

Fast and Reliable Hybrid DFT Calculations using ADMM

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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?

	Mae (G2)	Mae (G2-1)	Max ae (G2)	Max ae (G2-1)
SVWN ^a	121.2	39.6	229	94
LSD(SVWN5)	83.7	36.4	216	84
PBE	17.1	8.6	52	26
BLYP ^a	7.1	4.7	28	15
VSXC ^b	2.7	2.5	12	8
B3LYP ^a	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 ^a	-1.14	-1.13	-0.98	-0.17
MAE ^b	1.14	1.13	0.98	0.26
rms ^c	1.24	1.25	1.12	0.34
Max (+) ^d	0.32
Max (-) ^e	-2.30	-2.88	-2.66	-0.72

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

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

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

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

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)

Interaction potential

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

- 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 $\hat{P} \approx P$

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

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

- 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)

MOLOPT basis set format

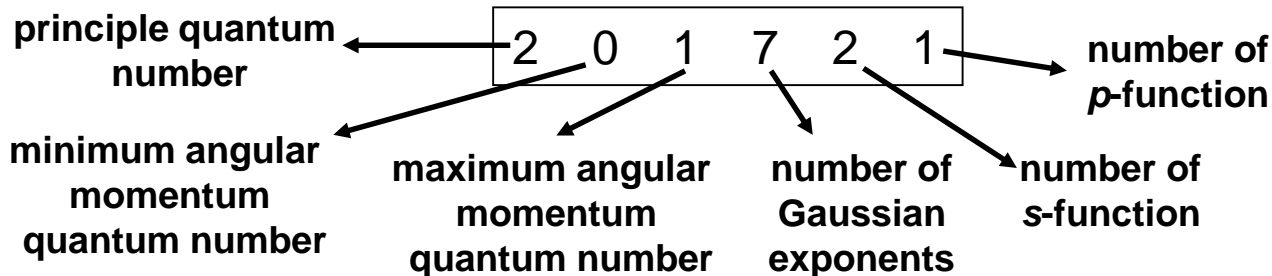
element basis set name number of valence electrons in pseudo

H	DZVP -MOLOPT-GTH DZVP -MOLOPT-GTH-q1		
1	number of CGTO	contraction coefficients	
2 0 1 7 2 1			
11.478000339908	0.0249162432	-0.0125124214	0.0245109182
3.700758562763	0.0798254900	-0.0564490711	0.0581407941
1.446884268432	0.1288626753	0.0112426847	0.4447094985
0.716814589696	0.3794488946	-0.4185875483	0.6462079731
0.247918564176	0.3245524326	0.5903632167	0.8033850182
0.066918004004	0.0371481214	0.4387031330	0.8929712087
0.021708243634	-0.0011251955	-0.0596931713	0.1201013165

Gaussian exponents

s-function

p-function



ADMM basis set format

uncontracted

H <i>aug-pFIT3 (1s¹)</i>	
5	
1 0 0 1 1	
0.11329 1.0	
1 0 0 1 1	
0.55125 1.0	
1 0 0 1 1	
3.58503 1.0	
1 1 1 1 1	
1.00000 1.0	
1 0 0 1 1	
0.03776 1.0	

3 × s

1 × p

1 × s (*aug-*)

uncontracted

Ti <i>FIT11 (3s² 3p⁶ 3d² 4s²)</i>		
11		
1 0 0 1 1		
0.10001738	1.000	
1 0 0 1 1		
1.22453356	1.000	
1 0 0 1 1		
0.51778507	1.000	
1 0 0 1 1		
4.22013330	1.000	
1 1 1 1 1		
0.53247041	1.000	
1 1 1 1 1		
1.57742596	1.000	
1 1 1 1 1		
11.78131390	1.000	
1 2 2 1 1		
0.24966492	1.000	
1 2 2 1 1		
1.01468694	1.000	
1 2 2 1 1		
4.19817352	1.000	
1 3 3 1 1		
0.32508090	1.000	

4 × s

3 × p

3 × d

1 × f

contracted

Ti <i>cFIT11 (3s² 3p⁶ 3d² 4s²)</i>			
7			
1 0 0 1 1			
0.10001738	1.00000000		
1 0 0 3 2			
0.51778507	0.66923159	0.10374122	
1.22453356	0.63752925	0.42847815	
4.22013330	0.38168794	-0.89757681	
1 1 1 1 1			
0.53247041	1.00000000		
1 1 1 2 1			
1.57742596	1.00000000		
11.78131390	-0.09732223		
1 2 2 1 1			
0.24966492	1.00000000		
1 2 2 2 1			
1.01468694	0.88730943		
4.19817352	0.46117452		
1 3 3 1 1			
0.32508090	1.00000000		

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)

ADMM basis sets

<http://chemistry.about.com>
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 About Chemistry

1A												3A					4A	5A	6A	7A	8A
1 H 1s ¹												5 B 1s ² 2s ² p ¹	6 C 1s ² 2s ² p ²	7 N 1s ² 2s ² p ³	8 O 1s ² 2s ² p ⁴	9 F 1s ² 2s ² p ⁵	10 Ne 1s ² 2s ² p ⁶				
3 Li 1s ² 2s ¹	4 Be 1s ² 2s ²											13 Al [Ne]3s ² p ¹	14 Si [Ne]3s ² p ²	15 P [Ne]3s ² p ³	16 S [Ne]3s ² p ⁴	17 Cl [Ne]3s ² p ⁵	18 Ar [Ne]3s ² p ⁶				
11 Na [Ne]3s ¹	12 Mg [Ne]3s ²	3B	4B	5B	6B	7B	8B		1B	2B											
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 p ¹	32 Ge [Ar]3d ¹⁰ 4s ² p ²	33 As [Ar]3d ¹⁰ 4s ² p ³	34 Se [Ar]3d ¹⁰ 4s ² p ⁴	35 Br [Ar]3d ¹⁰ 4s ² p ⁵	36 Kr [Ar]3d ¹⁰ 4s ² p 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 p ¹	50 Sn [Kr]4d ¹⁰ 5s ² p ²	51 Sb [Kr]4d ¹⁰ 5s ² p ³	52 Te [Kr]4d ¹⁰ 5s ² p ⁴	53 I [Kr]4d ¹⁰ 5s ² p ⁵	54 Xe [Kr]4d ¹⁰ 5s ² p 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 p ¹	82 Pb [Xe]4f ¹⁴ 5d ¹⁰ 6s ² p ²	83 Bi [Xe]4f ¹⁴ 5d ¹⁰ 6s ² p ³	84 Po [Xe]4f ¹⁴ 5d ¹⁰ 6s ² p ⁴	85 At [Xe]4f ¹⁴ 5d ¹⁰ 6s ² p ⁵	86 Rn [Xe]4f ¹⁴ 5d ¹⁰ 6s ² p 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 ⁸ 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 p ¹	114 F1 [Rn]5f ¹⁴ 6d ¹⁰ 7s ² p ²	115 Uup [Rn]5f ¹⁴ 6d ¹⁰ 7s ² p ³	116 Lv [Rn]5f ¹⁴ 6d ¹⁰ 7s ² p ⁴	117 Uus [Rn]5f ¹⁴ 6d ¹⁰ 7s ² p ⁵	118 Uuo [Rn]5f ¹⁴ 6d ¹⁰ 7s ² p ⁶				

(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- ζ quality)

- cFIT10 / cFIT11 / cFIT12 / cFIT13

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

Common Warning/Error Message

“...The Kohn Sham matrix is not 100% occupied...”

Solutions:

- decrease EPS_PGF_ORB (e.g. to 1.0E-32)
- decrease EPS_SCHWARZ
- ignore it (if you know what you are doing)
- **see** https://www.cp2k.org/faq:hfx_eps_warning **and** <https://groups.google.com/d/msg/cp2k/GVnd7pmdOo4/vjHC3q2A4B0J>

Common Warning/Error Message

“... Periodic Hartree Fock calculation requested with use of a truncated or shortrange potential. The cutoff radius is larger than half the minimal cell dimension...”

Solutions:

- ignore it if you use HSE06
- decrease CUTOFF_RADIUS if you use PBE0-TC
- go to a larger simulation box
- **see** <https://groups.google.com/d/msg/cp2k/g1sFck3SYF8/jkseHHuCGQAJ>

Common Warning/Error Message

“OOM killer terminated this process”

Solutions:

- **increase MAX_MEMORY in &MEMORY**
- **increase the total number of processors**
- **use large memory nodes (“bigmem=true” option)**
- **use less number of cores per node (“-S” flag)**
- **use smaller ADMM basis sets**
- **decrease CUTOFF_RADIUS if you use PBE0-TC**
- **increase EPS_SCHWARZ**
- **use smaller supercell**

Use of ELPA Library

```

&GLOBAL
  PREFERRED_DIAG_LIBRARY ELPA
  ...
&END GLOBAL
  
```

- **Default is SL (Standard ScaLAPACK)**
- **Can be very useful for SCF calculations based on direct diagonalization (e.g. metallic systems)**

	Wall time (seconds)
Default (SL)	415.4
ELPA	202.3

(Ag surface slab, 96 atoms, 5 GEO_OPT steps, 8 nodes on ARCHER)

- **May be useful for SCF calculations based on &OT**

Primary and ADMM basis sets for Lanthanides

<http://chemistry.about.com>
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 About Chemistry

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

Lanthanides	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	[Xe]5d ¹ 6s ²	[Xe]4f ¹ 5d ¹ 6s ²	[Xe]4f ² 6s ²	[Xe]4f ³ 6s ²	[Xe]4f ⁴ 6s ²	[Xe]4f ⁵ 6s ²	[Xe]4f ⁶ 6s ²	[Xe]4f ⁷ 5d ¹ 6s ²	[Xe]4f ⁷ 6s ²	[Xe]4f ⁹ 6s ²	[Xe]4f ¹¹ 6s ²	[Xe]4f ¹² 6s ²	[Xe]4f ¹³ 6s ²	[Xe]4f ¹⁴ 6s ²	[Xe]4f ¹⁴ 5d ¹ 6s ²
Actinides	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
	[Rn]6d ¹ 7s ²	[Rn]6d ² 7s ²	[Rn]5f ² 6d ¹ 7s ²	[Rn]5f ² 6d ¹ 7s ²	[Rn]5f ³ 6d ¹ 7s ²	[Rn]5f ⁴ 7s ²	[Rn]5f ⁵ 7s ²	[Rn]5f ⁶ 6d ¹ 7s ²	[Rn]5f ⁷ 7s ²	[Rn]5f ⁹ 7s ²	[Rn]5f ¹¹ 7s ²	[Rn]5f ¹² 7s ²	[Rn]5f ¹³ 7s ²	[Rn]5f ¹⁴ 7s ²	[Rn]5f ¹⁴ 6d ¹ 7s ²

- Based on new GTH-PBE pseudopotentials produced by Dr Matthias Krack
- Primary and ADMM basis sets available upon request (E-mail: S.Ling@ucl.ac.uk)

Further Reading

Hybrid Functionals (by Prof Joost VandeVondele)

http://www.cecaml.org/upload/talk/presentation_5766.pdf

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

http://www.cecaml.org/upload/talk/presentation_2988.pdf

Exchange-Correlation Functionals (by Dr Manuel Guidon)

http://www.cecaml.org/upload/talk/presentation_2987.pdf

Hybrid Functionals in CP2K (by Sanliang Ling)

https://www.cp2k.org/_media/events:2015_cecaml_tutorial:ling_hybrids.pdf

Optimization of Pseudopotential and Basis Set (by Sanliang Ling)

https://www.cp2k.org/_media/events:2015_cecaml_tutorial:ling_basis_pseudo.pdf

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) 26

Which functional to use?

- **PBE0-TC-LRC**

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

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

- **HSE06**

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

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

“Empirical” parameters: \mathbf{a} , R_c , and ω

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)