



University of
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UK | CHINA | MALAYSIA

Hybrid Functionals and ADMM

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A quick survey:

What is your favourite DFT functional?

What others say?

Results for the 2014 edition of the Annual DFT Popularity Poll: Primera Divisió

	functional	like	neutral	hate	blanc	none	#votes	points average
1	PBE	99 61.5%	30 18.6%	6 3.7%	9 5.6%	17 10.6%	135 83.9%	321 1.99
2	PBE0	87 54.0%	23 14.3%	10 6.2%	11 6.8%	30 18.6%	120 74.5%	274 1.70
3	B3LYP	56 34.8%	44 27.3%	33 20.5%	7 4.3%	21 13.0%	133 82.6%	179 1.11
4	wB97X-D	49 30.4%	21 13.0%	12 7.5%	45 28.0%	34 21.1%	82 50.9%	156 0.97
5	PW91	38 23.6%	47 29.2%	13 8.1%	32 19.9%	31 19.3%	98 60.9%	148 0.92
6	B3LYP-D	41 25.5%	38 23.6%	14 8.7%	34 21.1%	34 21.1%	93 57.8%	147 0.91
7	LDA	50 31.1%	33 20.5%	37 23.0%	19 11.8%	22 13.7%	120 74.5%	146 0.91
8	M06-2X	46 28.6%	27 16.8%	31 19.2%	26 16.1%	31 19.2%	104 64.6%	134 0.83
9	CAM-B3LYP	39 24.2%	29 18.0%	14 8.7%	42 26.1%	37 23.0%	82 50.9%	132 0.82
10	BP86	35 21.7%	33 20.5%	16 9.9%	41 25.5%	36 22.4%	84 52.2%	122 0.76
11	HSE	29 18.0%	47 29.2%	12 7.5%	43 26.7%	30 18.6%	88 54.7%	122 0.76
12	B97-D	26 16.1%	39 24.2%	13 8.1%	43 26.7%	40 24.8%	78 48.4%	104 0.65
13	B2PLYP	24 14.9%	33 20.5%	18 11.2%	45 28.0%	41 25.5%	75 46.6%	87 0.54
14	RPA	22 13.7%	33 20.5%	12 7.5%	54 33.5%	40 24.8%	67 41.6%	87 0.54
15	B3PW91	21 13.0%	40 24.8%	19 11.8%	42 26.1%	39 24.2%	80 49.7%	84 0.52
16	revPBE	19 11.8%	42 26.1%	17 10.6%	42 26.1%	41 25.5%	78 48.4%	82 0.51
17	RPBE	18 11.2%	34 21.1%	18 11.2%	54 33.5%	37 23.0%	70 43.5%	70 0.43
18	LC-wPBE	15 9.3%	37 23.0%	13 8.1%	54 33.5%	42 26.1%	65 40.4%	69 0.43
19	B3LYPstar	17 10.6%	30 18.6%	23 14.3%	52 32.3%	39 24.2%	70 43.5%	58 0.36
20	BHandH	9 5.6%	33 20.5%	23 14.3%	56 34.8%	40 24.8%	65 40.4%	37 0.23

total number of participants: 161

Year: 2014



What others say?

Results for the 2015 edition of the Annual DFT Popularity Poll: Primera Divisió

	functional	like	neutral	hate	blanc	none	#votes	points average
1	PBE	36 47.4%	18 23.7%	3 3.9%	5 6.6%	14 18.4%	62 81.6%	123 1.62
2	PBE0	34 44.7%	19 25.0%	2 2.6%	4 5.3%	17 22.4%	59 77.6%	119 1.57
3	B3LYP	23 30.3%	21 27.6%	15 19.7%	3 3.9%	14 18.4%	62 81.6%	75 0.99
4	wB97X-D	22 28.9%	11 14.5%	4 5.3%	20 26.3%	19 25.0%	57 75.0%	73 0.96
5	B3LYP-D	17 22.4%	23 30.3%	7 9.2%	11 14.5%	18 23.7%	58 76.3%	67 0.88
6	LDA	20 26.3%	14 18.4%	13 17.1%	12 15.8%	17 22.4%	59 77.6%	61 0.80
7	PW91	14 18.4%	22 28.9%	5 6.6%	13 17.1%	22 28.9%	54 71.1%	59 0.78
8	B97-D	16 21.1%	16 21.1%	7 9.2%	17 22.4%	20 26.3%	56 73.7%	57 0.75
9	M06-2X	20 26.3%	10 13.2%	13 17.1%	14 18.4%	19 25.0%	57 75.0%	57 0.75
10	B2PLYP	16 21.1%	14 18.4%	6 7.9%	19 25.0%	21 27.6%	55 72.4%	56 0.74
11	CAM-B3LYP	12 15.8%	19 25.0%	5 6.6%	19 25.0%	21 27.6%	55 72.4%	50 0.66
12	HSE	12 15.8%	17 22.4%	3 3.9%	20 26.3%	24 31.6%	52 68.4%	50 0.66
13	BP86	14 18.4%	14 18.4%	9 11.8%	16 21.1%	23 30.3%	53 69.7%	47 0.62
14	M06	11 14.5%	19 25.0%	12 15.8%	15 19.7%	19 25.0%	57 75.0%	40 0.53
15	B3PW91	10 13.2%	17 22.4%	8 10.5%	16 21.1%	25 32.9%	51 67.1%	39 0.51
16	revTPSS	6 7.9%	21 27.6%	4 5.3%	22 28.9%	23 30.3%	53 69.7%	35 0.46
17	RPA	8 10.5%	13 17.1%	5 6.6%	25 32.9%	25 32.9%	51 67.1%	32 0.42
18	TPSSh	6 7.9%	18 23.7%	5 6.6%	22 28.9%	25 32.9%	51 67.1%	31 0.41
19	M06-L	7 9.2%	15 19.7%	12 15.8%	18 23.7%	24 31.6%	52 68.4%	24 0.32
20	BLYP	6 7.9%	18 23.7%	17 22.4%	14 18.4%	21 27.6%	55 72.4%	19 0.25

total number of participants: 76

Year: 2015



What others say?

Results for the 2016 edition of the Annual DFT Popularity Poll: Primera Divisi6

	functional	like	neutral	hate	blanc	none	#votes	points average
1	PBE	49 49.5%	23 23.2%	7 7.1%	6 6.1%	14 14.1%	85 85.9%	163 1.65
2	PBE0	43 43.4%	19 19.2%	9 9.1%	4 4.0%	24 24.2%	75 75.8%	139 1.40
3	B3LYP	33 33.3%	24 24.2%	20 20.2%	2 2.0%	20 20.2%	79 79.8%	103 1.04
4	wB97X-D	30 30.3%	19 19.2%	7 7.1%	17 17.2%	26 26.3%	73 73.7%	102 1.03
5	B3LYP-D	23 23.2%	26 26.3%	14 14.1%	11 11.1%	25 25.3%	74 74.7%	81 0.82
6	CAM-B3LYP	22 22.2%	24 24.2%	12 12.1%	14 14.1%	27 27.3%	72 72.7%	78 0.79
7	BP86	20 20.2%	23 23.2%	10 10.1%	16 16.2%	30 30.3%	69 69.7%	73 0.74
8	LDA	21 21.2%	27 27.3%	21 21.2%	13 13.1%	17 17.2%	82 82.8%	69 0.70
9	M06-2X	24 24.2%	16 16.2%	22 22.2%	12 12.1%	25 25.3%	74 74.7%	66 0.67
10	B97-D	15 15.2%	27 27.3%	8 8.1%	19 19.2%	30 30.3%	69 69.7%	64 0.65
11	PW91	12 12.1%	33 33.3%	11 11.1%	15 15.2%	28 28.3%	71 71.7%	58 0.59
12	HSE	10 10.1%	33 33.3%	9 9.1%	19 19.2%	28 28.3%	71 71.7%	54 0.55
13	B2PLYP	12 12.1%	27 27.3%	10 10.1%	21 21.2%	29 29.3%	70 70.7%	53 0.54
14	revPBE	11 11.1%	27 27.3%	9 9.1%	21 21.2%	31 31.3%	68 68.7%	51 0.52
15	LC-wPBE	10 10.1%	25 25.3%	7 7.1%	25 25.3%	32 32.3%	67 67.7%	48 0.48
16	M06	18 18.2%	17 17.2%	25 25.3%	15 15.2%	24 24.2%	75 75.8%	46 0.46
17	PWPB95-D3	6 6.1%	32 32.3%	8 8.1%	21 21.2%	32 32.3%	67 67.7%	42 0.42
18	RPBE	7 7.1%	30 30.3%	9 9.1%	25 25.3%	28 28.3%	71 71.7%	42 0.42
19	B3PW91	4 4.0%	32 32.3%	13 13.1%	20 20.2%	30 30.3%	69 69.7%	31 0.31
20	optB88-vdW	3 3.0%	24 24.2%	10 10.1%	30 30.3%	32 32.3%	67 67.7%	23 0.23

total number of participants: 99

Year: 2016



What others say?

Results for the 2017 edition of the Annual DFT Popularity Poll: Primera Divisió

	functional	like	neutral	hate	blanc	none	#votes	points average
1	PBE0	31 48.4 %	8 12.5 %	7 10.9 %	0 0.0 %	18 28.1 %	46 71.9 %	94 1.47
2	PBE	29 45.3 %	11 17.2 %	8 12.5 %	0 0.0 %	16 25.0 %	48 75.0 %	90 1.41
3	wB97X-D	26 40.6 %	10 15.6 %	3 4.7 %	7 10.9 %	18 28.1 %	46 71.9 %	85 1.33
4	B3LYP-D	22 34.4 %	12 18.8 %	5 7.8 %	5 7.8 %	20 31.2 %	44 68.8 %	73 1.14
5	CAM-B3LYP	19 29.7 %	15 23.4 %	5 7.8 %	5 7.8 %	20 31.2 %	44 68.8 %	67 1.05
6	B97-D	18 28.1 %	14 21.9 %	2 3.1 %	7 10.9 %	23 35.9 %	41 64.1 %	66 1.03
7	B3LYP	21 32.8 %	16 25.0 %	14 21.9 %	1 1.6 %	12 18.8 %	52 81.2 %	65 1.02
8	TPSSh	13 20.3 %	14 21.9 %	7 10.9 %	6 9.4 %	24 37.5 %	40 62.5 %	46 0.72
9	BP86	13 20.3 %	12 18.8 %	9 14.1 %	6 9.4 %	24 37.5 %	40 62.5 %	42 0.66
10	B2PLYP	12 18.8 %	13 20.3 %	8 12.5 %	9 14.1 %	22 34.4 %	42 65.6 %	41 0.64
11	PW91	7 10.9 %	20 31.2 %	6 9.4 %	7 10.9 %	24 37.5 %	40 62.5 %	35 0.55
12	HSE	8 12.5 %	16 25.0 %	6 9.4 %	12 18.8 %	22 34.4 %	42 65.6 %	34 0.53
13	LC-wPBE	8 12.5 %	15 23.4 %	6 9.4 %	11 17.2 %	24 37.5 %	40 62.5 %	33 0.52
14	M06-2X	12 18.8 %	14 21.9 %	20 31.2 %	3 4.7 %	15 23.4 %	49 76.6 %	30 0.47
15	revPBE	7 10.9 %	14 21.9 %	5 7.8 %	11 17.2 %	27 42.2 %	37 57.8 %	30 0.47
16	BLYP	5 7.8 %	20 31.2 %	10 15.6 %	5 7.8 %	24 37.5 %	40 62.5 %	25 0.39
17	RPA	6 9.4 %	12 18.8 %	5 7.8 %	15 23.4 %	26 40.6 %	38 59.4 %	25 0.39
18	OLYP	4 6.2 %	14 21.9 %	7 10.9 %	13 20.3 %	26 40.6 %	38 59.4 %	19 0.30
19	LDA	4 6.2 %	17 26.6 %	14 21.9 %	7 10.9 %	22 34.4 %	42 65.6 %	15 0.23
20	BHandH	2 3.1 %	16 25.0 %	10 15.6 %	12 18.8 %	24 37.5 %	40 62.5 %	12 0.19

total number of participants: 64

Year: 2017

What others say?

Results for the 2017 edition of the Annual DFT Popularity Poll: 1. Reaction barriers

	functional	love (++)		like (+)		neutral (0)		dislike (-)		hate (--)		#votes	points average		
1	wB97X-D	5	7.8%	9	14.1%	3	4.7%	0	0.0%	1	1.6%	18	28.1%	21	0.33
2	M06-2X	5	7.8%	4	6.2%	0	0.0%	1	1.6%	2	3.1%	12	18.8%	12	0.19
3	B3LYP-D	4	6.2%	3	4.7%	1	1.6%	1	1.6%	1	1.6%	10	15.6%	11	0.17
4	PBE0	3	4.7%	3	4.7%	0	0.0%	0	0.0%	1	1.6%	7	10.9%	9	0.14
5	B3LYP	4	6.2%	4	6.2%	2	3.1%	3	4.7%	2	3.1%	15	23.4%	7	0.11
6	PBE-D	2	3.1%	0	0.0%	0	0.0%	1	1.6%	0	0.0%	3	4.7%	5	0.08
7	wB97M-V	2	3.1%	1	1.6%	1	1.6%	0	0.0%	1	1.6%	5	7.8%	4	0.06
8	B3PW91	2	3.1%	1	1.6%	0	0.0%	1	1.6%	1	1.6%	5	7.8%	3	0.05
9	SCAN	2	3.1%	0	0.0%	1	1.6%	0	0.0%	1	1.6%	4	6.2%	3	0.05
10	DSD-PBEP86	2	3.1%	0	0.0%	0	0.0%	0	0.0%	2	3.1%	4	6.2%	0	0.00
11	PWPB95-D3	1	1.6%	1	1.6%	0	0.0%	1	1.6%	1	1.6%	4	6.2%	0	0.00
12	wB97X-V	1	1.6%	0	0.0%	0	0.0%	0	0.0%	1	1.6%	2	3.1%	0	0.00
13	B97M-V	1	1.6%	0	0.0%	1	1.6%	0	0.0%	1	1.6%	3	4.7%	0	0.00
14	PW6B95	1	1.6%	0	0.0%	0	0.0%	1	1.6%	1	1.6%	3	4.7%	-1	-0.02
15	CAM-B3LYP	0	0.0%	2	3.1%	0	0.0%	1	1.6%	1	1.6%	4	6.2%	-2	-0.03
16	M06	2	3.1%	1	1.6%	0	0.0%	0	0.0%	3	4.7%	6	9.4%	-2	-0.03
17	OLYP	0	0.0%	1	1.6%	1	1.6%	0	0.0%	1	1.6%	3	4.7%	-2	-0.03
18	revTPSS	0	0.0%	1	1.6%	0	0.0%	0	0.0%	1	1.6%	2	3.1%	-2	-0.03
19	S12g	0	0.0%	1	1.6%	0	0.0%	0	0.0%	1	1.6%	2	3.1%	-2	-0.03
20	S12h	0	0.0%	1	1.6%	0	0.0%	0	0.0%	1	1.6%	2	3.1%	-2	-0.03
21	SSB-D	0	0.0%	1	1.6%	0	0.0%	0	0.0%	1	1.6%	2	3.1%	-2	-0.03
22	BP86	1	1.6%	0	0.0%	1	1.6%	0	0.0%	2	3.1%	4	6.2%	-3	-0.05
23	LC-wPBE	0	0.0%	0	0.0%	2	3.1%	0	0.0%	1	1.6%	3	4.7%	-3	-0.05
24	PBE	1	1.6%	4	6.2%	1	1.6%	1	1.6%	3	4.7%	10	15.6%	-3	-0.05
25	revTPSS-D	1	1.6%	0	0.0%	0	0.0%	0	0.0%	2	3.1%	3	4.7%	-3	-0.05

Property:
reaction barriers



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 ^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

- 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

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

- Hartree-Fock exchange energy

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

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

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



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

- Permutational symmetry of the ERIs

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

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

trick	number of integrals	memory [MB]
none	365'216'351'984	2'786'380
symmetry	45'652'043'998	345'297



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

(see EPS_SCHWARZ keyword in &SCREENING subsection)

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

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

trick	number of integrals	memory [MB]
none	365'216'351'984	2'786'380
symmetry	45'652'043'998	345'297
$\epsilon = 10^{-16}$	10'236'358'844	78'097
$\epsilon = 10^{-12}$	6'499'520'364	49'587
$\epsilon = 10^{-6}$	1'300'799'772	9'924

- Density matrix screening

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

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

$$\mathbf{O(N^2)} \longrightarrow \mathbf{O(N)}$$

(see SCREEN_ON_INITIAL_P keyword in &SCREENING subsection)

trick	number of integrals	memory [MB]
none	365'216'351'984	2'786'380
symmetry	45'652'043'998	345'297
$\epsilon = 10^{-6}$	1'300'799'772	9'924
P - screening	532'091'877	4'060



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)



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

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

short-range long-range

(used in HSE06, etc)

(see POTENTIAL_TYPE keyword in &INTERACTION_POTENTIAL subsection)



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

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

parameter ↑

(used in PBE0-TC-LRC, etc)

(see POTENTIAL_TYPE keyword in &INTERACTION_POTENTIAL subsection)



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 $\hat{P} \approx P$

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

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

original
density matrix

auxiliary
density matrix

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

$$\hat{P}^{uv} = \sum_i \hat{C}^{ui} \hat{C}^{vi} \Leftrightarrow \hat{C}\hat{C}^T$$



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

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

- Construction of auxiliary density matrix

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

$$\hat{P}^{uv} = \sum_i \hat{C}^{ui} \hat{C}^{vi} \Leftrightarrow \hat{C} \hat{C}^T$$

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

(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)

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

(see \$CP2K/cp2k/data/BASIS_ADMM)



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
	3.700758562763	0.0798254900	-0.0564490711
	1.446884268432	0.1288626753	0.0112426847
	0.716814589696	0.3794488946	-0.4185875483
	0.247918564176	0.3245524326	0.5903632167
	0.066918004004	0.0371481214	0.4387031330
	0.021708243634	-0.0011251955	-0.0596931713
			0.1201013165

Gaussian exponents

s-function

p-function

principle quantum number

minimum angular momentum quantum number

maximum angular momentum quantum number

number of Gaussian exponents

number of p-function

number of s-function

2 0 1 7 2 1



ADMM basis set format

uncontracted

H	aug-pFIT3	(1s ¹)		
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	FIT11	(3s ² 3p ⁶ 3d ² 4s ²)		
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	cFIT11	(3s ² 3p ⁶ 3d ² 4s ²)		
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			

(see \$CP2K/cp2k/data/[BASIS_ADMM_MOLOPT](#))



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

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1A												3A					4A	5A	6A	7A	8A
1 H 1s ¹												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				
3 Li 1s ² 2s ¹	4 Be 1s ² 2s 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				
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 3p ¹	32 Ge [Ar]3d ¹⁰ 4s ² 3p ²	33 As [Ar]3d ¹⁰ 4s ² 3p ³	34 Se [Ar]3d ¹⁰ 4s ² 3p ⁴	35 Br [Ar]3d ¹⁰ 4s ² 3p ⁵	36 Kr [Ar]3d ¹⁰ 4s ² 3p 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 3p ¹	50 Sn [Kr]4d ¹⁰ 5s ² 3p ²	51 Sb [Kr]4d ¹⁰ 5s ² 3p ³	52 Te [Kr]4d ¹⁰ 5s ² 3p ⁴	53 I [Kr]4d ¹⁰ 5s ² 3p ⁵	54 Xe [Kr]4d ¹⁰ 5s ² 3p 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 3p ¹	82 Pb [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 3p ²	83 Bi [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 3p ³	84 Po [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 3p ⁴	85 At [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 3p ⁵	86 Rn [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 3p 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 3p ¹	114 Fll [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 3p ²	115 Uup [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 3p ³	116 Lvv [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 3p ⁴	117 Uus [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 3p ⁵	118 Uuo [Rn]5f ¹⁴ 6d ¹⁰ 7s ² 3p 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 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)
- 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



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 (files can be found in $CP2K/cp2k/data)
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
&SUBSYS
    &KIND Si
        BASIS_SET DZVP-MOLOPT-SR-GTH
        BASIS_SET AUX_FIT FIT3 (note: the old AUX_FIT_BASIS_SET keyword is now deprecated)
        POTENTIAL GTH-PBE-q4
    &END KIND
&END SUBSYS
```

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



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

```
&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)

“...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>

“... 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>**

“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**



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: Bulk Silicon

Cutoff radius (Å)	Band gap (eV)	Integrals
2	1.16 ^a	77799946176
4	1.54 ^a	154325979000
6	1.71 ^a	265868148312
8	1.78 ^a	422457823080

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

Cutoff radius

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

ADMM basis	Band gap (eV)	Integrals
cFIT3	1.78 ^a	422457823080
FIT3	1.80 ^a	424426850352
pFIT3	1.98 ^a	1447428361680
Ref. (VASP)	1.93 ^b (indirect)	

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

Polarisation
function is
important for
covalent solids!

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



Further Reading

Hybrid Functionals (by Prof Joost VandeVondele)

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

Exchange-Correlation Functionals (by Dr Manuel Guidon)

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

PRACE Workshop talk on CP2K (by Dr Manuel Guidon)

http://www.training.prace-ri.eu/uploads/tx_pracetmo/manuelguidon.pdf

Hybrid functionals in CP2K (by myself)

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

Optimization of Pseudopotential and Basis Set (by myself)

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



University of
Nottingham

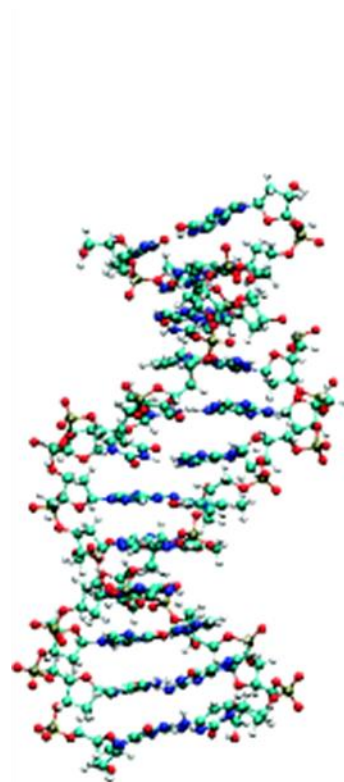
UK | CHINA | MALAYSIA

van der Waals corrected DFT

Sanliang Ling

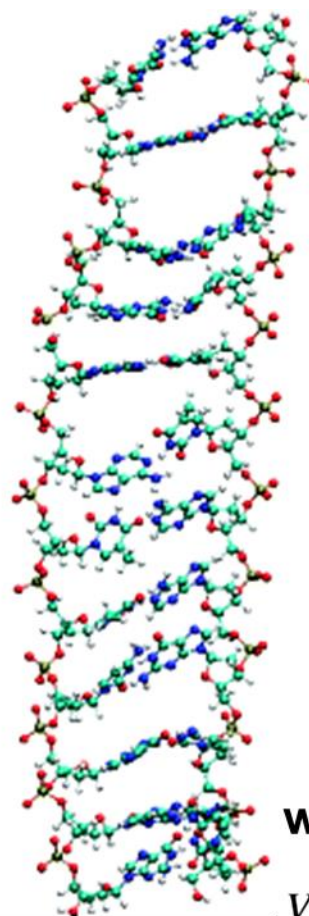


Why van der Waals force is important?



experimental crystal structure

Loss of
→
dispersion

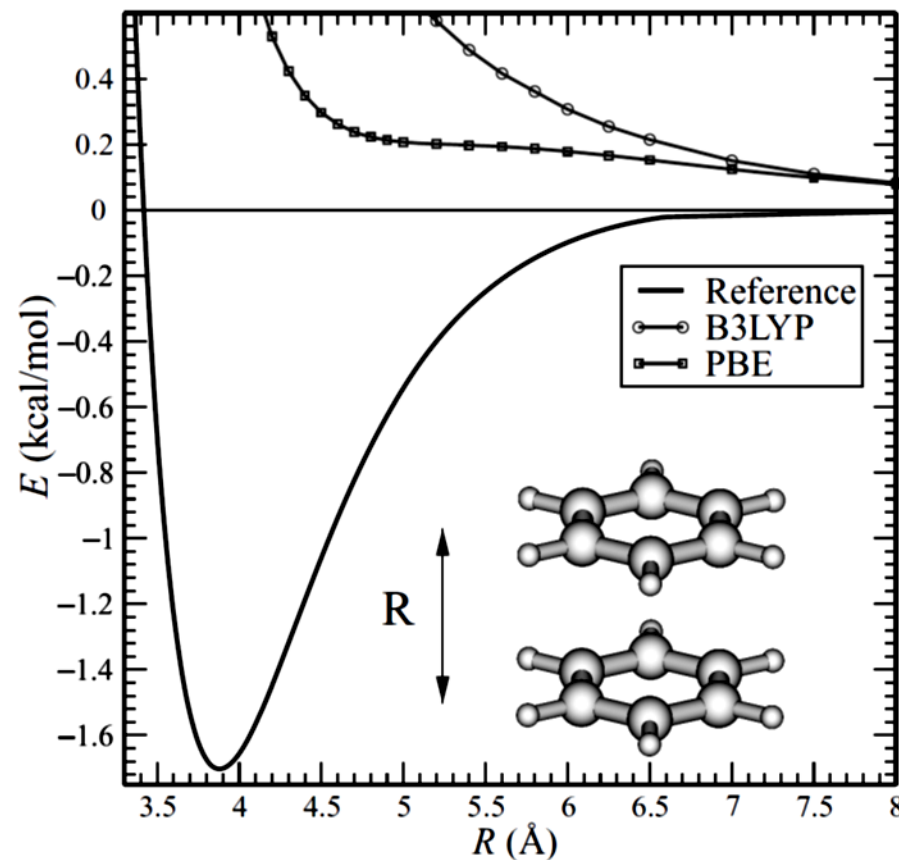
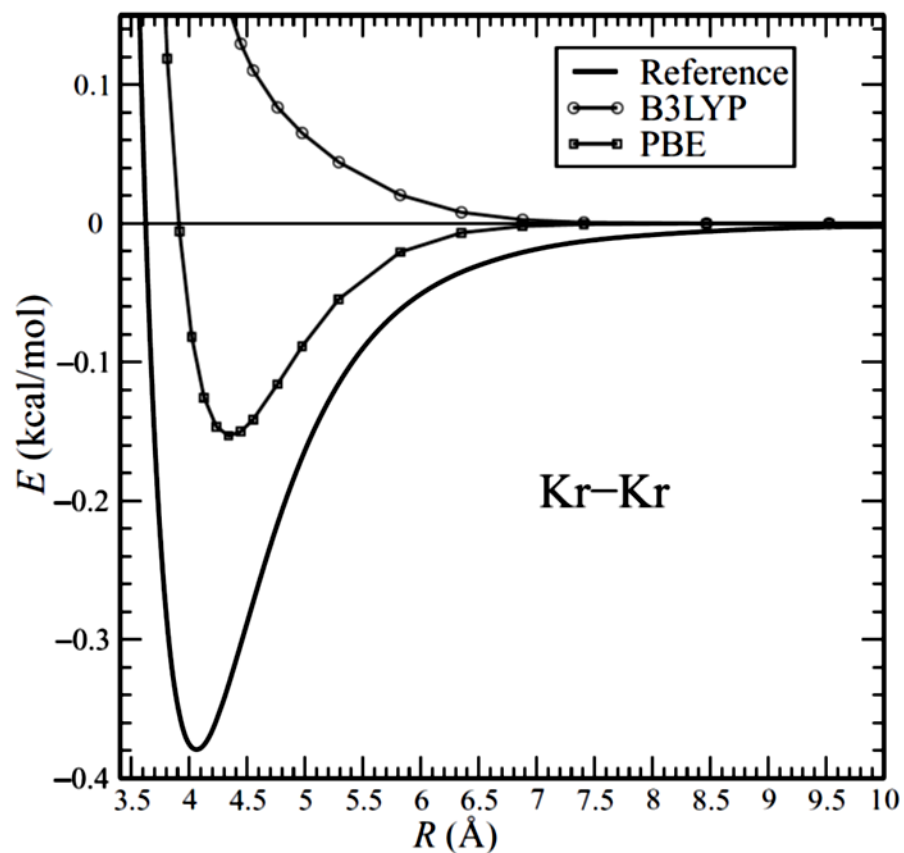


after MD simulation
without dispersion term

$$V(r) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$

helical to ladder structural transition in DNA

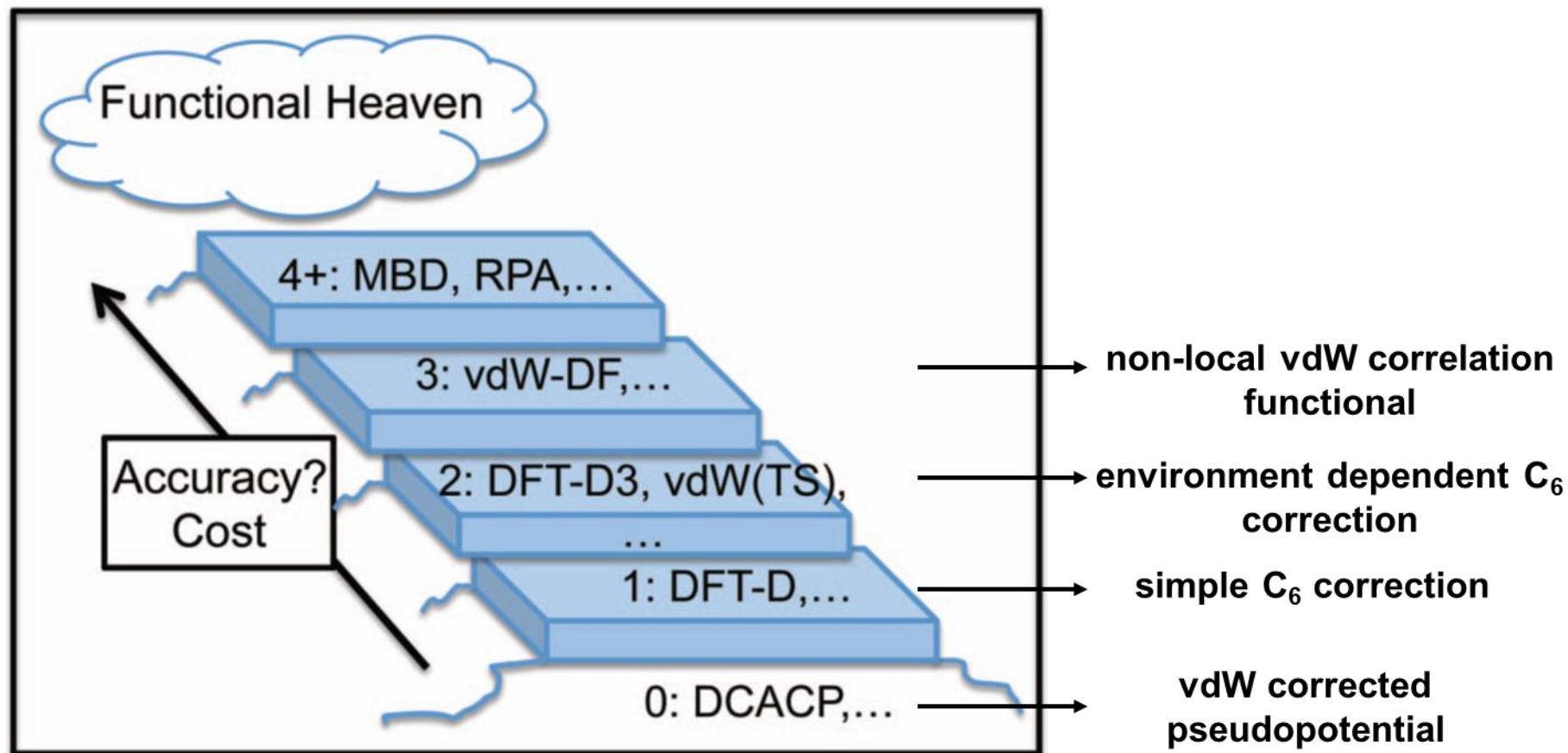
Conventional DFT Fails for vdW Force



Reference: CCSD(T), see Grimme, WIREs Comput. Mol. Sci., 1, 211 (2011)

Conventional DFT methods cannot provide correct $-1/R^6$ dependence of vdW force on R

Methods to include vdW force in Conventional DFT



Michaelides et al., J. Chem. Phys., 137, 120901 (2012)

“stairway to heaven” for long range dispersion interactions



Simple C6 Correction

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

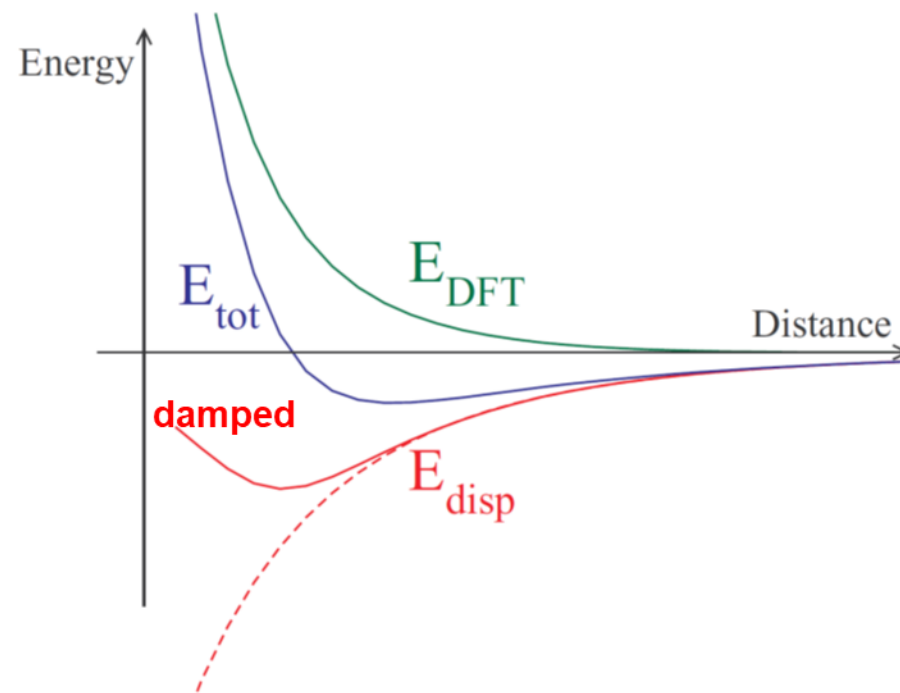
pairwise additive dispersion coefficients

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

↓
conventional DFT



Damped C6 Correction



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



$$C_6^{ij} = \sqrt{C_6^i C_6^j}$$

$$C_6^a = 0.05 N I_p^a \alpha^a$$

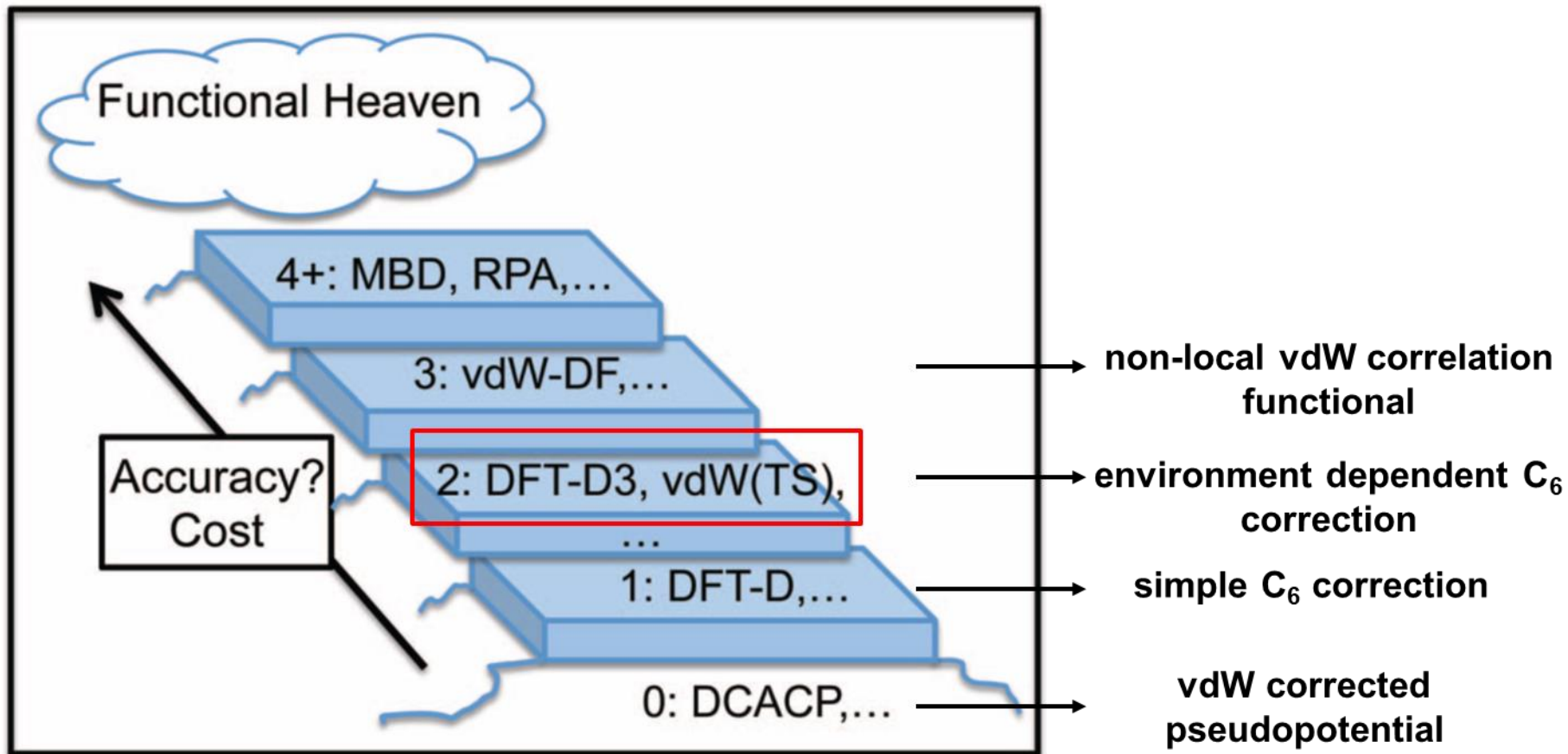
atomic ionization potentials

static polarizability



```
&XC
  &XC_FUNCTIONAL PBE
  &END XC_FUNCTIONAL
  &vdW_POTENTIAL
    DISPERSION_FUNCTIONAL PAIR_POTENTIAL
    &PAIR_POTENTIAL
      TYPE DFTD2
      REFERENCE_FUNCTIONAL PBE
      SCALING ??? ← XC-dependent
      R_CUTOFF ??? ← cutoff radius to calculate Edisp
    &END PAIR_POTENTIAL
  &END vdW_POTENTIAL
&END XC
```

Methods to include vdW force in Conventional DFT



Michaelides et al., J. Chem. Phys., 137, 120901 (2012)

“stairway to heaven” for long range dispersion interactions

DFT-D3: pre-calculated C₆ coefficients for various pairs of elements in different hybridisation states

Grimme et al., J. Chem. Phys, 132, 154104 (2010)

DFT-TS: Hirshfeld partitioning of the molecular electron density, compare effective atomic volume with a free atom, and then scale the C₆ coefficients of a free-atom reference

Tkatchenko & Scheffler, Phys. Rev. Letts., 102, 073005 (2009)



$$C_6^{AB}(\text{CN}^A, \text{CN}^B) = \frac{Z}{W},$$

$$Z = \sum_i^{N_A} \sum_j^{N_B} C_{6,\text{ref}}^{AB}(\text{CN}_i^A, \text{CN}_j^B) L_{ij},$$

$$W = \sum_i^{N_A} \sum_j^{N_B} L_{ij},$$

$$L_{ij} = e^{-k_3[(\text{CN}^A - \text{CN}_i^A)^2 + (\text{CN}^B - \text{CN}_j^B)^2]},$$

$$\text{CN}^A = \sum_{B \neq A}^{N_{\text{at}}} \frac{1}{1 + e^{-k_1(k_2(R_{A,\text{cov}} + R_{B,\text{cov}})/r_{AB} - 1)}}$$

**coordination
number**



$$E^{ABC} = \frac{C_9^{ABC} (3 \cos \theta_a \cos \theta_b \cos \theta_c + 1)}{(r_{AB} r_{BC} r_{CA})^3}$$

three-body term

$$C_9^{ABC} \approx - \sqrt{C_6^{AB} C_6^{AC} C_6^{BC}}$$



&XC

&XC_FUNCTIONAL PBE

&END XC_FUNCTIONAL

&vdW_POTENTIAL

DISPERSION_FUNCTIONAL PAIR_POTENTIAL

&PAIR_POTENTIAL

TYPE DFTD3 ### or DFTD3(BJ) ← type of damping

CALCULATE_C9_TERM .TRUE. ← include three-body term

PARAMETER_FILE_NAME dftd3.dat

REFERENCE_FUNCTIONAL PBE

D3_SCALING ??? ← XC and basis set dependent

R_CUTOFF ??? ← cutoff radius to calculate E_{disp}

&END PAIR_POTENTIAL

&END vdW_POTENTIAL

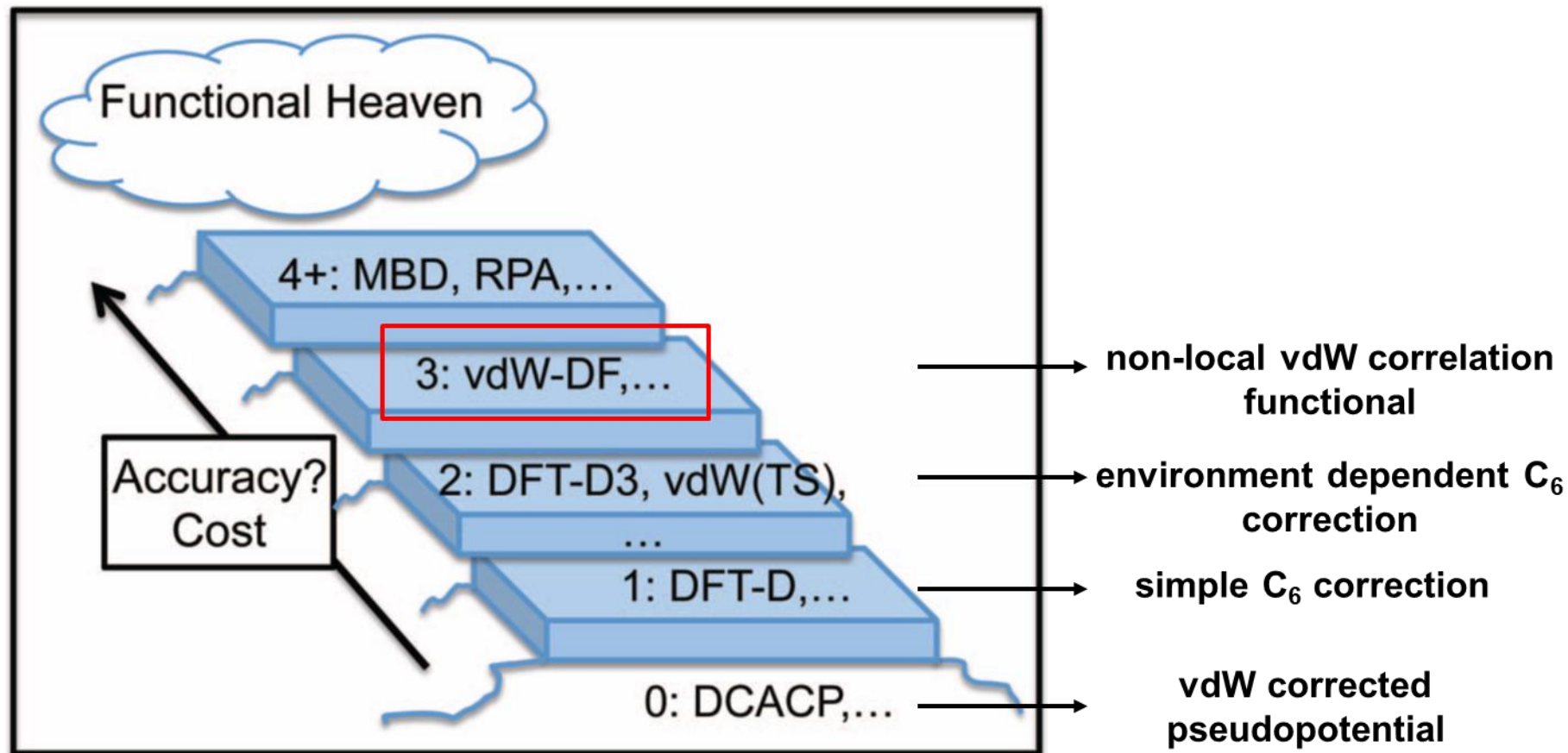
&END XC

(see more examples in \$CP2K/cp2k/tests/QS/regtest-dft-vdw-corr-2; for additional scaling parameters optimised for **moderate** basis set calculations, see Supporting Information of the D3 paper)



```
&QS  
METHOD PM3  
&SE  
DISPERSION T  
DISPERSION_RADIUS 15.  
D3_SCALING 1.0 1.2 1.4  
DISPERSION_PARAMETER_FILE dftd3.dat  
&END SE  
&END QS
```

Methods to include vdW force in Conventional DFT



Michaelides et al., J. Chem. Phys., 137, 120901 (2012)

“stairway to heaven” for long range dispersion interactions



Non-local vdW Correlation Functional

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

$$E_{\text{c}}^{\text{nl}} = \frac{1}{2} \int \int \rho(\mathbf{r}) \Phi(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') d^3 r d^3 r'$$

$$\Phi(\mathbf{r}, \mathbf{r}') = \Phi(\rho(\mathbf{r}), \rho(\mathbf{r}'), |\nabla \rho(\mathbf{r})|, |\nabla \rho(\mathbf{r}')|, |\mathbf{r} - \mathbf{r}'|)$$



Non-local vdW Correlation Functional

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 _x -vdW	29	C09 _x	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



&XC

&XC_FUNCTIONAL

&PBE

PARAMETRIZATION revPBE

SCALE_C 0.0

&END PBE

&VWN

&END VWN

&END XC_FUNCTIONAL

&vdW_POTENTIAL

DISPERSION_FUNCTIONAL NON_LOCAL

&NON_LOCAL

TYPE DRSLL ← **type of non-local vdW correlation functional**

KERNEL_FILE_NAME vdW_kernel_table.dat

CUTOFF ??? ← **cutoff of FFT grid used to calculate E_c^{nl}**

&END NON_LOCAL

&END vdW_POTENTIAL

&END XC

revPBE exchange

LDA correlation



```
&XC
  &XC_FUNCTIONAL
    &LIBXC
      FUNCTIONAL XC_GGA_X_RPW86 XC_GGA_C_PBE
    &END LIBXC
  &END XC_FUNCTIONAL
  &vdW_POTENTIAL
    DISPERSION_FUNCTIONAL NON_LOCAL
    &NON_LOCAL
      TYPE rVV10 ← type of non-local vdW correlation functional
      PARAMETERS 6.3 0.0093 ← parameters relevant to rVV10
      KERNEL_FILE_NAME rVV10_kernel_table.dat
      CUTOFF ??? ← cutoff of FFT grid used to calculate  $E_c^{nl}$ 
    &END NON_LOCAL
  &END vdW_POTENTIAL
&END XC
```



```
&XC  
  &XC_FUNCTIONAL  
    &LIBXC T  
      FUNCTIONAL XC_MGGA_X_M06_L XC_MGGA_C_M06_L  
    &END LIBXC  
  &END XC_FUNCTIONAL  
&END XC
```

Truhlar et al., J. Chem. Phys., 125, 194101 (2006)

- maybe combined with D3 correction
- analytical stress tensor has not been implemented, i.e. cannot be used
for CELL_OPT

Comparison of various methods

Method	Step	Reference for C_6	C_6 depend on	Additional computational cost ^a
Minnesota	0	None	N/A	None
DCACP	0	None	N/A	Small
DFT-D	1	Various	Constant	Small
DFT-D3	2	TDDFT	Structure	Small
vdW(TS)	2	Polarizabilities and atomic C_6	Atomic volume	Small
BJ	2	Polarizabilities	Atomic volume, X hole	Large
LRD	3	C_6 calculated	Density	Small
vdW-DF	3	C_6 calculated	Density	≈50%
Dbl. hybrids	4	None or as “-D”	Orbitals	Large

A few more remarks ...

- **use higher planewave cutoff and tighter energy/force convergence criteria for meta-GGAs and functionals from Libxc**
- **to use functionals from Libxc, you will need to install Libxc and link CP2K with Libxc, see `$CP2K/cp2k/INSTALL` for more details**
- **Basis set superposition error may “mimick” the missing dispersion interactions by DFT; check convergence on basis sets**

Available in CP2K

- Random phase approximation
- Møller–Plesset perturbation theory

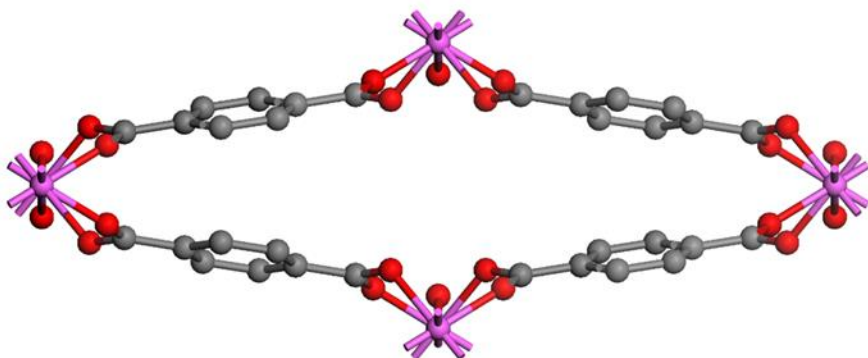
Not available in CP2K

- quantum Monte Carlo
- Symmetry adapted perturbation theory (SAPT) based on DFT
- Coupled cluster theory



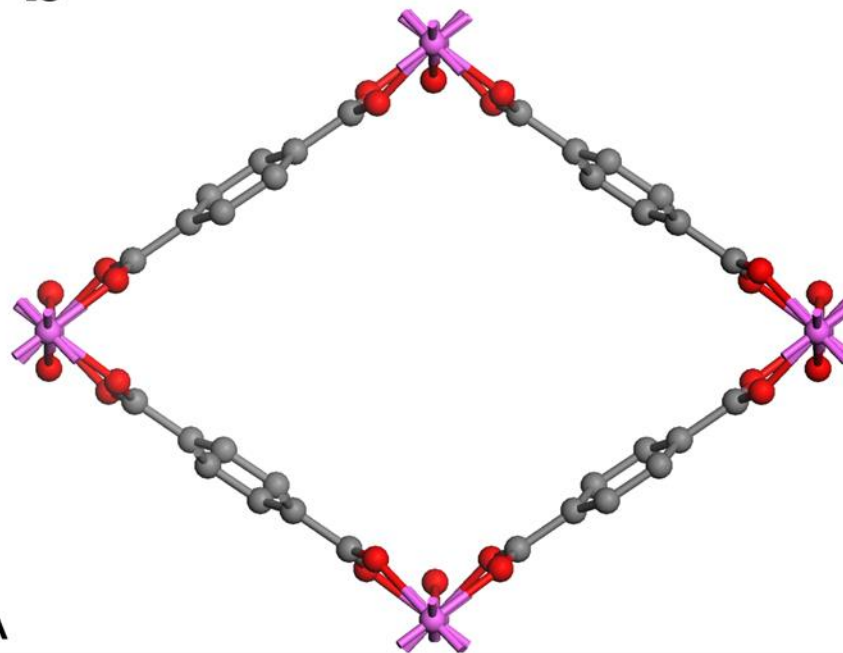
Example: “breathing” metal-organic framework MIL-53

a

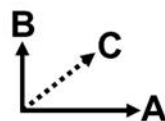


***np*-MIL-53:**
low temperature closed form

b

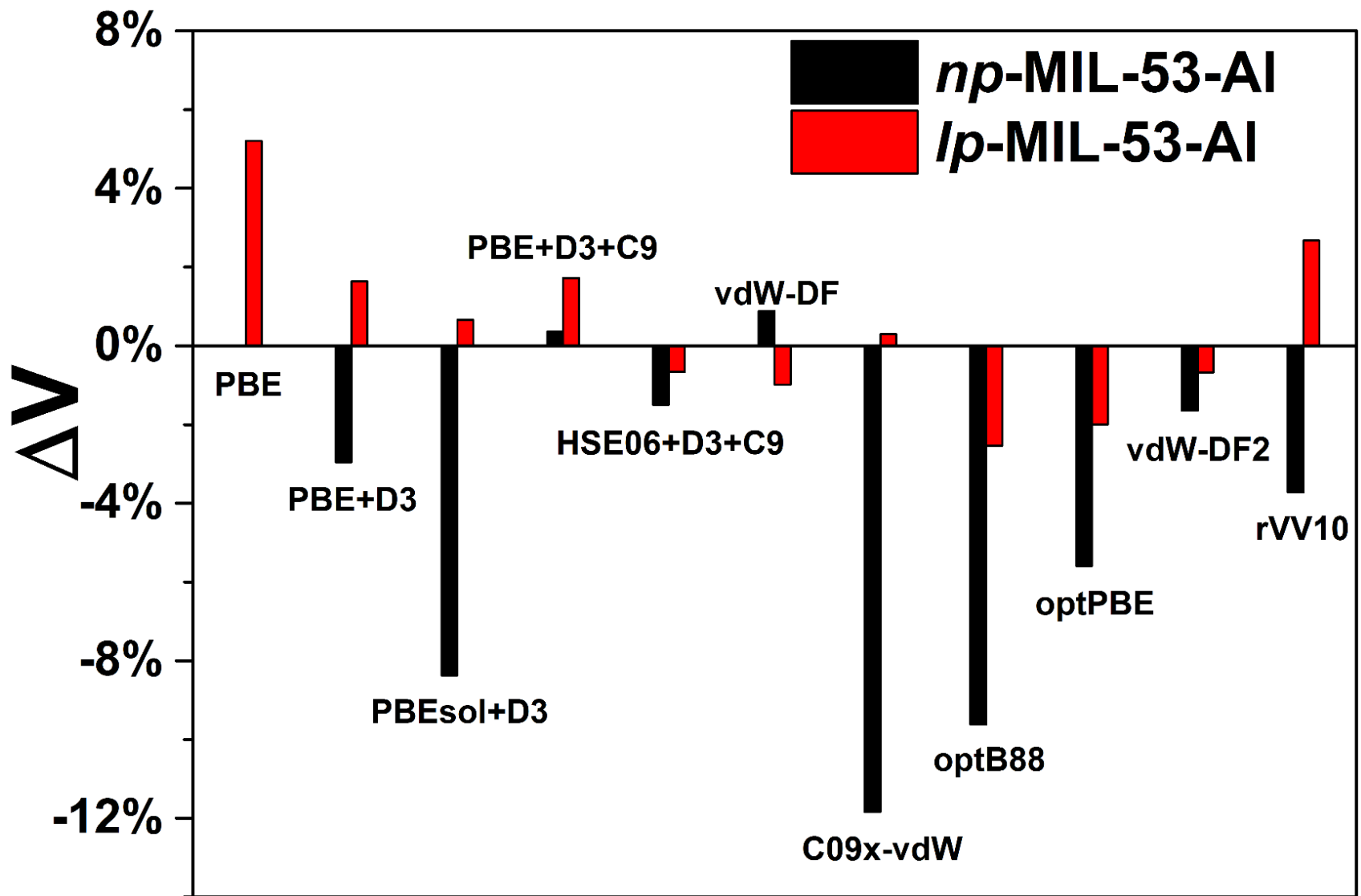


***lp*-MIL-53:**
high temperature open form





Example: “breathing” metal-organic framework MIL-53





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

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

Van der Waals Corrections to DFT (by Dr Ari Paavo Seitsonen)

http://www.cecami.org/upload/talk/presentation_5738.pdf

Post HF: MP2 and RPA in CP2K (by Jan Wilhelm)

https://www.cp2k.org/_media/events:2015_cecami_tutorial:wilhelm_posthf.pdf

Van der Waals corrected DFT (by myself)

https://www.cp2k.org/_media/events:2015_cecami_tutorial:ling_vdw.pdf