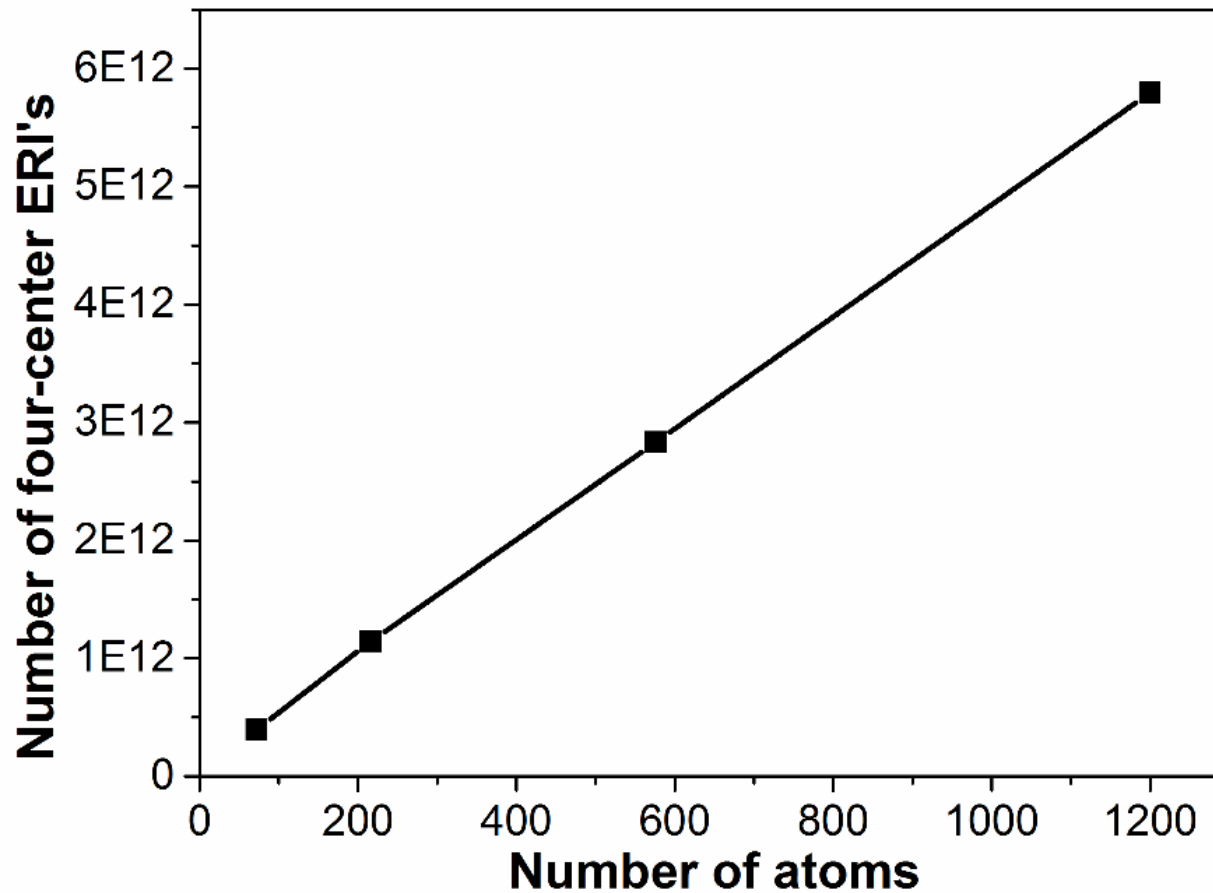
PBE0-TC-LRC with 8 Å cutoff radius, 3x3x3 supercell

Polarisation function is important for covalent solids!

<sup>a</sup> Ling & Slater, unpublished; <sup>b</sup> J. Chem. Phys. 124, 154709 (2006)



# Example: Rutile $\text{TiO}_2$



**Computational cost: Linear scaling!**

# GGA with on-site Coulomb interaction: GGA+U

$$E_{\text{LSDA}+U} = E_{\text{LSDA}}[\{\epsilon_i\}] + \frac{(\overline{U} - \overline{J})}{2} \sum_{l,j,\sigma} \rho_{lj}^{\sigma} \rho_{jl}^{\sigma}$$

Phys. Rev. B, 57, 1505 (1998)

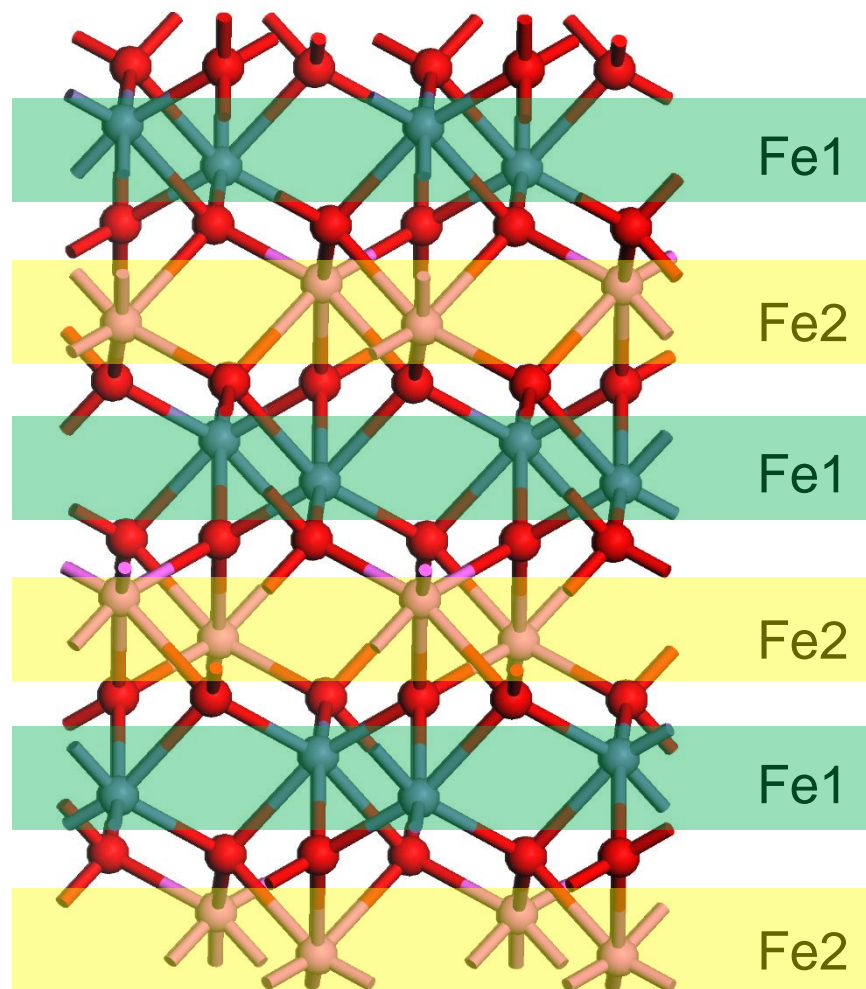
## Input Structure: GGA+U

```

&KIND Ti
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-PBE-q12
  &DFT_PLUS_U T
    L 2 → specify which orbital to add GGA+U
    U_MINUS_J [eV] 3.9 → specify effective on-site Coulomb interaction parameter
  &END DFT_PLUS_U
&END KIND
  
```

(see examples in \$CP2K/cp2k/tests/QS/regtest-plus\_u)

# Magnetic systems



Fe1

Fe2

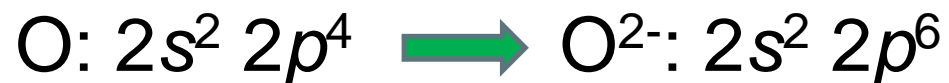
Fe1

Fe2

Fe1

Fe2

Hematite ( $\text{Fe}_2\text{O}_3$ ) – antiferromagnetic

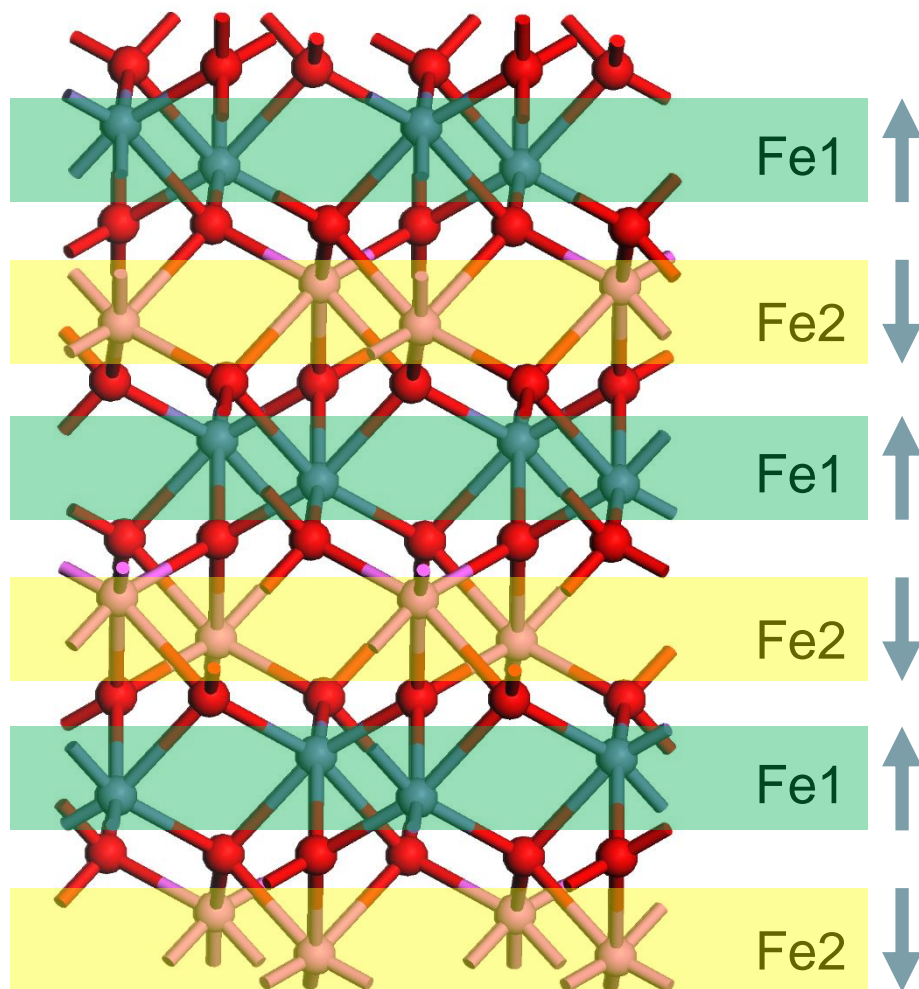


```

&KIND O
BASIS_SET DZVP-MOLOPT-SR-GTH
POTENTIAL GTH-PBE-q6
&BS
  &ALPHA → spin channel
  NEL +2 → orbital occupation change
  L 1 → angular momentum quantum number
  N 2 → principal quantum number
&END ALPHA
&BETA
  NEL +2
  L 1
  N 2
&END BETA
&END BS
&END KIND
  
```

(see examples in \$CP2K/cp2k/tests/QS/regtest-bs)

# Magnetic systems



Hematite ( $\text{Fe}_2\text{O}_3$ ) – antiferromagnetic

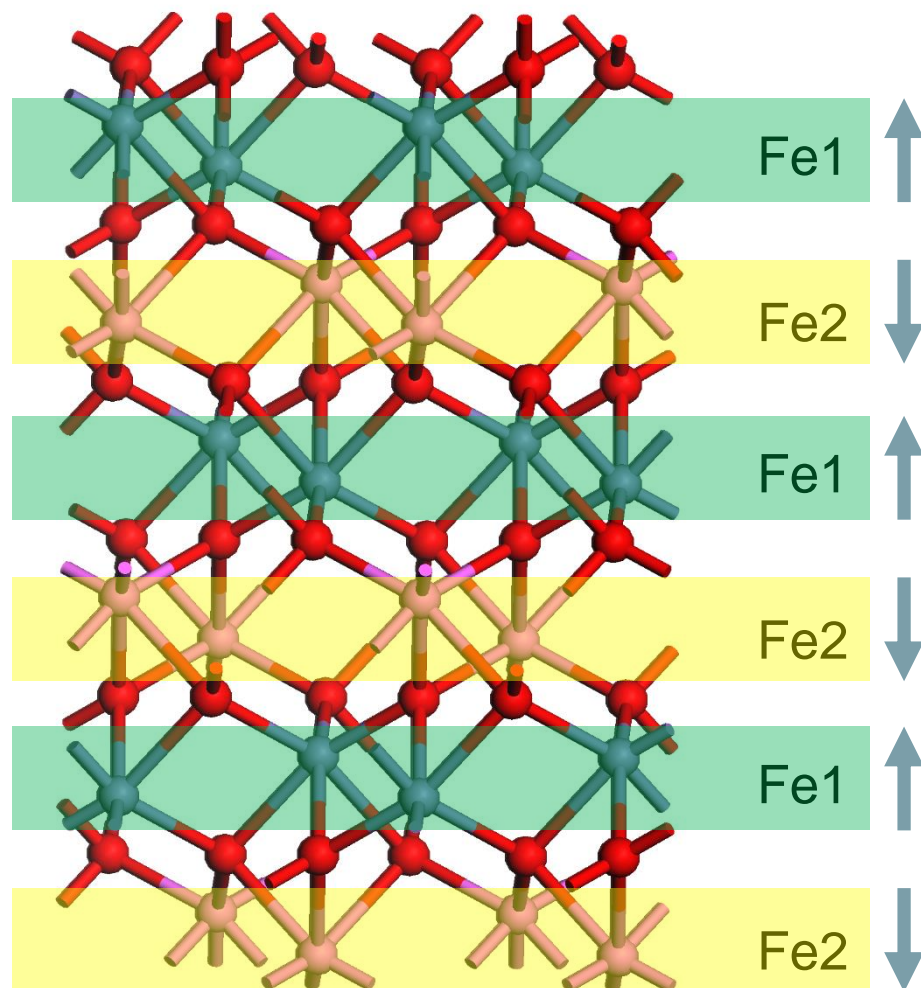


```

&KIND Fe1
ELEMENT Fe
BASIS_SET DZVP-MOLOPT-SR-GTH
POTENTIAL GTH-PBE-q16
&DFT_PLUS_U
L 2
U_MINUS_J [eV] 5.0
&END DFT_PLUS_U
&BS
&ALPHA
NEL +4 -2
L 2 0
N 3 4
&END ALPHA
&BETA
NEL -6 -2
L 2 0
N 3 4
&END BETA
&END BS
&END KIND
    
```

(see examples in  $\$CP2K/cp2k/tests/QS/regtest-bs$ )

# Magnetic systems



Hematite ( $\text{Fe}_2\text{O}_3$ ) – antiferromagnetic



```

&KIND Fe2
ELEMENT Fe
BASIS_SET DZVP-MOLOPT-SR-GTH
POTENTIAL GTH-PBE-q16
&DFT_PLUS_U
L 2
U_MINUS_J [eV] 5.0
&END DFT_PLUS_U
&BS
&ALPHA
NEL -6 -2
L 2 0
N 3 4
&END ALPHA
&BETA
NEL +4 -2
L 2 0
N 3 4
&END BETA
&END BS
&END KIND
  
```

(see examples in  $\$CP2K/cp2k/tests/QS/regtest-bs$ )

# Some general suggestions

- Always check the convergence of CUTOFF

(see [http://www.cp2k.org/howto:converging\\_cutoff](http://www.cp2k.org/howto:converging_cutoff))

- Always start from a pre-converged GGA (e.g. PBE)

wavefunction

- For GGA+U calculations, do not use **U\_MINUS\_J**

values derived from other codes directly

# Van der Waals corrected DFT methods

- **Stefan Grimme's DFT+D2/D3**
- **nonlocal van der Waals functionals**
- **functionals from Libxc**

# Van der Waals corrected DFT methods

## ➤ Stefan Grimme's DFT+D2/D3

$$E_{\text{tot}} = E_{\text{DFT}} + E_{\text{disp}}$$

$$E_{\text{disp}} = - \sum_{A,B} C_6^{\text{AB}} / r_{\text{AB}}^6$$

## ➤ nonlocal van der Waals functionals

$$E_{\text{xc}} = E_{\text{x}}^{\text{GGA}} + E_{\text{c}}^{\text{LDA}} + E_{\text{c}}^{\text{nl}}$$



# nonlocal van der Waals functionals

Functional	Reference	Exchange	Correlation
LDA	1 and 33	LDA	LDA
PBE	5	PBE	PBE
vdW-DF	19	revPBE	LDA+DRSLL
vdW-DF2	26	PW86R	LDA+LMKLL
C09 <sub>x</sub> -vdW	29	C09 <sub>x</sub>	LDA+DRSLL
optB88-vdW	30	optB88	LDA+DRSLL
RPBec2/3+nl	31	RPBE	$\frac{1}{3}$ LDA+ $\frac{2}{3}$ PBE+DRSLL
rVV10	34	PW86R	PBE+rVV10
PBE-D3	18	PBE	PBE+D3
revPBE-D3	18	revPBE	PBE+D3
B97D-D3	18	B97D	B97D+D3

# Input Structure: PBE+D3

```

&XC
&XC_FUNCTIONAL NO_SHORTCUT
  &PBE T
  &END PBE
&END XC_FUNCTIONAL
&VDW_POTENTIAL
  POTENTIAL_TYPE PAIR_POTENTIAL
  &PAIR_POTENTIAL
    TYPE DFTD3  $\longrightarrow$  specify DFT+D3
    PARAMETER_FILE_NAME ./dftd3.dat (can be found in $CP2K/cp2k/tests/QS)
    REFERENCE_FUNCTIONAL PBE
    #D3_SCALING 1.000 1.277 0.777  $\longrightarrow$  XC dependent scaling parameters
    CALCULATE_C9_TERM T  $\longrightarrow$  calculate the three-body term
    #R_CUTOFF 50.2  $\longrightarrow$  range of potential, check convergence
  &END PAIR_POTENTIAL
&END VDW_POTENTIAL
&END XC
  
```

(see <http://www.thch.uni-bonn.de/tc/downloads/DFT-D3/functionals.html> for a complete list of scaling parameters (zero-damping); see Supporting Information of J. Chem. Phys. 132, 154104 (2010) for scaling parameters relevant to calculations with BSSE)

# Input Structure: M06L+D3

&XC

&XC\_FUNCTIONAL NO\_SHORTCUT

&LIBXC T

FUNCTIONAL XC\_MGGA\_X\_M06\_L XC\_MGGA\_C\_M06\_L

&END LIBXC

&END XC\_FUNCTIONAL

&VDW\_POTENTIAL

POTENTIAL\_TYPE PAIR\_POTENTIAL

&PAIR\_POTENTIAL

TYPE DFTD3

PARAMETER\_FILE\_NAME ./dftd3.dat

REFERENCE\_FUNCTIONAL M06L

CALCULATE\_C9\_TERM T

&END PAIR\_POTENTIAL

&END VDW\_POTENTIAL

&END XC

# Input Structure: vdW-DF

&XC

&XC\_FUNCTIONAL NO\_SHORTCUT

&PBE T

PARAMETRIZATION REVPBE

SCALE\_C 0.000E+00

&END PBE

&VWN T

&END VWN

&END XC\_FUNCTIONAL

&VDW\_POTENTIAL

POTENTIAL\_TYPE NON\_LOCAL

&NON\_LOCAL

TYPE DRSLL → **type of nonlocal vdW correlation functional**

VERBOSE\_OUTPUT T

KERNEL\_FILE\_NAME **./vdW\_kernel\_table.dat** (can be found in \$CP2K/cp2k/tests/QS)

#CUTOFF 160 → **cutoff of FFT grid for vdW calculation, check convergence**

&END NON\_LOCAL

&END VDW\_POTENTIAL

&END XC

(see examples in \$CP2K/cp2k/tests/QS/regtest-dft-vdw-corr)

# Input Structure: vdW-DF2

```
&XC
```

```
  &XC_FUNCTIONAL NO_SHORTCUT
```

```
  &LIBXC T
```

```
    FUNCTIONAL XC_GGA_X_RPW86
```

```
  &END LIBXC
```

```
  &VWN T
```

```
  &END VWN
```

```
&END XC_FUNCTIONAL
```

```
&VDW_POTENTIAL
```

```
  POTENTIAL_TYPE NON_LOCAL
```

```
  &NON_LOCAL
```

```
    TYPE LMKLL
```

```
    VERBOSE_OUTPUT T
```

```
    KERNEL_FILE_NAME ./vdW_kernel_table.dat
```

```
    CUTOFF 160
```

```
  &END NON_LOCAL
```

```
&END VDW_POTENTIAL
```

```
&END XC
```

# Input Structure: c09x-vdW

```

&XC
  &XC_FUNCTIONAL
    &LIBXC
      FUNCTIONAL XC_GGA_X_C09X
    &END LIBXC
  &VWN
  &END VWN
&END XC_FUNCTIONAL
&VDW_POTENTIAL
  POTENTIAL_TYPE NON_LOCAL
  &NON_LOCAL
    TYPE DRSL
    VERBOSE_OUTPUT T
    KERNEL_FILE_NAME ./vdW_kernel_table.dat
    CUTOFF 160
  &END NON_LOCAL
&END VDW_POTENTIAL
&END XC

```

# Input Structure: rVV10

```

&XC
  &XC_FUNCTIONAL NO_SHORTCUT
  &LIBXC T
    FUNCTIONAL XC_GGA_X_RPW86 XC_GGA_C_PBE
  &END LIBXC
&END XC_FUNCTIONAL
&VDW_POTENTIAL
  POTENTIAL_TYPE NON_LOCAL
  &NON_LOCAL
    TYPE RVV10
    VERBOSE_OUTPUT T
    KERNEL_FILE_NAME ./rVV10_kernel_table.dat
    CUTOFF 160
    PARAMETERS 6.2999999999999998E+00 9.2999999999999992E-03
  &END NON_LOCAL
&END VDW_POTENTIAL
&END XC

```

# Input Structure: optPBE

```

&XC
  &XC_FUNCTIONAL NO_SHORTCUT
  &LIBXC T
    FUNCTIONAL XC_GGA_X_OPTPBE_VDW
  &END LIBXC
  &VWN T
  &END VWN
&END XC_FUNCTIONAL
&VDW_POTENTIAL
  POTENTIAL_TYPE NON_LOCAL
  &NON_LOCAL
    TYPE DRSL
    VERBOSE_OUTPUT T
    KERNEL_FILE_NAME ./vdW_kernel_table.dat
    CUTOFF 160
  &END NON_LOCAL
&END VDW_POTENTIAL
&END XC

```



# Input Structure: optB88

```
&XC
```

```
  &XC_FUNCTIONAL NO_SHORTCUT
```

```
  &LIBXC T
```

```
    FUNCTIONAL XC_GGA_X_OPTB88_VDW
```

```
  &END LIBXC
```

```
  &VWN T
```

```
  &END VWN
```

```
&END XC_FUNCTIONAL
```

```
&VDW_POTENTIAL
```

```
  POTENTIAL_TYPE NON_LOCAL
```

```
  &NON_LOCAL
```

```
    TYPE DRSL
```

```
    VERBOSE_OUTPUT T
```

```
    KERNEL_FILE_NAME ./vdW_kernel_table.dat
```

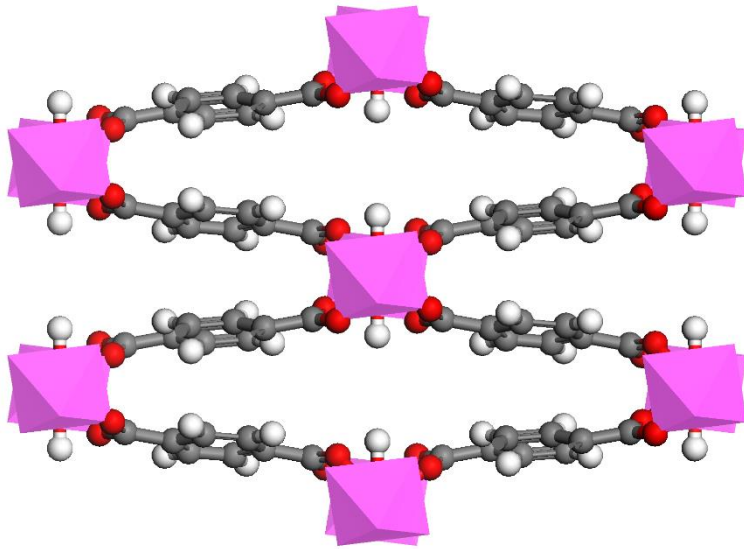
```
    CUTOFF 160
```

```
  &END NON_LOCAL
```

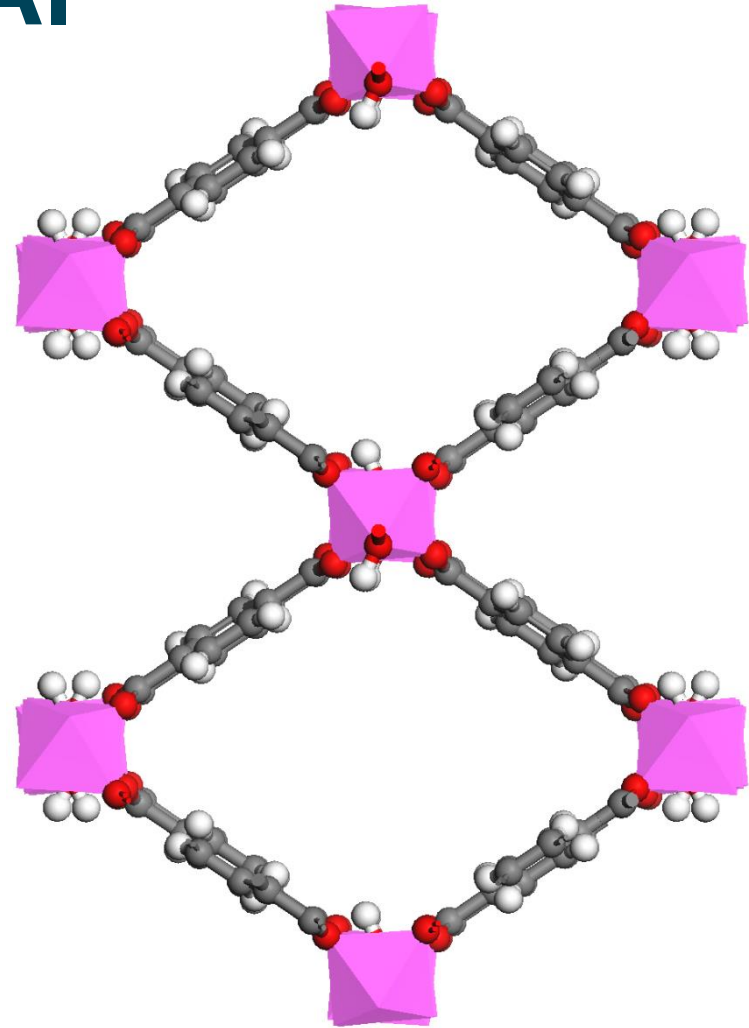
```
&END VDW_POTENTIAL
```

```
&END XC
```

# Example: MIL-53-Al



narrow pore  
(low temperature)



large pore  
(high temperature)

# Example: MIL-53-AI

Method	Volume (Å <sup>3</sup> ) / LT	Volume (Å <sup>3</sup> ) / HT	ΔE (kcal/mol/AI centre) / E(LT)-E(HT) <sup>a</sup>
PBE	-	1488.867	-
PBE+D3	837.158	1398.908	-2.07
PBE+D3+C9	866.867	1438.995	-0.56
PBEsol+D3	790.132	1384.009	-2.54
vdW-DF	841.140	1403.985	-2.50
optPBE	789.082	1386.546	-4.97
optB88	763.734	1377.982	-6.03
c09x-vdW	745.767	1374.714	-6.86
vdW-DF2	822.296	1426.049	-1.63
vdW-DF-cx	771.156	1381.084	-4.37
rVV10	799.396	1409.608	-3.81
HSE06+D3+C9	850.307	1399.016	-0.39
<b>Expt<sup>b</sup></b>	<b>863.9</b>	<b>1419</b>	

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Pioneering research  
and skills

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