

# DFT with Hybrid Functionals

**Sanliang Ling**

University College London

4th CP2K Tutorial, 31st August – 4th September 2015, Zurich

# What are hybrid functionals?

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

## Hybrid functionals:

**mixing non-local Hartree-Fock exchange with local/semi-local DFT/GGA exchange**

# Why do we need hybrid DFT?

- 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 and band gaps of semiconductors and insulators

# Why do we need hybrid DFT?

	Mae (G2)	Mae (G2-1)	Max ae (G2)	Max ae (G2-1)
SVWN <sup>a</sup>	121.2	39.6	229	94
LSD(SVWN5)	83.7	36.4	216	84
PBE	17.1	8.6	52	26
BLYP <sup>a</sup>	7.1	4.7	28	15
VSXC <sup>b</sup>	2.7	2.5	12	8
B3LYP <sup>a</sup>	3.1	2.4	20	10
PBE1PBE/PBE0	4.8	3.5	24	10

**Mean absolute errors (Mae) for atomisation energies (kcal/mol)**

# Why do we need hybrid DFT?

Solid	LSDA	PBE	TPSS	HSE
ME <sup>a</sup>	-1.14	-1.13	-0.98	-0.17
MAE <sup>b</sup>	1.14	1.13	0.98	0.26
rms <sup>c</sup>	1.24	1.25	1.12	0.34
Max (+) <sup>d</sup>	...	...	...	0.32
Max (-) <sup>e</sup>	-2.30	-2.88	-2.66	-0.72

**Band gap error (eV) statistics for the SC/40 test set**

# Hybrid DFT Calculations with CP2K

- 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

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

# Hybrid DFT Calculations with CP2K

- Hartree-Fock exchange energy

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

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

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



**Four-centre two-electron integrals (ERIs):  $O(N^4)$  scaling**

# Hybrid DFT Calculations with CP2K

- Permutational symmetry of the ERIs

$$\begin{aligned}(\mu\nu|\lambda\sigma)_g &= (\nu\mu|\lambda\sigma)_g = (\nu\mu|\sigma\lambda)_g = (\mu\nu|\sigma\lambda)_g \\ &= (\lambda\sigma|\mu\nu)_g = (\lambda\sigma|\nu\mu)_g = (\sigma\lambda|\nu\mu)_g \\ &= (\sigma\lambda|\mu\nu)_g.\end{aligned}$$

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



# Hybrid DFT Calculations with CP2K

- Integral screening: Schwarz inequality

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

**upper bound for ERIs**

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

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

(see EPS\_SCHWARZ keyword in &SCREENING subsection)

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

# Hybrid DFT Calculations with CP2K

- Density matrix screening

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

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

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

(see SCREEN\_ON\_INITIAL\_P keyword in &SCREENING subsection)

# Interaction potential

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

- Standard Coulomb potential

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

(used in B3LYP, PBE0, etc)

(see POTENTIAL\_TYPE keyword in &INTERACTION\_POTENTIAL subsection)

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

# Interaction potential

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

- Range-separated Coulomb potential

$$\frac{1}{r} = \underbrace{\frac{\text{erfc}(\overset{\text{parameter}}{\omega}r)}{r}}_{\text{short-range}} + \underbrace{\frac{\text{erf}(\omega r)}{r}}_{\text{long-range}}$$

(used in HSE06, etc)

(see POTENTIAL\_TYPE keyword in &INTERACTION\_POTENTIAL subsection)

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

Heyd & Scuseria, J. Chem. Phys., 118, 8207 (2003)

# Interaction potential

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

- Truncated Coulomb potential

$$g_{\text{TC}}(r_{12}) = \begin{cases} \frac{1}{r_{12}}, & r_{12} \leq \overset{\text{parameter}}{\uparrow} R_c \\ 0, & r_{12} > R_c \end{cases}$$

(used in PBE0-TC-LRC, etc)

(see POTENTIAL\_TYPE keyword in &INTERACTION\_POTENTIAL subsection)

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

Spencer & Alavi, Phys. Rev. B, 77, 193110 (2008)

# Auxiliary Density Matrix Methods

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

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

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

$$E_x^{\text{HFX}}[P] = E_x^{\text{HFX}}[\hat{P}] + (E_x^{\text{HFX}}[P] - E_x^{\text{HFX}}[\hat{P}])$$

$$\approx E_x^{\text{HFX}}[\hat{P}] + (E_x^{\text{DFT}}[P] - E_x^{\text{DFT}}[\hat{P}])$$

**approximation**

**original  
density matrix**

**auxiliary  
density matrix**

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

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

# Auxiliary Density Matrix Methods

- The total energy with ADMM

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

- Kohn-Sham Matrix with ADMM

$$K_{\text{total}} = \frac{dE[P]}{dP} + \frac{d\tilde{E}[\tilde{P}]}{dP} = K + \frac{d\tilde{E}[\tilde{P}]}{dP}$$

- The Kohn-Sham equation

$$K_{\text{total}}C = SC\varepsilon$$

# Auxiliary Density Matrix Methods

- Construction of auxiliary density matrix

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

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

$$\min_{\hat{C}} = \sum_i \int (\psi_j(\mathbf{r}) - \hat{\psi}_j(\mathbf{r}))^2 d\mathbf{r}$$

(see ADMM\_PURIFICATION\_METHOD keyword in &AUXILIARY\_DENSITY\_MATRIX\_METHOD subsection)



# Auxiliary Density Matrix Methods

- Construction of auxiliary density matrix: enforcing orthonormality

$$\min_{\tilde{C}} \left[ \sum_j \int (\psi_j(\mathbf{r}) - \tilde{\psi}_j(\mathbf{r}))^2 d\mathbf{r} + \sum_{k,l} \Lambda_{kl} \left( \int \tilde{\psi}_k(\mathbf{r}) \tilde{\psi}_l(\mathbf{r}) d\mathbf{r} - \delta_{kl} \right) \right]$$

↓  
**Lagrangian multipliers**

(see ADMM\_PURIFICATION\_METHOD keyword in &AUXILIARY\_DENSITY\_MATRIX\_METHOD subsection)

# Auxiliary Density Matrix Methods

- Construction of auxiliary density matrix:  
constraint on total charge

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

(see EXCH\_SCALING\_MODEL keyword in &AUXILIARY\_DENSITY\_MATRIX\_METHOD subsection)

# Auxiliary Density Matrix Methods

- GGA exchange corrections using different functions

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

**DFT = B88, PBE, OPTX, KT3X**

(see EXCH\_CORRECTION\_FUNC keyword in &AUXILIARY\_DENSITY\_MATRIX\_METHOD subsection)

# ADMM basis sets

<http://chemistry.about.com>  
 ©2012 Todd Helmenstine  
 About Chemistry

1A		2A												3A 4A 5A 6A 7A					8A			
1 <b>H</b> 1s <sup>1</sup>																					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> 2p <sup>1</sup>	6 <b>C</b> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup>	7 <b>N</b> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>3</sup>	8 <b>O</b> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>4</sup>	9 <b>F</b> 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup>	10 <b>Ne</b> 1s <sup>2</sup> 2s <sup>2</sup> 2p <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> 2p <sup>1</sup>	14 <b>Si</b> [Ne]3s <sup>2</sup> 2p <sup>2</sup>	15 <b>P</b> [Ne]3s <sup>2</sup> 2p <sup>3</sup>	16 <b>S</b> [Ne]3s <sup>2</sup> 2p <sup>4</sup>	17 <b>Cl</b> [Ne]3s <sup>2</sup> 2p <sup>5</sup>	18 <b>Ar</b> [Ne]3s <sup>2</sup> 2p <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> 2p <sup>1</sup>	32 <b>Ge</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup> 2p <sup>2</sup>	33 <b>As</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup> 2p <sup>3</sup>	34 <b>Se</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup> 2p <sup>4</sup>	35 <b>Br</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup> 2p <sup>5</sup>	36 <b>Kr</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup> 2p <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> 2p <sup>1</sup>	50 <b>Sn</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup> 2p <sup>2</sup>	51 <b>Sb</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup> 2p <sup>3</sup>	52 <b>Te</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup> 2p <sup>4</sup>	53 <b>I</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup> 2p <sup>5</sup>	54 <b>Xe</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup> 2p <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> 2p <sup>1</sup>	82 <b>Pb</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 2p <sup>2</sup>	83 <b>Bi</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 2p <sup>3</sup>	84 <b>Po</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 2p <sup>4</sup>	85 <b>At</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 2p <sup>5</sup>	86 <b>Rn</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 2p <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> 2p <sup>1</sup>	114 <b>F1</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> 2p <sup>2</sup>	115 <b>Uup</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> 2p <sup>3</sup>	116 <b>Lv</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> 2p <sup>4</sup>	117 <b>Uus</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> 2p <sup>5</sup>	118 <b>Uuo</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> 2p <sup>6</sup>					

(see \$CP2K/cp2k/data/BASIS\_ADMM)

# ADMM basis sets

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)

# Basis optimisation 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

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

# ADMM basis sets

<http://chemistry.about.com>  
 ©2012 Todd Helmenstine  
 About Chemistry

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

(see \$CP2K/cp2k/data/**BASIS\_ADMM\_MOLOPT**)

# ADMM basis sets

## Uncontracted basis sets

- FIT10:  $4s + 3p + 3d$
- FIT11:  $4s + 3p + 3d + 1f$  → recommended for solids
- FIT12:  $4s + 3p + 4d + 1f$
- FIT13:  $4s + 4p + 4d + 1f$

## Contracted basis sets (double- $\zeta$ 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.



# 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 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

# Work Flow

**1. Convergence test (primary basis, CUTOFF, supercell, etc)**



**2. GGA optimisation with selected primary basis**



**3. Name GGA wave function file for use with ADMM**



**4. Construct ADMM input with auxiliary basis (e.g. FIT3)**



**5. Run calculations and check convergence of ADMM basis**

# Input Structure: ADMM

&DFT

```

...
BASIS_SET_FILE_NAME ./BASIS_MOLOPT
BASIS_SET_FILE_NAME ./BASIS_ADMM
WFN_RESTART_FILE_NAME ${project}-RESTART.wfn
&SCF

```

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

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

&SUBSYS

&KIND Si

BASIS\_SET DZVP-MOLOPT-SR-GTH

AUX\_FIT\_BASIS\_SET **FIT3**

POTENTIAL GTH-PBE-q4

&END KIND

&END SUBSYS

(see examples in \$CP2K/cp2k/tests/QS/regtest-admm-1/2/3/4) 27

# Which functional to use?

- PBE0-TC-LRC

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

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

- HSE06

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

Scuseria et al., 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 2.0
      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 2.0
    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

(t\_c\_g.dat can be found in \$CP2K/cp2k/data)

```

&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

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

## A few more remarks ...

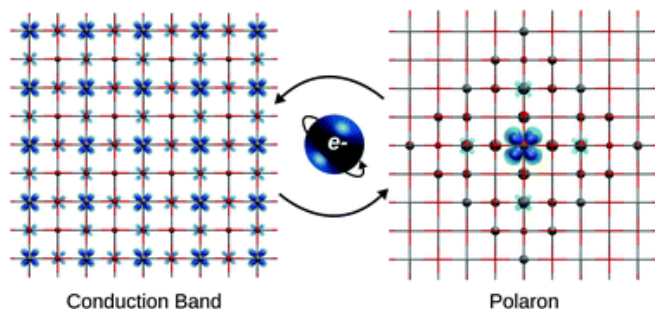
- **Libint library is used to calculate ERIs and their analytic derivatives, see `$CP2K/cp2k/INSTALL` for more details on installation and linking with CP2K**
- **Hybrid DFT calculations of large systems are memory demanding, try to increase `MAX_MEMORY` or run the job with more MPI processes**
- **For extremely large hybrid DFT calculations, try hybrid MPI/OpenMP binary (i.e. `cp2k.psmmp`)**

# Example: Diamond Band Gap

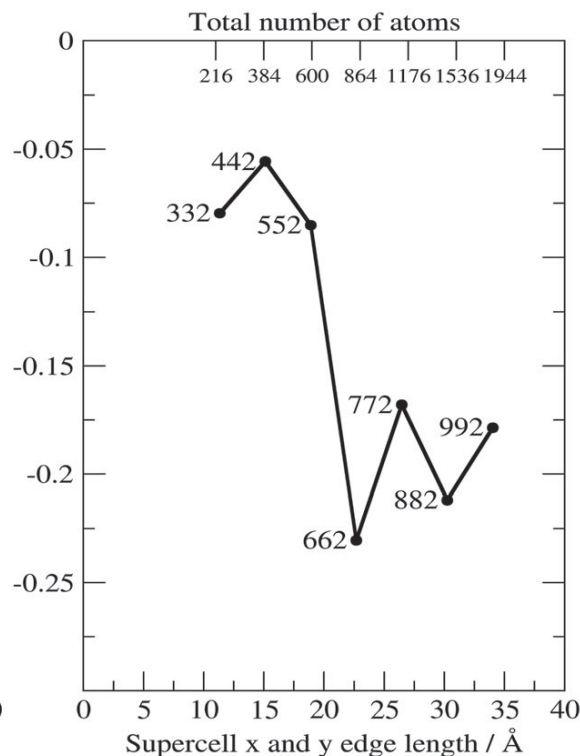
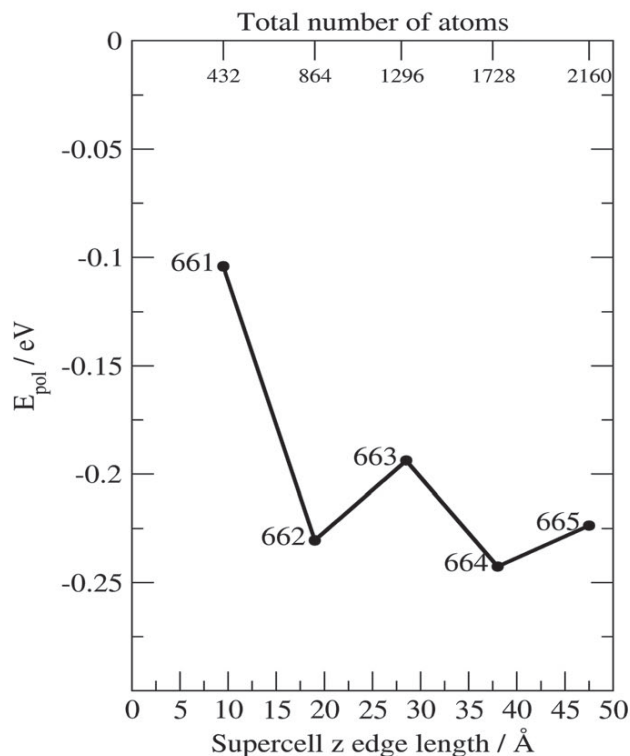
method	number of integrals	gap [eV]
PBE (PBS)		4.17
PBE (ABS)		4.37
PBE0 (PBS)	40 787 850 778 591	6.07
PBE0 (ABS)	23 561 509 497	6.25
PBE0 ADMM1	24 816 897 009	6.03
PBE0 ADMM2	24 795 460 638	6.02

**3x3x3 supercell**

# Example: excess electrons in $\text{TiO}_2$



$$E_{\text{pol}} = E_{\text{loc}(N+1)} - E_{\text{deloc}(N+1)}$$





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

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

Dudarev et al., Phys. Rev. B, 57, 1505 (1998)

## Input Structure: GGA+U

```
&DFT
```

```
...
```

```
PLUS_U_METHOD MULLIKEN ###LOWDIN
```

```
...
```

```
&END DFT
```

```
&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

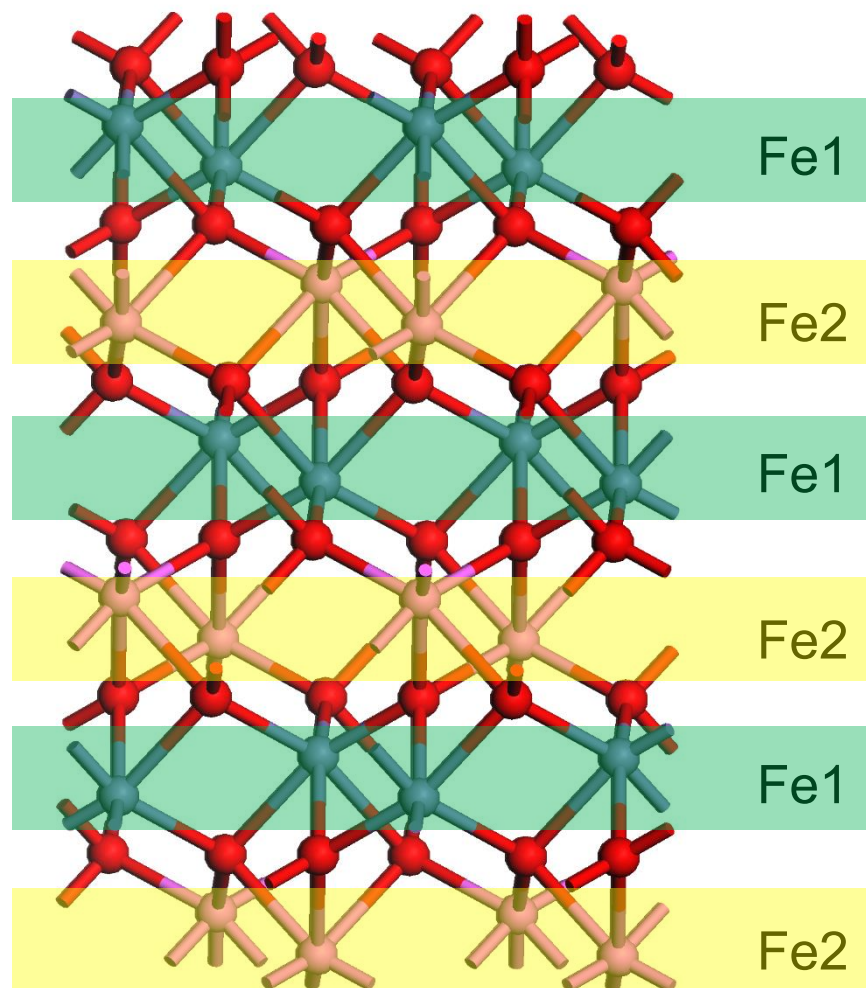
```
U_MINUS_J [eV] 3.9
```

→ specify effective on-site Coulomb interaction parameter

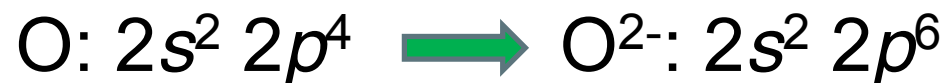
```
&END DFT_PLUS_U
```

```
&END KIND
```

# Magnetic systems



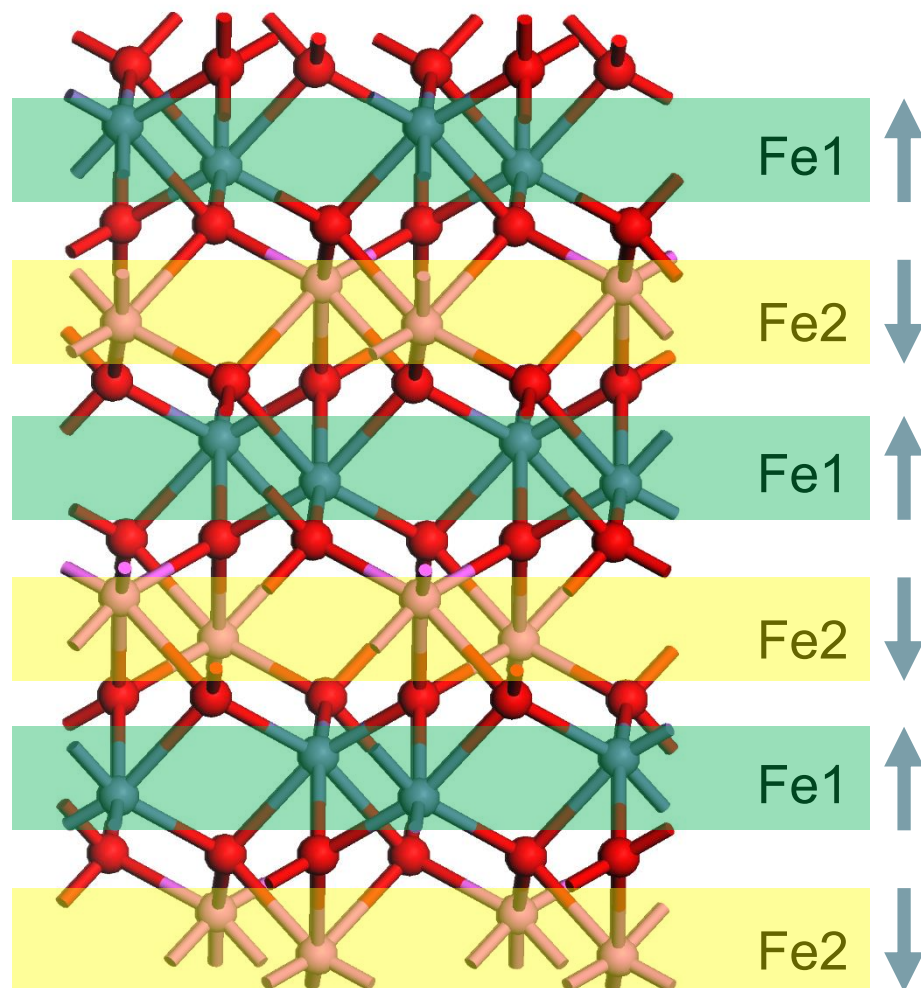
Hematite ( $\text{Fe}_2\text{O}_3$ ) – antiferromagnetic



```

&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
  
```

# Magnetic systems



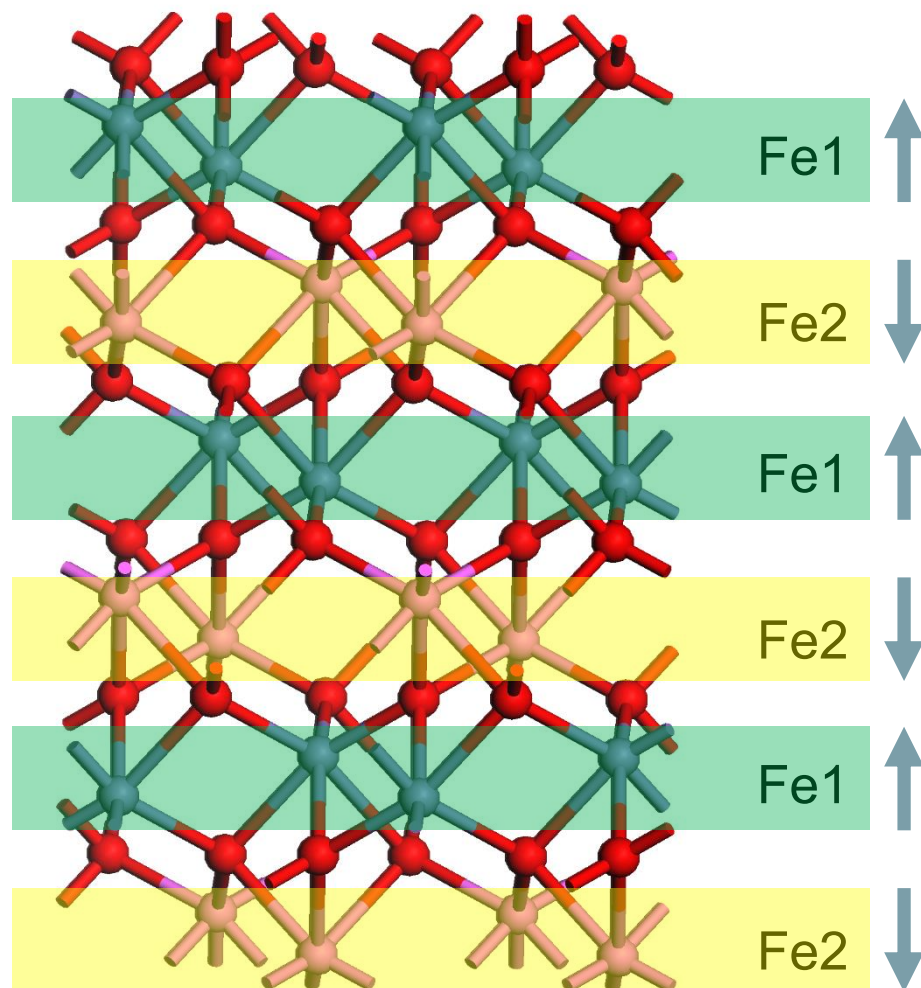
Hematite ( $\text{Fe}_2\text{O}_3$ ) – antiferromagnetic



```

&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
  
```

# 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
  
```

# 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 and geometry

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

derived from other codes directly

# Further Reading

**Hybrid Functionals (by Prof Joost VandeVondele)**

[http://www.cecam.org/upload/talk/presentation\\_5766.pdf](http://www.cecam.org/upload/talk/presentation_5766.pdf)

**Self-Interaction Energy and Dispersion (by Prof Juerg Hutter)**

[http://www.cecam.org/upload/talk/presentation\\_2988.pdf](http://www.cecam.org/upload/talk/presentation_2988.pdf)

**Exchange-Correlation Functionals (by Dr Manuel Guidon)**

[http://www.cecam.org/upload/talk/presentation\\_2987.pdf](http://www.cecam.org/upload/talk/presentation_2987.pdf)