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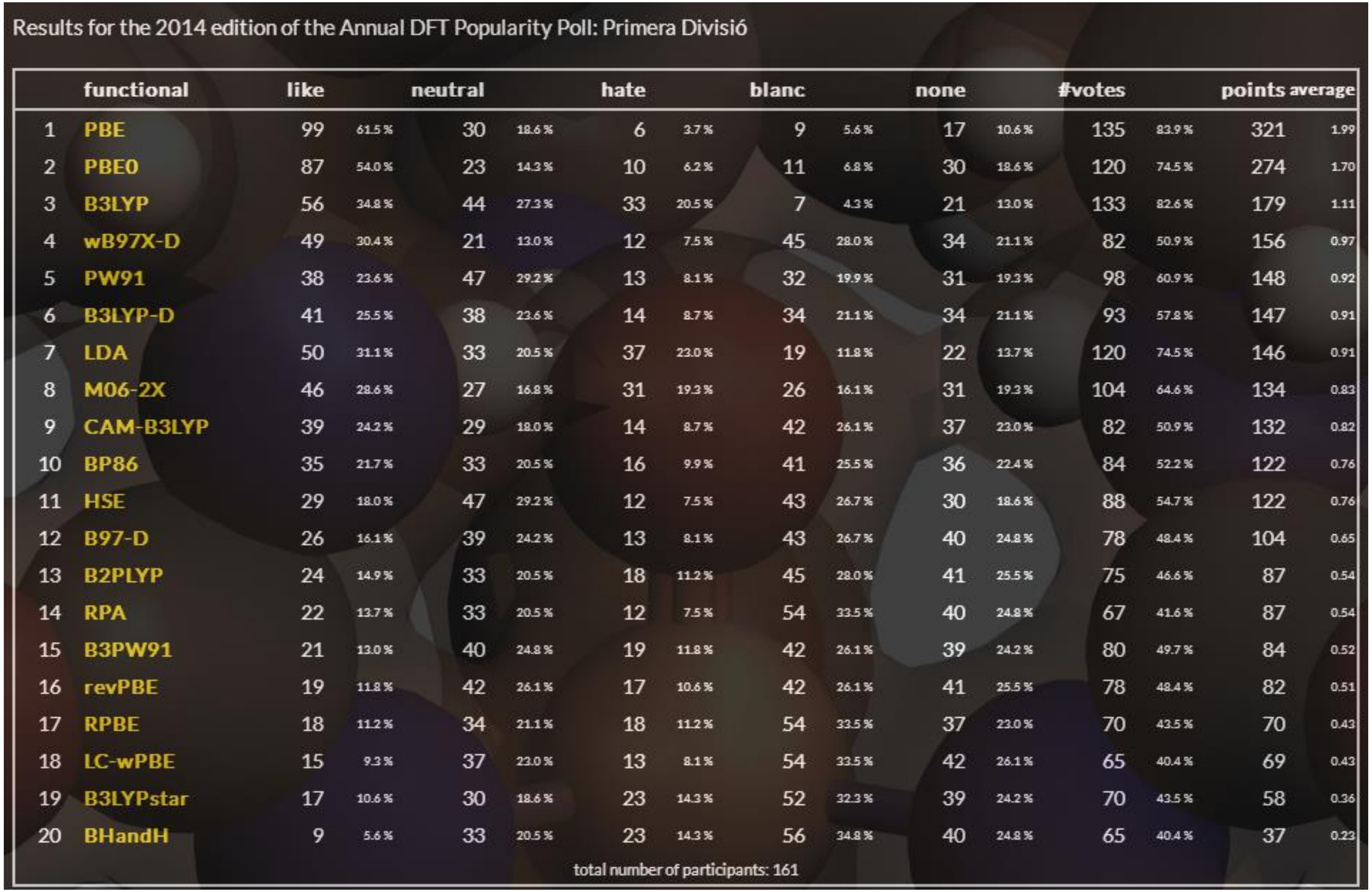
Hybrid Functionals and ADMM

Sanliang Ling

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

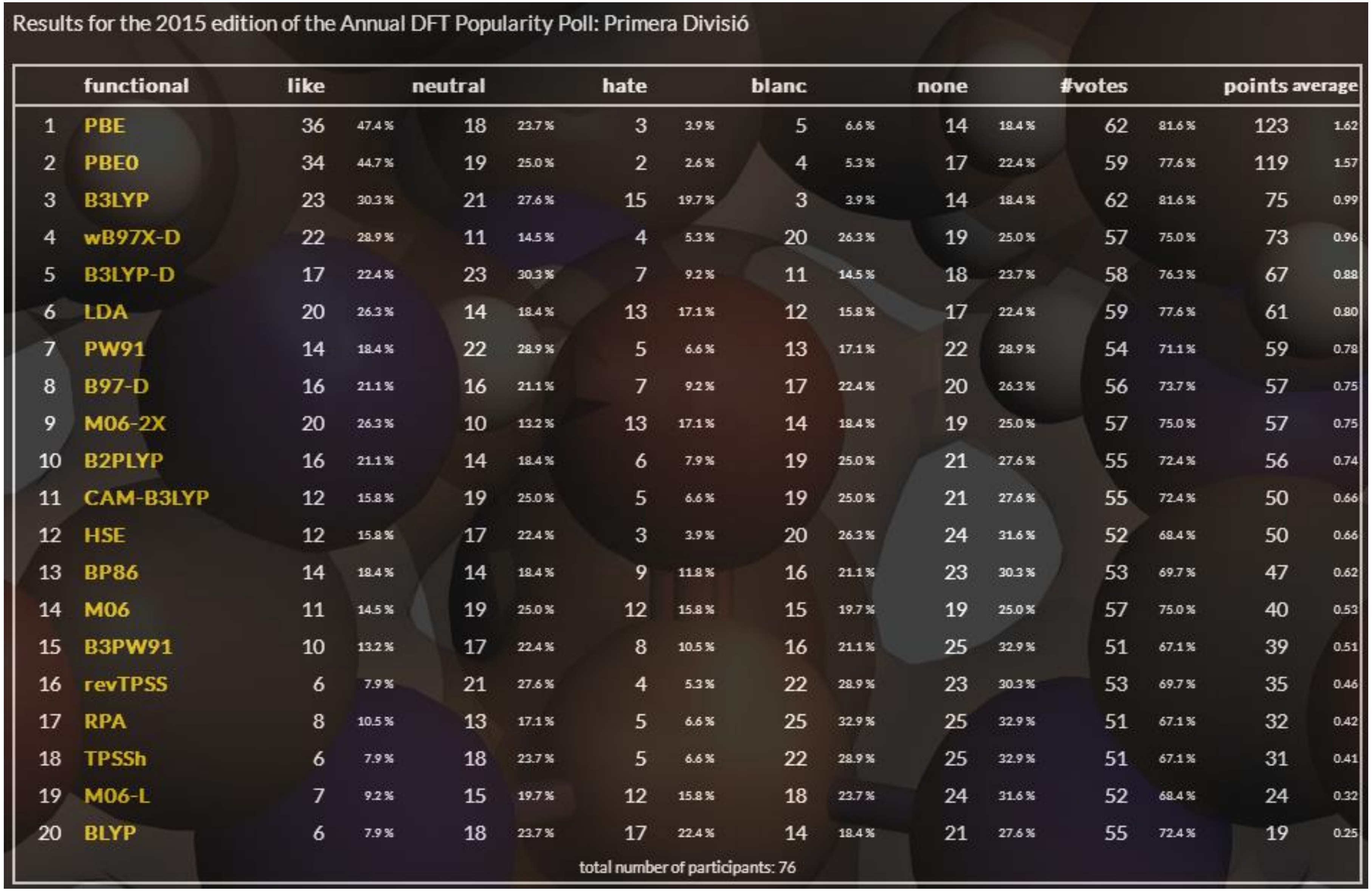
	functional	like		neutral		hate		blanc		none		#votes		points	average
1	PBE	99	61.5 %	30	18.6 %	6	3.7 %	9	5.6 %	17	10.6 %	135	83.9 %	321	1.99
2	PBE0	87	54.0 %	23	14.3 %	10	6.2 %	11	6.8 %	30	18.6 %	120	74.5 %	274	1.70
3	B3LYP	56	34.8 %	44	27.3 %	33	20.5 %	7	4.3 %	21	13.0 %	133	82.6 %	179	1.11
4	wB97X-D	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	19.3 %	26	16.1 %	31	19.3 %	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

(source: http://www.marcelswart.eu/dft-poll/)

What others say?



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

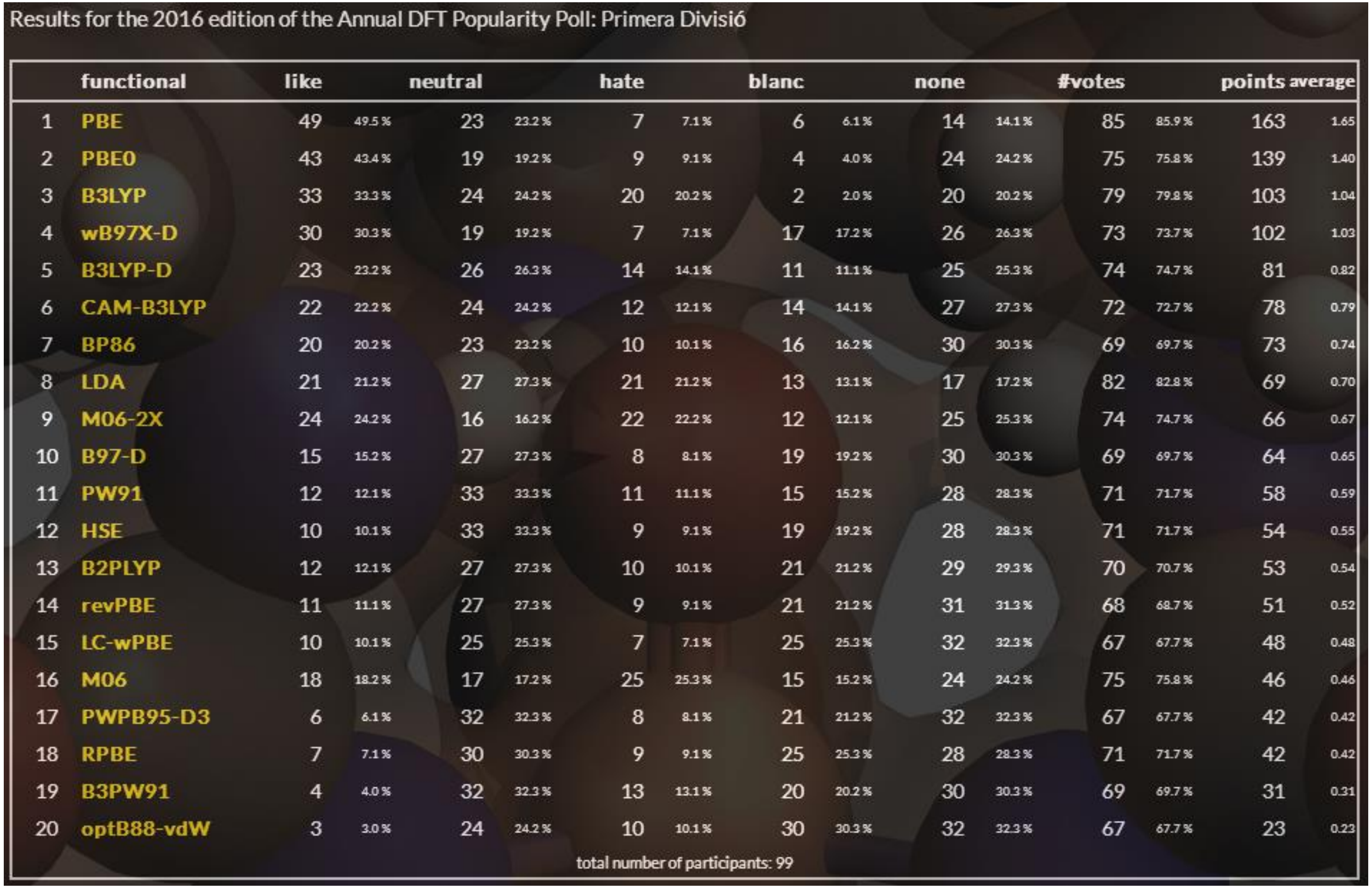
	functional	like		neutral		hate		blanc		none		#votes		points	average
1	PBE	36	47.4 %	18	23.7 %	3	3.9 %	5	6.6 %	14	18.4 %	62	81.6 %	123	1.62
2	PBE0	34	44.7 %	19	25.0 %	2	2.6 %	4	5.3 %	17	22.4 %	59	77.6 %	119	1.57
3	B3LYP	23	30.3 %	21	27.6 %	15	19.7 %	3	3.9 %	14	18.4 %	62	81.6 %	75	0.99
4	wB97X-D	22	28.9 %	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

(source: http://www.marcelswart.eu/dft-poll/)

What others say?



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

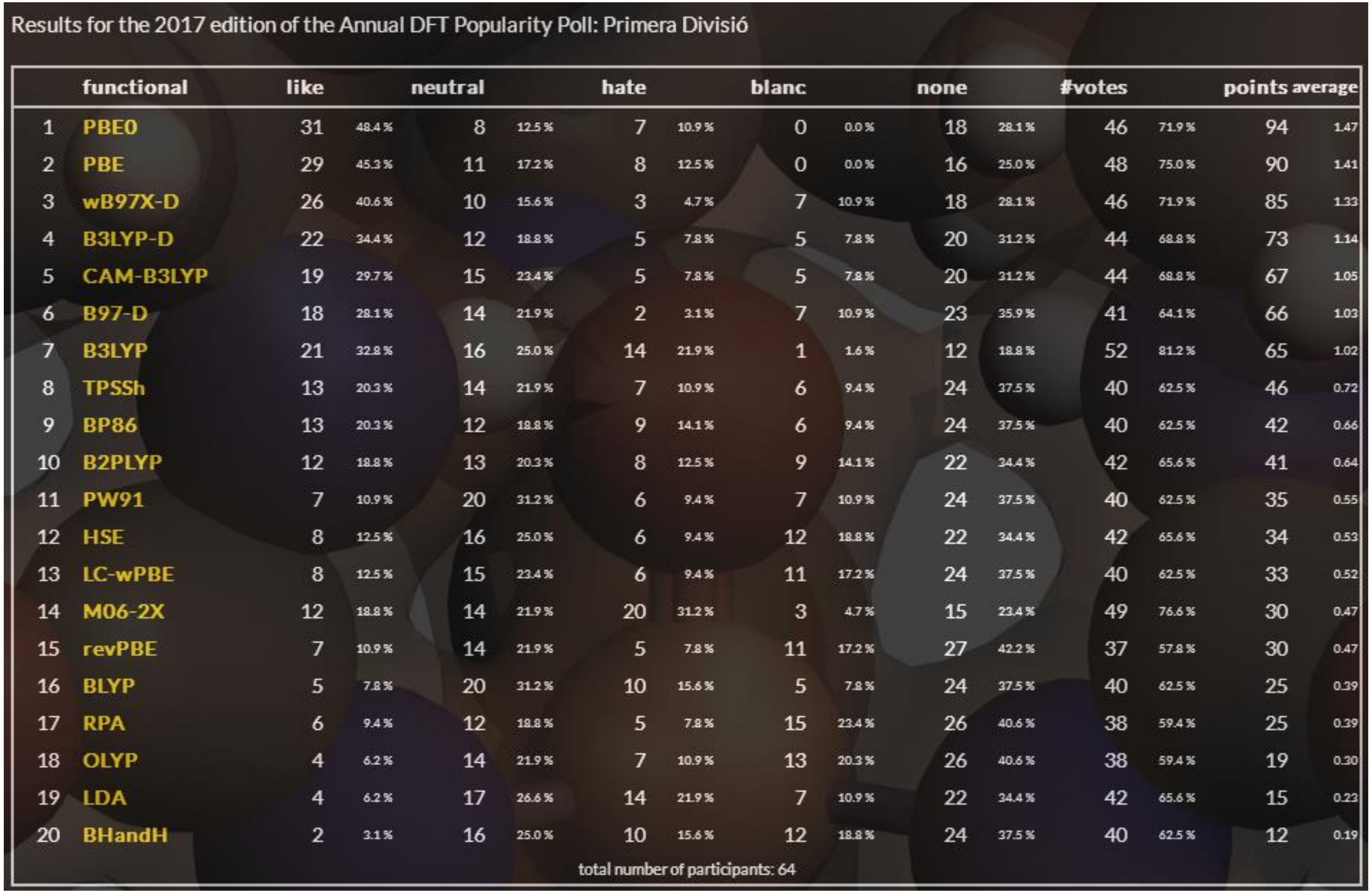
	functional	like		neutral		hate		blanc		none		#votes		points	average
1	PBE	49	49.5 %	23	23.2 %	7	7.1 %	6	6.1 %	14	14.1 %	85	85.9 %	163	1.65
2	PBE0	43	43.4 %	19	19.2 %	9	9.1 %	4	4.0 %	24	24.2 %	75	75.8 %	139	1.40
3	B3LYP	33	33.3 %	24	24.2 %	20	20.2 %	2	2.0 %	20	20.2 %	79	79.8 %	103	1.04
4	wB97X-D	30	30.3 %	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

(source: http://www.marcelswart.eu/dft-poll/)

What others say?



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

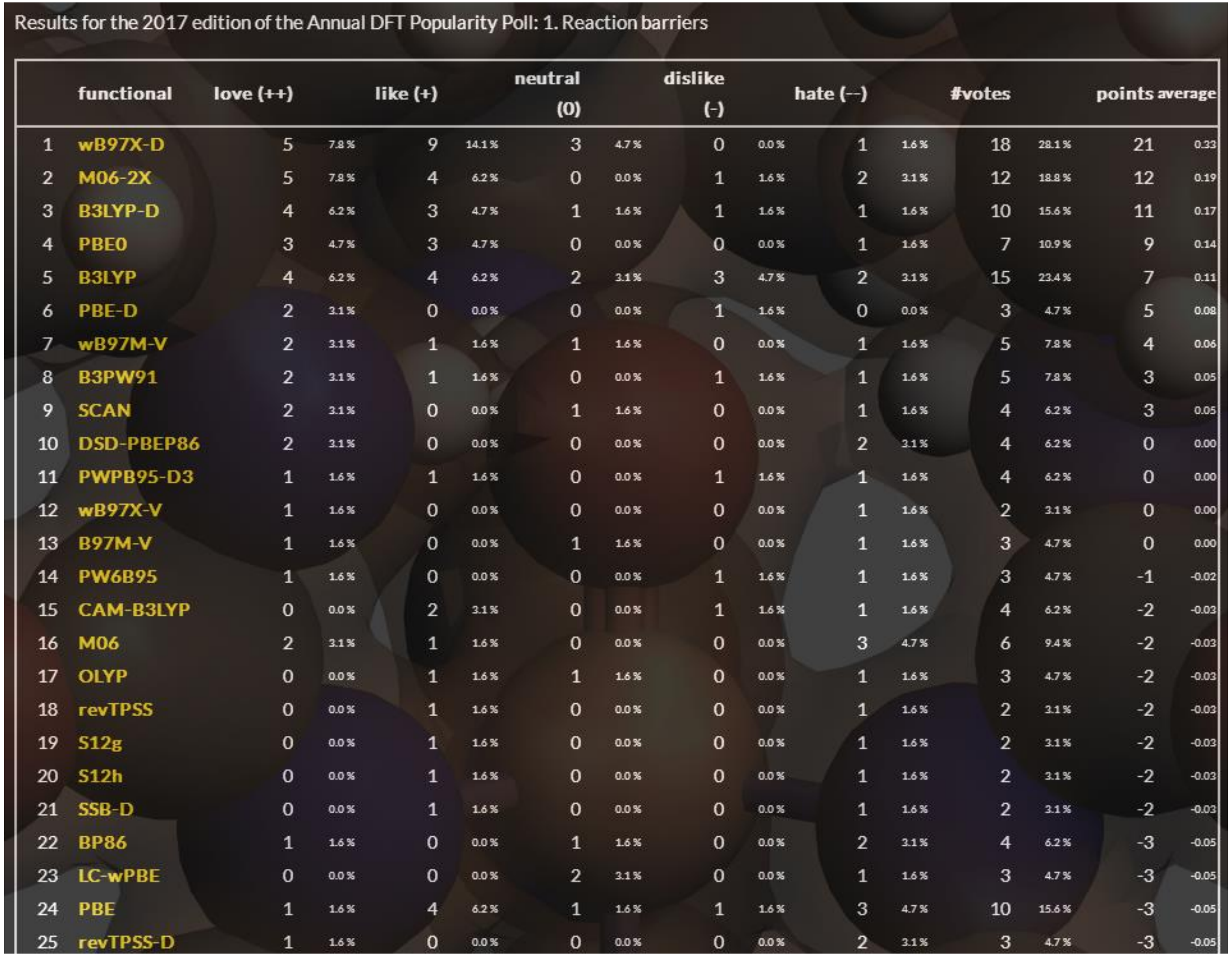
	functional	like		neutral		hate		blanc		none		#votes		points	average
1	PBE0	31	48.4 %	8	12.5 %	7	10.9 %	0	0.0 %	18	28.1 %	46	71.9 %	94	1.47
2	PBE	29	45.3 %	11	17.2 %	8	12.5 %	0	0.0 %	16	25.0 %	48	75.0 %	90	1.41
3	wB97X-D	26	40.6 %	10	15.6 %	3	4.7 %	7	10.9 %	18	28.1 %	46	71.9 %	85	1.33
4	B3LYP-D	22	34.4 %	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

(source: http://www.marcelswart.eu/dft-poll/)

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

(source: http://www.marcelswart.eu/dft-poll/)

What are hybrid functionals?

$$E_{\mathrm{xc}}[\rho] = \alpha E_{\mathrm{x}}^{\mathrm{HFX}}[\{\psi_i\}] + (1 - \alpha)E_{\mathrm{x}}^{\mathrm{DFT}}[\rho] + E_{\mathrm{c}}^{\mathrm{DFT}}[\rho]$$

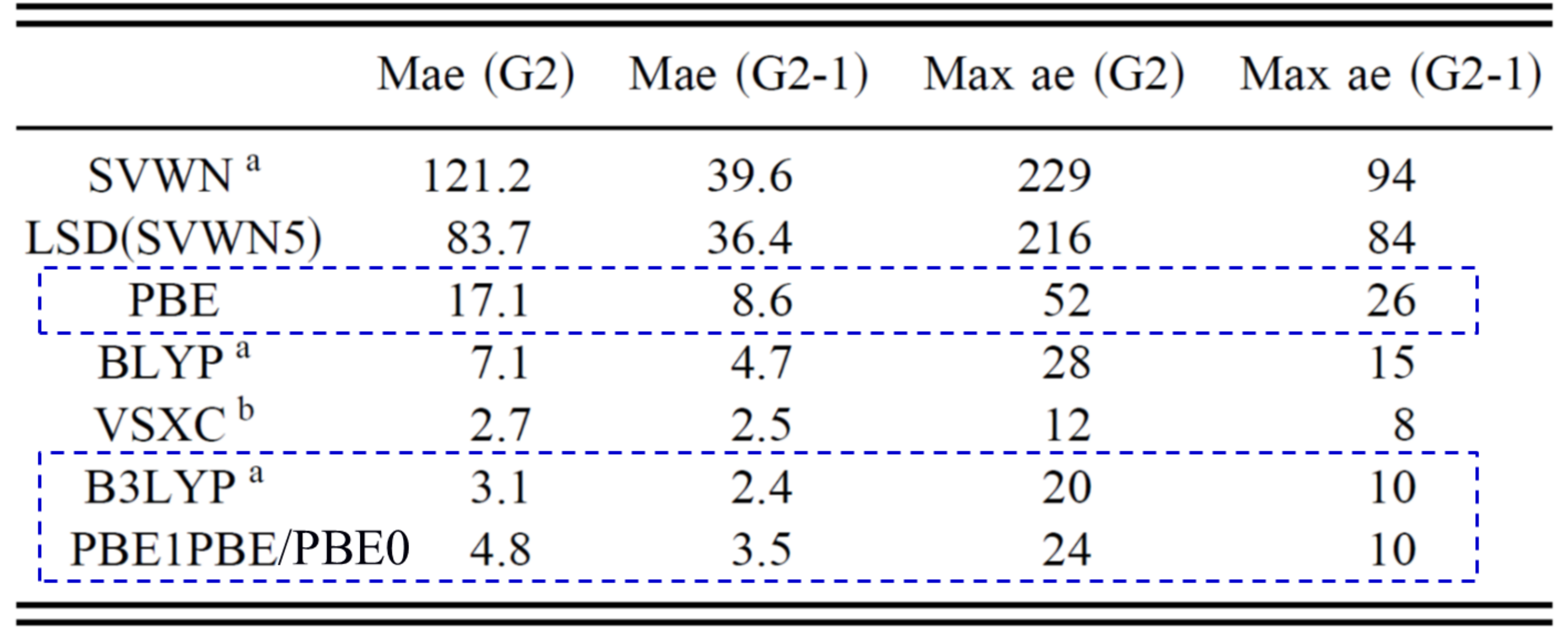
Hybrid functionals:

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?

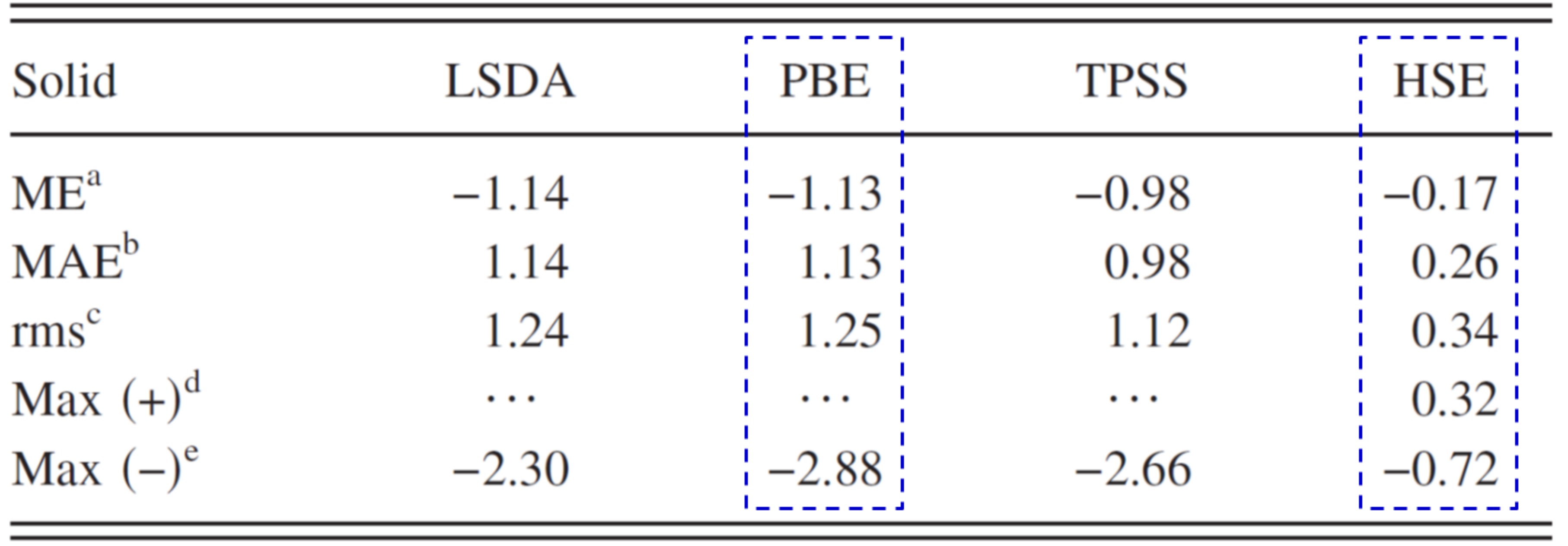


	Mae (G2)	Mae (G2-1)	Max ae (G2)	Max ae (G2-1)
SVWN [a]	121.2	39.6	229	94
LSD(SVWN5)	83.7	36.4	216	84
PBE	17.1	8.6	52	26
BLYP [a]	7.1	4.7	28	15
VSXC [b]	2.7	2.5	12	8
B3LYP [a]	3.1	2.4	20	10
PBE1PBE/PBE0	4.8	3.5	24	10

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

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

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

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

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Hybrid DFT Calculations with CP2K

- Total energy as a functional of the electron density

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

- Exchange-correlation energy with a hybrid functional

$$E_{\mathrm{xc}}[\rho] = \alpha E_{\mathrm{x}}^{\mathrm{HFX}}[\{\psi_i\}] + (1-\alpha)E_{\mathrm{x}}^{\mathrm{DFT}}[\rho] + E_{\mathrm{c}}^{\mathrm{DFT}}[\rho]$$

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

Hybrid DFT Calculations with CP2K

- Hartree-Fock exchange energy

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

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

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

$$\downarrow$$

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

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

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Hybrid DFT Calculations with CP2K

- Permutational symmetry of the ERIs

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

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

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

Guidon et al., J. Chem. Phys., 128, 214104 (2008); Guidon, [PRACE Workshop talk on CP2K]

Hybrid DFT Calculations with CP2K

- Integral screening: Schwarz inequality

$$\left|(\mu\nu\,|\,\lambda\sigma)_g\right| \le \underbrace{[(\mu\nu|\mu\nu)_g]^{1/2}[(\lambda\sigma|\lambda\sigma)_g]^{1/2}}_{\textbf{upper bound for ERIs}}$$

(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

Guidon et al., J. Chem. Phys., 128, 214104 (2008); Guidon, PRACE Workshop talk on CP2K

Hybrid DFT Calculations with CP2K

- Density matrix screening

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

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

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

(see SCREEN_ON_INITIAL_P keyword in &SCREENING subsection)

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

Guidon et al., J. Chem. Phys., 128, 214104 (2008); Guidon, PRACE Workshop talk on CP2K

Interaction potential

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

- 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

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

- Range-separated Coulomb potential

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

(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

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

- Truncated Coulomb potential

parameter

$$g_{\mathrm{TC}}(r_{12}) = \begin{cases} \dfrac{1}{r_{12}}, & r_{12} \le \overset{\uparrow}{R_c} \\ 0, & r_{12} > R_c \end{cases}$$

(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

$$E_{\mathrm{xc}}[\rho] = \alpha E_{\mathrm{x}}^{\mathrm{HFX}}[\{\psi_i\}] + (1-\alpha)E_{\mathrm{x}}^{\mathrm{DFT}}[\rho] + E_{\mathrm{c}}^{\mathrm{DFT}}[\rho]$$

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

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

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

approximation

original density matrix

auxiliary density matrix

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

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

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

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

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

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

Auxiliary Density Matrix Methods

- Construction of auxiliary density matrix

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

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

$$\boxed{\min_{\hat{C}} = \sum_{i} \int (\psi_j(\mathbf{r}) - \hat{\psi}_j(\mathbf{r}))^2 \, \mathrm{d}\mathbf{r}}$$

(see ADMM_PURIFICATION_METHOD keyword in &AUXILIARY_DENSITY_MATRIX_METHOD subsection)

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

Auxiliary Density Matrix Methods

- Construction of auxiliary density matrix: enforcing orthonormality

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

Lagrangian multipliers

(see ADMM_PURIFICATION_METHOD keyword in &AUXILIARY_DENSITY_MATRIX_METHOD subsection)

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

University of Nottingham
UK | CHINA | MALAYSIA

Auxiliary Density Matrix Methods

- Construction of auxiliary density matrix: constraint on total charge

$$W_{\mathrm{Q}} = \sum_{i}^{\mathrm{occ}} \langle (i - \tilde{i})^2 \rangle + \lambda \left(\frac{N}{2} - \sum_{i}^{\mathrm{occ}} \langle \tilde{i}^2 \rangle \right)$$

(see EXCH_SCALING_MODEL keyword in &AUXILIARY_DENSITY_MATRIX_METHOD subsection)

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

Auxiliary Density Matrix Methods

- GGA exchange corrections using different functions

$$\begin{aligned} E_{\mathrm{x}}^{\mathrm{HFX}}[P] &= E_{\mathrm{x}}^{\mathrm{HFX}}[\hat{P}] + \boxed{\left(E_{\mathrm{x}}^{\mathrm{HFX}}[P] - E_{\mathrm{x}}^{\mathrm{HFX}}[\hat{P}]\right)} \\ &\approx E_{\mathrm{x}}^{\mathrm{HFX}}[\hat{P}] + \boxed{\left(E_{\mathrm{x}}^{\mathrm{DFT}}[P] - E_{\mathrm{x}}^{\mathrm{DFT}}[\hat{P}]\right)} \end{aligned}$$

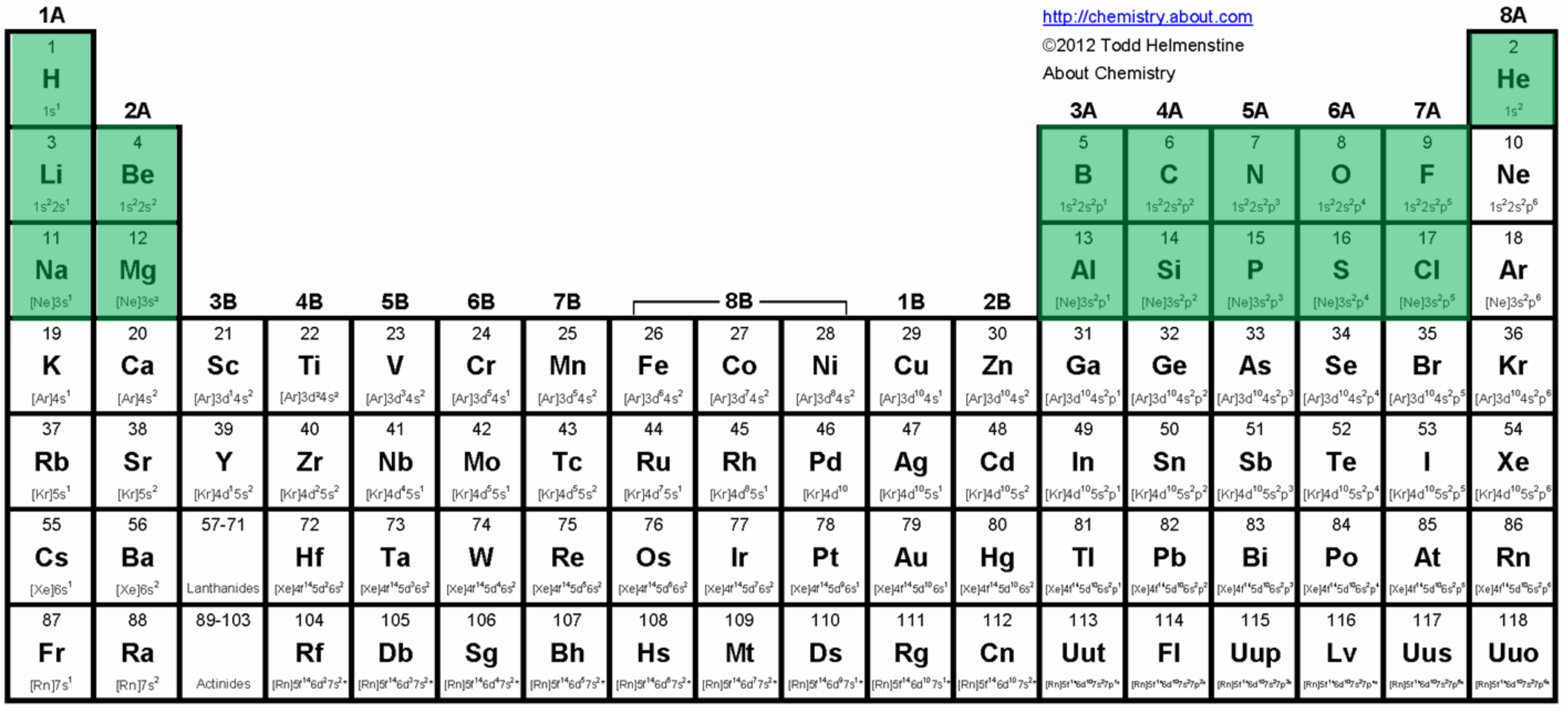
$\downarrow$

DFT = B88, PBE, OPTX, KT3X

(see EXCH_CORRECTION_FUNC keyword in &AUXILIARY_DENSITY_MATRIX_METHOD subsection)

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

ADMM basis sets



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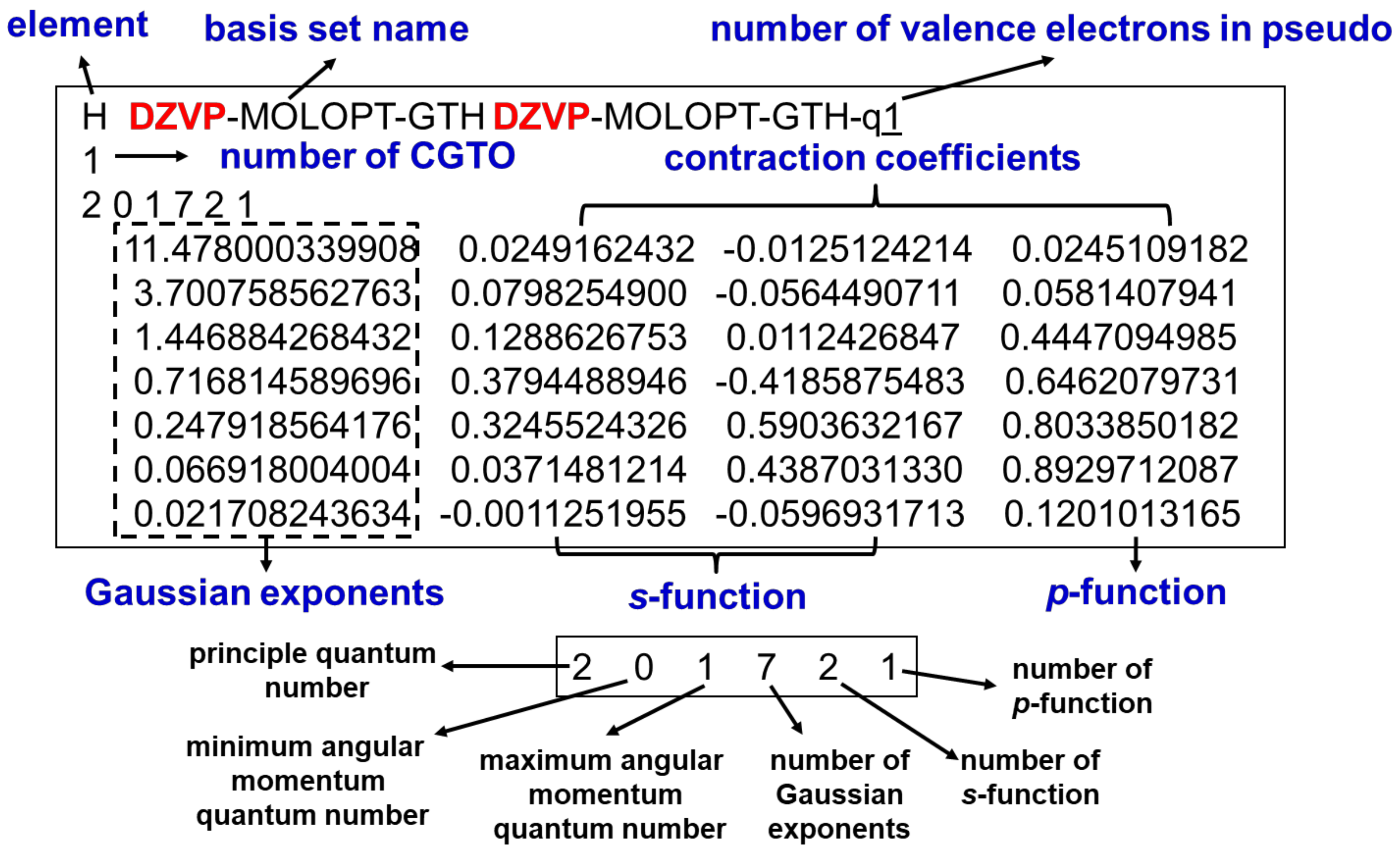
About Chemistry

1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
🟩 1 H $1s^1$																	🟩 2 He $1s^2$
🟩 3 Li $1s^22s^1$	🟩 4 Be $1s^22s^2$											🟩 5 B $1s^22s^2p^1$	🟩 6 C $1s^22s^2p^2$	🟩 7 N $1s^22s^2p^3$	🟩 8 O $1s^22s^2p^4$	🟩 9 F $1s^22s^2p^5$	10 Ne $1s^22s^2p^6$
🟩 11 Na $[Ne]3s^1$	🟩 12 Mg $[Ne]3s^2$											🟩 13 Al $[Ne]3s^2p^1$	🟩 14 Si $[Ne]3s^2p^2$	🟩 15 P $[Ne]3s^2p^3$	🟩 16 S $[Ne]3s^2p^4$	🟩 17 Cl $[Ne]3s^2p^5$	18 Ar $[Ne]3s^2p^6$
19 K $[Ar]4s^1$	20 Ca $[Ar]4s^2$	21 Sc $[Ar]3d^14s^2$	22 Ti $[Ar]3d^24s^2$	23 V $[Ar]3d^34s^2$	24 Cr $[Ar]3d^54s^1$	25 Mn $[Ar]3d^54s^2$	26 Fe $[Ar]3d^64s^2$	27 Co $[Ar]3d^74s^2$	28 Ni $[Ar]3d^84s^2$	29 Cu $[Ar]3d^{10}4s^1$	30 Zn $[Ar]3d^{10}4s^2$	31 Ga $[Ar]3d^{10}4s^2p^1$	32 Ge $[Ar]3d^{10}4s^2p^2$	33 As $[Ar]3d^{10}4s^2p^3$	34 Se $[Ar]3d^{10}4s^2p^4$	35 Br $[Ar]3d^{10}4s^2p^5$	36 Kr $[Ar]3d^{10}4s^2p^6$
37 Rb $[Kr]5s^1$	38 Sr $[Kr]5s^2$	39 Y $[Kr]4d^15s^2$	40 Zr $[Kr]4d^25s^2$	41 Nb $[Kr]4d^45s^1$	42 Mo $[Kr]4d^55s^1$	43 Tc $[Kr]4d^55s^2$	44 Ru $[Kr]4d^75s^1$	45 Rh $[Kr]4d^85s^1$	46 Pd $[Kr]4d^{10}$	47 Ag $[Kr]4d^{10}5s^1$	48 Cd $[Kr]4d^{10}5s^2$	49 In $[Kr]4d^{10}5s^2p^1$	50 Sn $[Kr]4d^{10}5s^2p^2$	51 Sb $[Kr]4d^{10}5s^2p^3$	52 Te $[Kr]4d^{10}5s^2p^4$	53 I $[Kr]4d^{10}5s^2p^5$	54 Xe $[Kr]4d^{10}5s^2p^6$
55 Cs $[Xe]6s^1$	56 Ba $[Xe]6s^2$	57-71 Lanthanides	72 Hf $[Xe]4f^{14}5d^26s^2$	73 Ta $[Xe]4f^{14}5d^36s^2$	74 W $[Xe]4f^{14}5d^46s^2$	75 Re $[Xe]4f^{14}5d^56s^2$	76 Os $[Xe]4f^{14}5d^66s^2$	77 Ir $[Xe]4f^{14}5d^76s^2$	78 Pt $[Xe]4f^{14}5d^96s^1$	79 Au $[Xe]4f^{14}5d^{10}6s^1$	80 Hg $[Xe]4f^{14}5d^{10}6s^2$	81 Tl $[Xe]4f^{14}5d^{10}6s^2p^1$	82 Pb $[Xe]4f^{14}5d^{10}6s^2p^2$	83 Bi $[Xe]4f^{14}5d^{10}6s^2p^3$	84 Po $[Xe]4f^{14}5d^{10}6s^2p^4$	85 At $[Xe]4f^{14}5d^{10}6s^2p^5$	86 Rn $[Xe]4f^{14}5d^{10}6s^2p^6$
87 Fr $[Rn]7s^1$	88 Ra $[Rn]7s^2$	89-103 Actinides	104 Rf $[Rn]5f^{14}6d^27s^{2*}$	105 Db $[Rn]5f^{14}6d^37s^{2*}$	106 Sg $[Rn]5f^{14}6d^47s^{2*}$	107 Bh $[Rn]5f^{14}6d^57s^{2*}$	108 Hs $[Rn]5f^{14}6d^67s^{2*}$	109 Mt $[Rn]5f^{14}6d^77s^{2*}$	110 Ds $[Rn]5f^{14}6d^97s^{1*}$	111 Rg $[Rn]5f^{14}6d^{10}7s^{1*}$	112 Cn $[Rn]5f^{14}6d^{10}7s^{2*}$	113 Uut $[Rn]5f^{14}6d^{10}7s^27p^{1*}$	114 Fl $[Rn]5f^{14}6d^{10}7s^27p^{2*}$	115 Uup $[Rn]5f^{14}6d^{10}7s^27p^{3*}$	116 Lv $[Rn]5f^{14}6d^{10}7s^27p^{4*}$	117 Uus $[Rn]5f^{14}6d^{10}7s^27p^{5*}$	118 Uuo $[Rn]5f^{14}6d^{10}7s^27p^{6*}$

(see $CP2K/cp2k/data/BASIS_ADMM)

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

MOLOPT basis set format



```
H  DZVP-MOLOPT-GTH DZVP-MOLOPT-GTH-q1
1
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
```

element

basis set name

number of valence electrons in pseudo

number of CGTO

contraction coefficients

Gaussian exponents

s-function

p-function

```
2  0  1  7  2  1
```

principle quantum number

minimum angular momentum quantum number

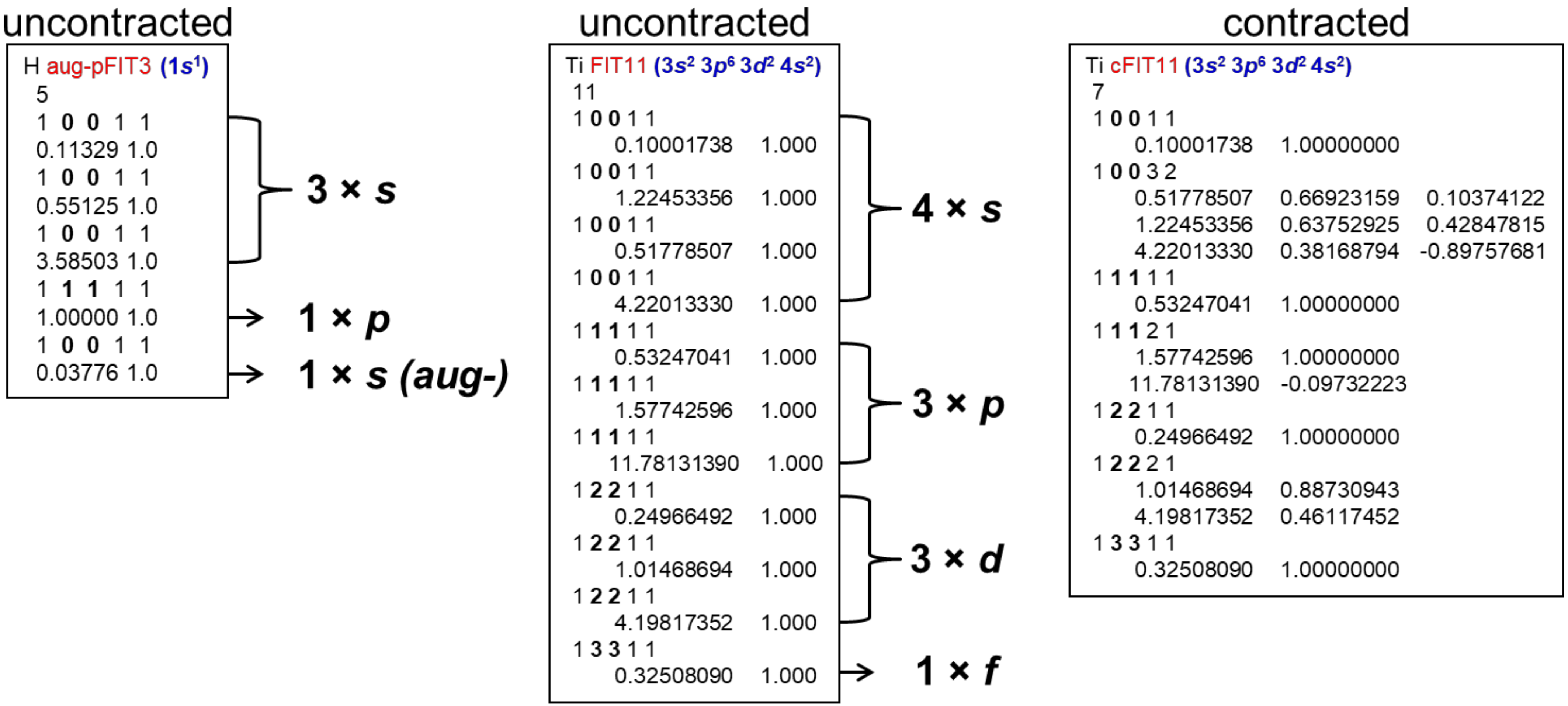
maximum angular momentum quantum number

number of Gaussian exponents

number of *s*-function

number of *p*-function

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**)

ADMM basis sets

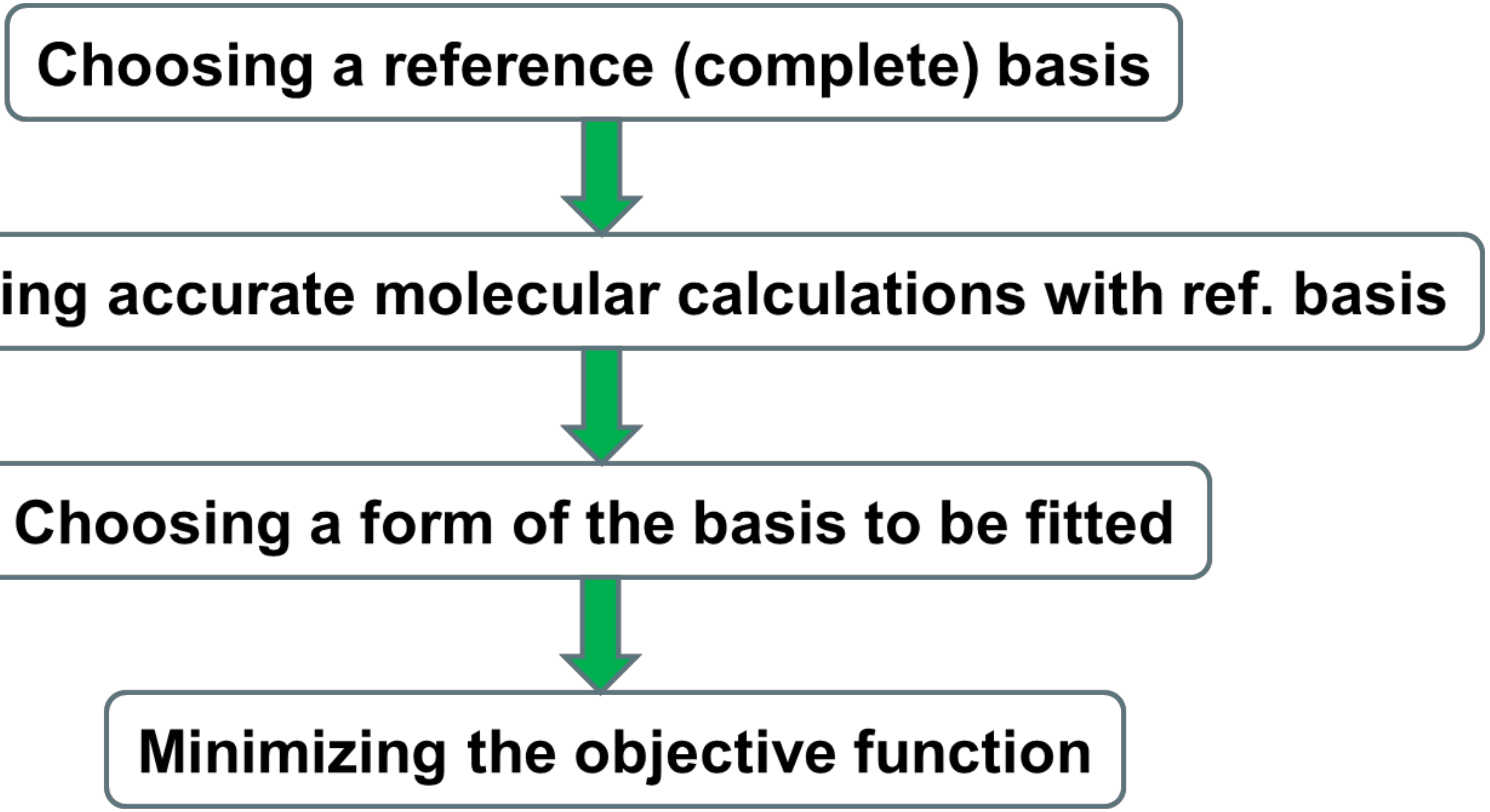
Choice of auxiliary basis set for ADMM

- 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)

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

Basis optimisation with OPTIMIZE_BASIS



Choosing a reference (complete) basis

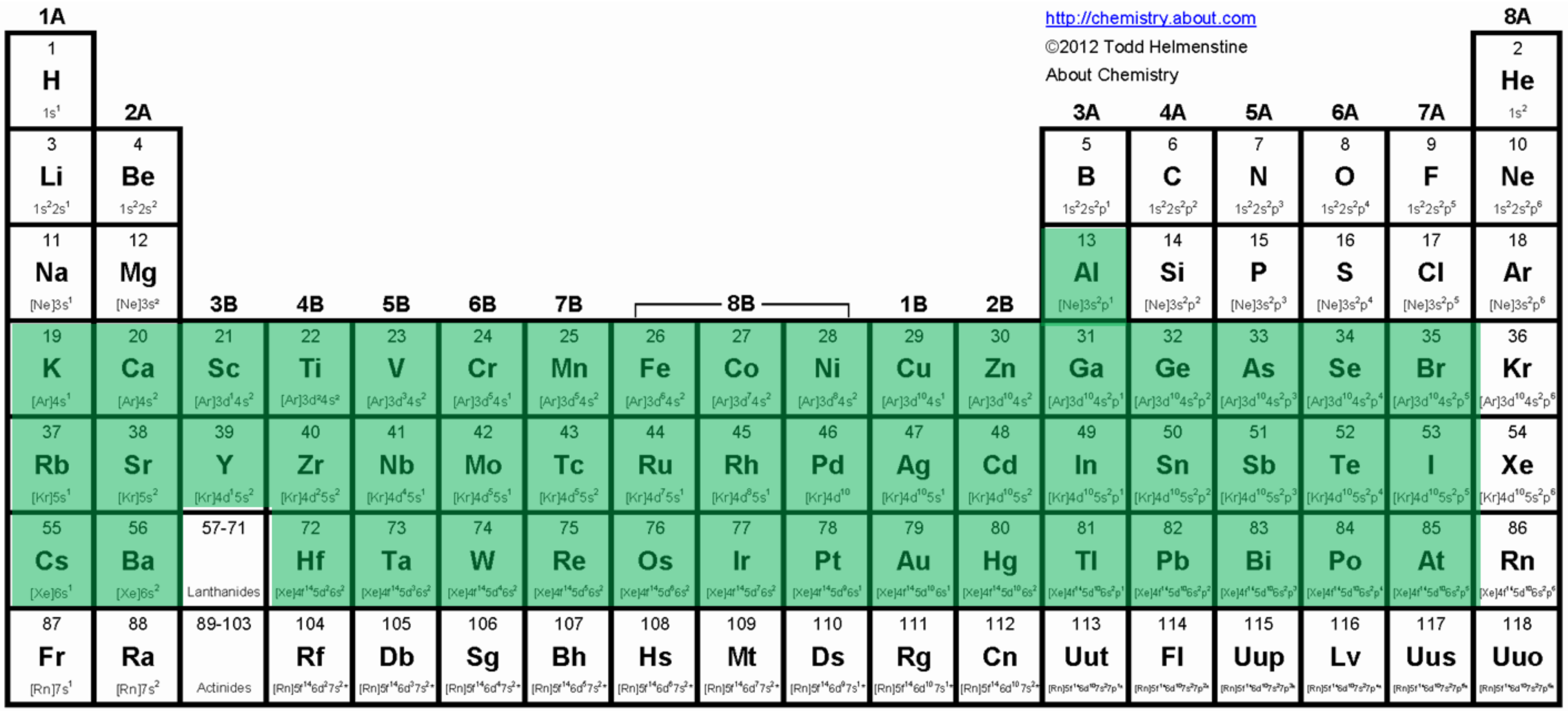
Performing accurate molecular calculations with ref. basis

Choosing a form of the basis to be fitted

Minimizing the objective function

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

ADMM basis sets



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About Chemistry

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	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** $1s^2 2s^2 p^1$	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** $1s^2 2s^2 p^6$
11 **Na** $[Ne]3s^1$	12 **Mg** $[Ne]3s^2$											🟩 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** $[Ne]3s^2 p^6$
🟩 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** $[Rn]5f^{14} 6d^9 7s^{1*}$	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** $[Rn]5f^{14} 6d^{10} 7s^2 7p^{6*}$

(see $CP2K/cp2k/data/**BASIS_ADMM_MOLOPT**)

ADMM basis sets

Uncontracted basis sets

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

Contracted basis sets (double-ζ quality)

- cFIT10 / cFIT11 / cFIT12 / cFIT13

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

(see $CP2K/cp2k/data/**BASIS_ADMM_MOLOPT**)

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

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
                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
                POTENTIAL GTH-PBE-q4
        &END KIND
&END SUBSYS
```

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

(note: the old AUX_FIT_BASIS_SET keyword is now deprecated)

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

Which functional to use?

- PBE0-TC-LRC

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

$$+(1-\boldsymbol{a})E_x^{PBE} + E_c^{PBE}$$

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

- HSE06

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

$$+E_x^{PBE,LR}(\boldsymbol{\omega}) + E_c^{PBE}$$

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

“Empirical” parameters: *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)

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

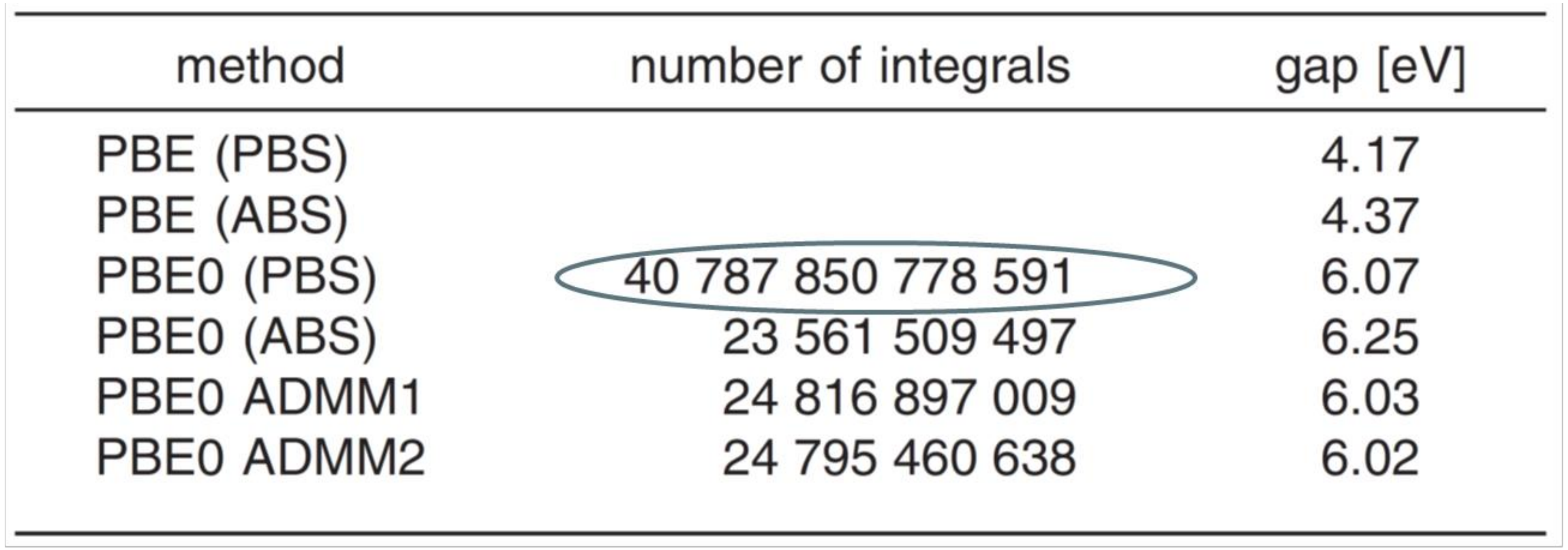
A few more remarks …

- 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.psmp)

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

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

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_cecam_tutorial:ling_hybrids.pdf

Optimization of Pseudopotential and Basis Set (by myself)
https://www.cp2k.org/_media/events:2015_cecam_tutorial:ling_basis_pseudo.pdf

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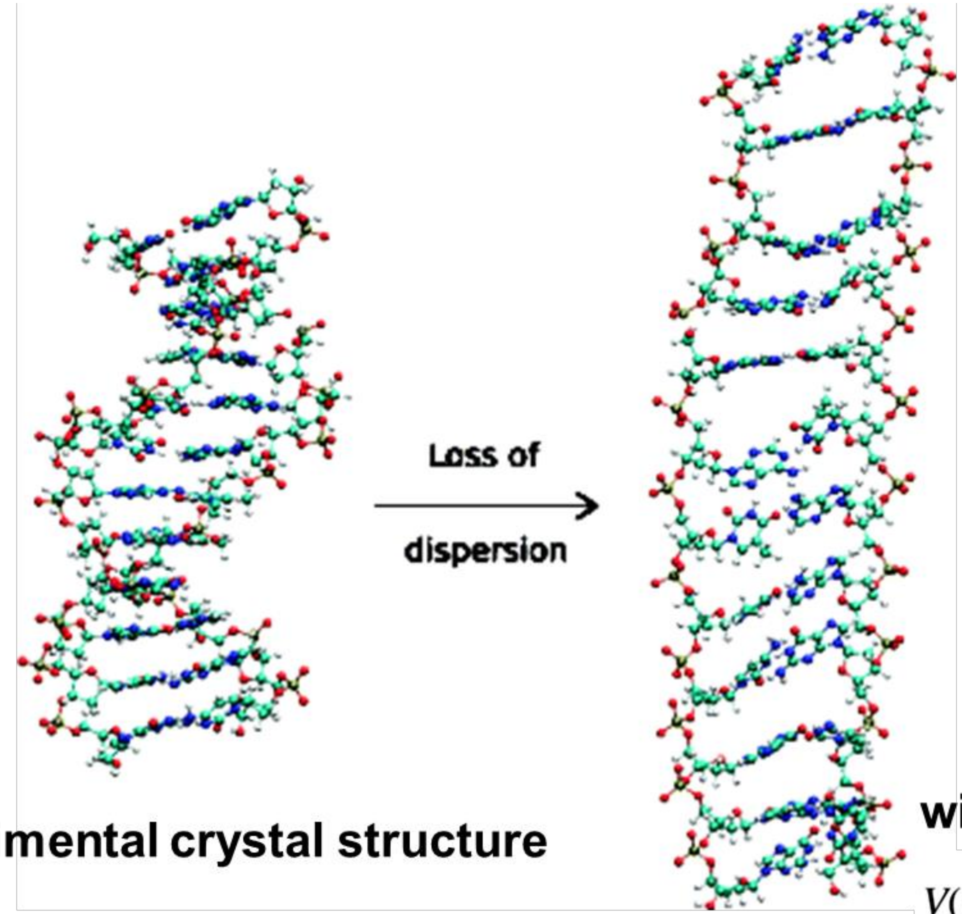
van der Waals corrected DFT

Sanliang Ling

Why van der Waals force is important?



experimental crystal structure

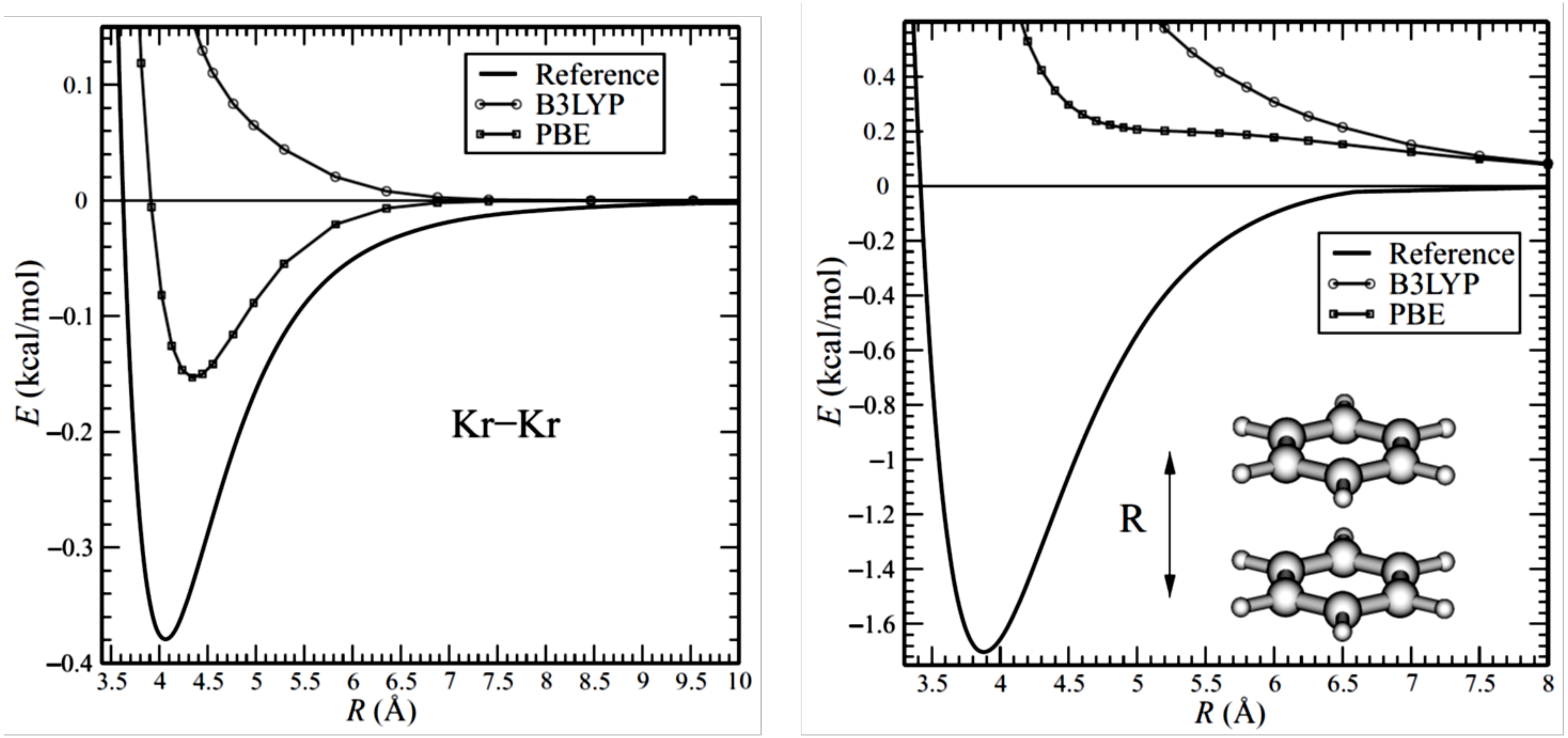
after MD simulation
without dispersion term

$$V(r) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

helical to ladder structural transition in DNA

Hobza et al. J. Am. Chem. Soc., 130, 16055 (2008)

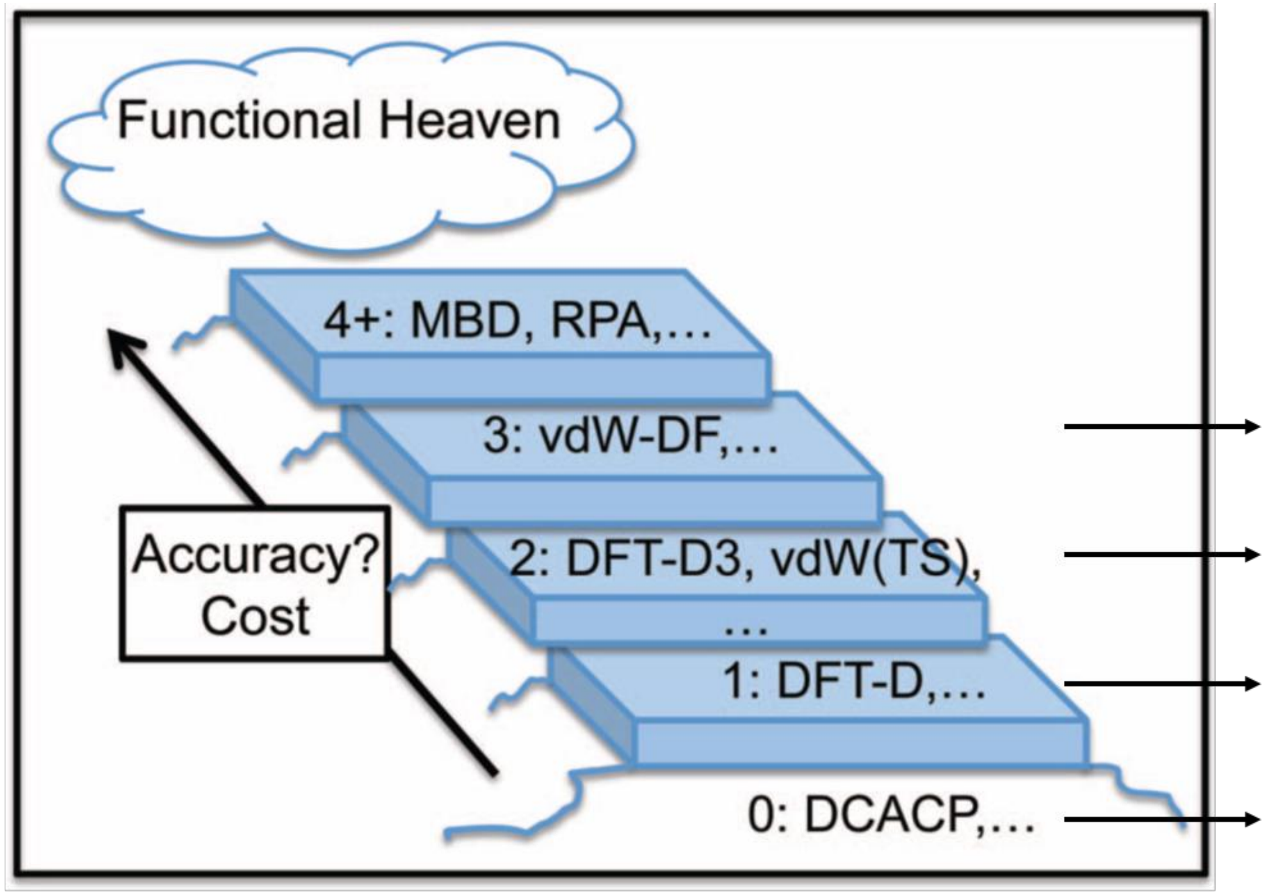
Conventional DFT Fails for vdW Force



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



→ non-local vdW correlation functional

→ environment dependent C_6 correction

→ simple C_6 correction

→ vdW corrected pseudopotential

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

“stairway to heaven” for long range dispersion interactions

Simple C6 Correction

$$E_{\mathrm{disp}} = -\sum_{\mathrm{A,B}} \underbrace{C_6^{\mathrm{AB}}}_{\text{dispersion coefficients}} / r_{\mathrm{AB}}^6$$

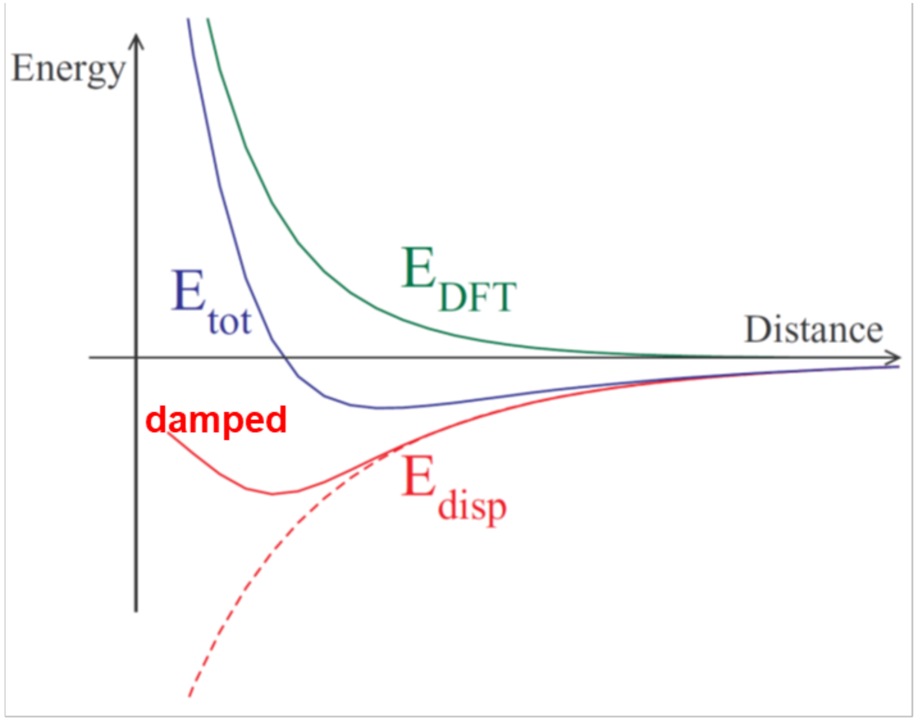
pairwise additive

dispersion coefficients

$$\boxed{E_{\mathrm{tot}} = \underbrace{E_{\mathrm{DFT}}}_{\text{conventional DFT}} + E_{\mathrm{disp}}}$$

conventional DFT

Damped C6 Correction



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

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

DFT+D2

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

$$C_6^{\mathrm{a}} = 0.05 N I_{\mathrm{p}}^{\mathrm{a}} \alpha^{\mathrm{a}}$$

atomic ionization potentials

static polarizability

Grimme, J. Comput. Chem., 27, 1787 (2006)

DFT+D2

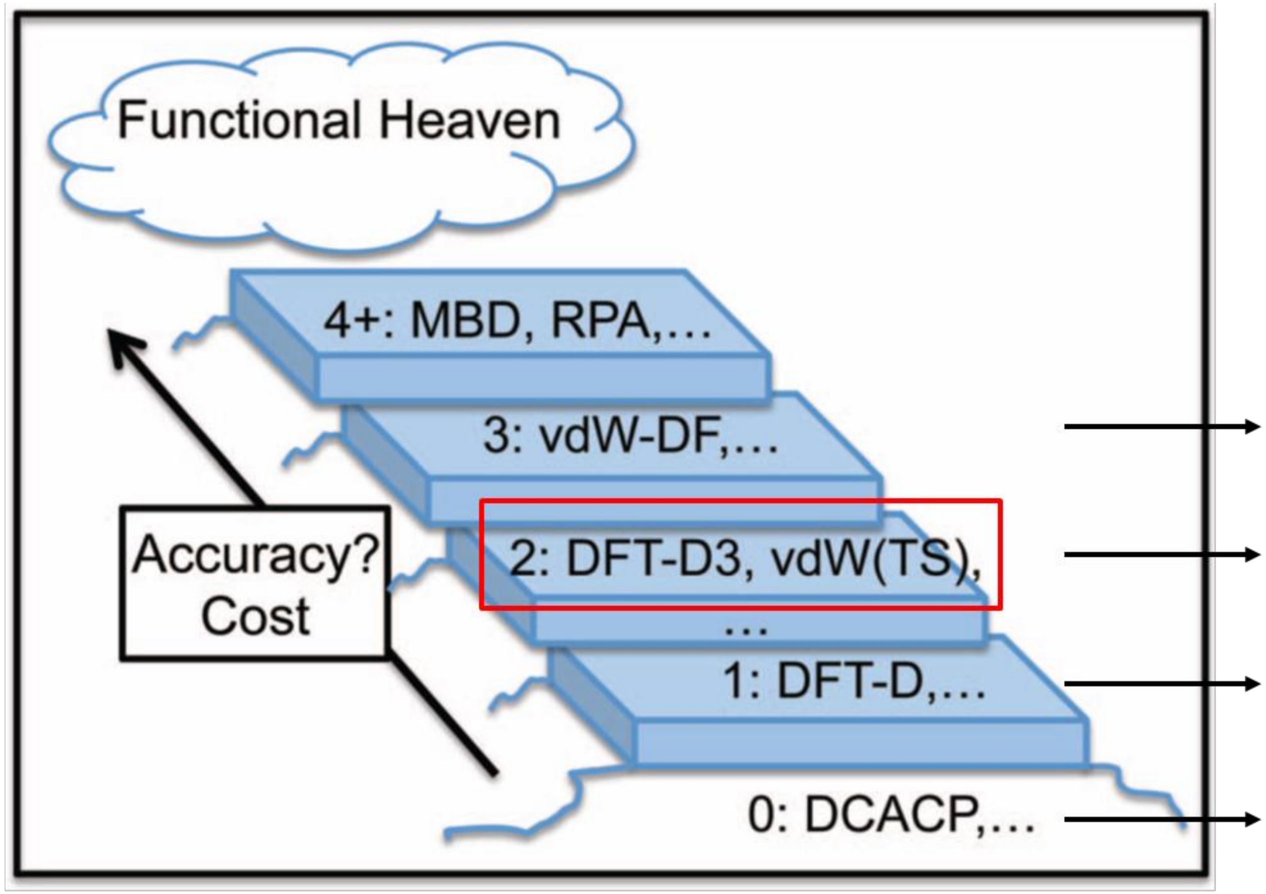
```
&XC
    &XC_FUNCTIONAL PBE
    &END XC_FUNCTIONAL
    &vdW_POTENTIAL
      DISPERSION_FUNCTIONAL PAIR_POTENTIAL
      &PAIR_POTENTIAL
        TYPE DFTD2
        REFERENCE_FUNCTIONAL PBE
        SCALING  ???
        R_CUTOFF ???
      &END PAIR_POTENTIAL
    &END vdW_POTENTIAL
&END XC
```

SCALING ??? ← XC-dependent

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

(see more examples in $CP2K/cp2k/tests/QS/regtest-dft-vdw-corr-1)

Methods to include vdW force in Conventional DFT



→ non-local vdW correlation functional

→ environment dependent C_6 correction

→ simple C_6 correction

→ vdW corrected pseudopotential

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

“stairway to heaven” for long range dispersion interactions

Environment Dependent C6 Correction

DFT-D3: pre-calculated C_6 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 C_6 coefficients of a free-atom reference

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

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DFT+D3

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

$$Z = \sum_{i}^{N_A} \sum_{j}^{N_B} C_{6,\mathrm{ref}}^{AB}(\mathrm{CN}_i^A,\mathrm{CN}_j^B) L_{ij},$$

$$W = \sum_{i}^{N_A} \sum_{j}^{N_B} L_{ij},$$

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

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

coordination number

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

DFT+D3

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

three-body term

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

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

DFT+D3

```
&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 Edisp
      &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)

Semi-empirical+D3

```
&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
```

(see more examples in $CP2K/cp2k/tests/SE/regtest-2)

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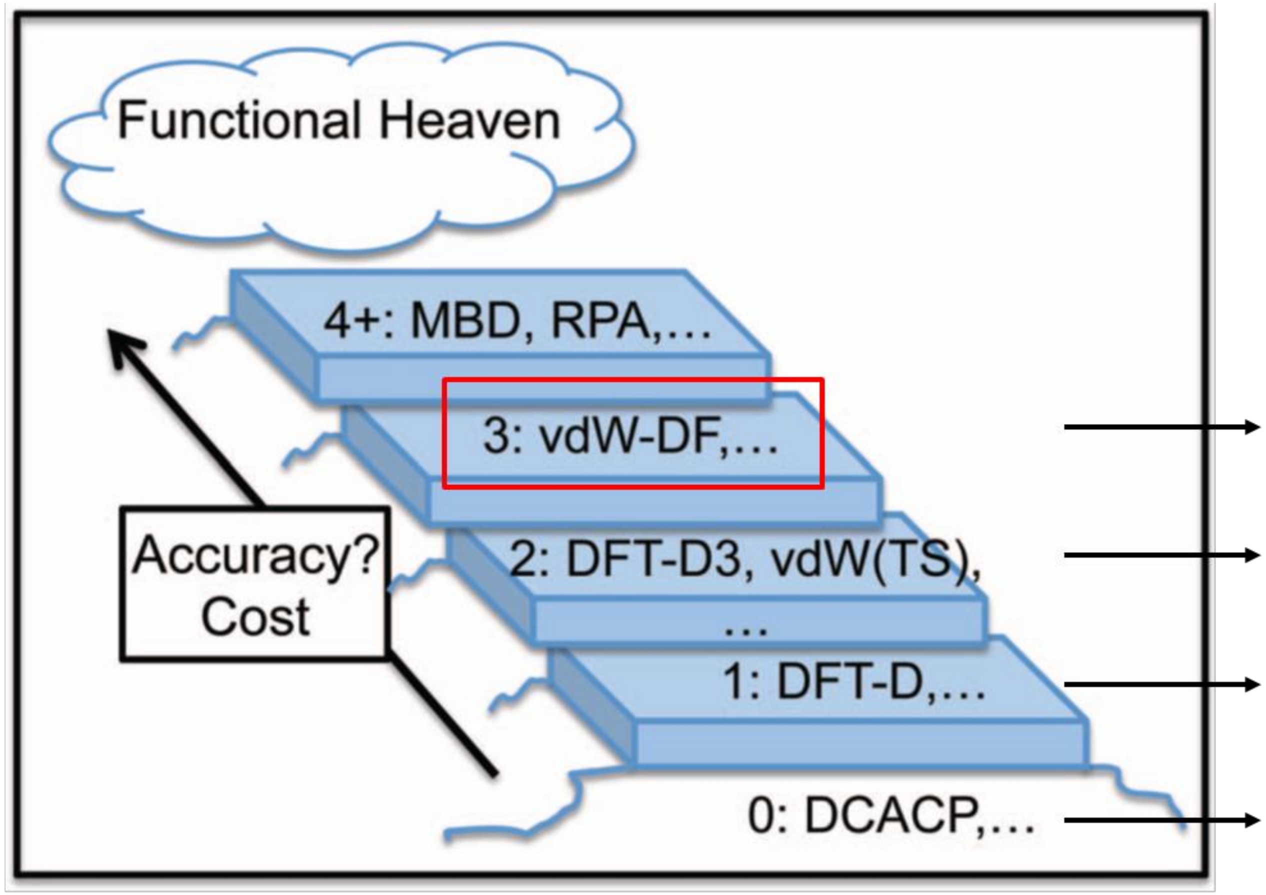
Methods to include vdW force in Conventional DFT



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

non-local vdW correlation functional

environment dependent C_6 correction

simple C_6 correction

vdW corrected pseudopotential

“stairway to heaven” for long range dispersion interactions

Non-local vdW Correlation Functional

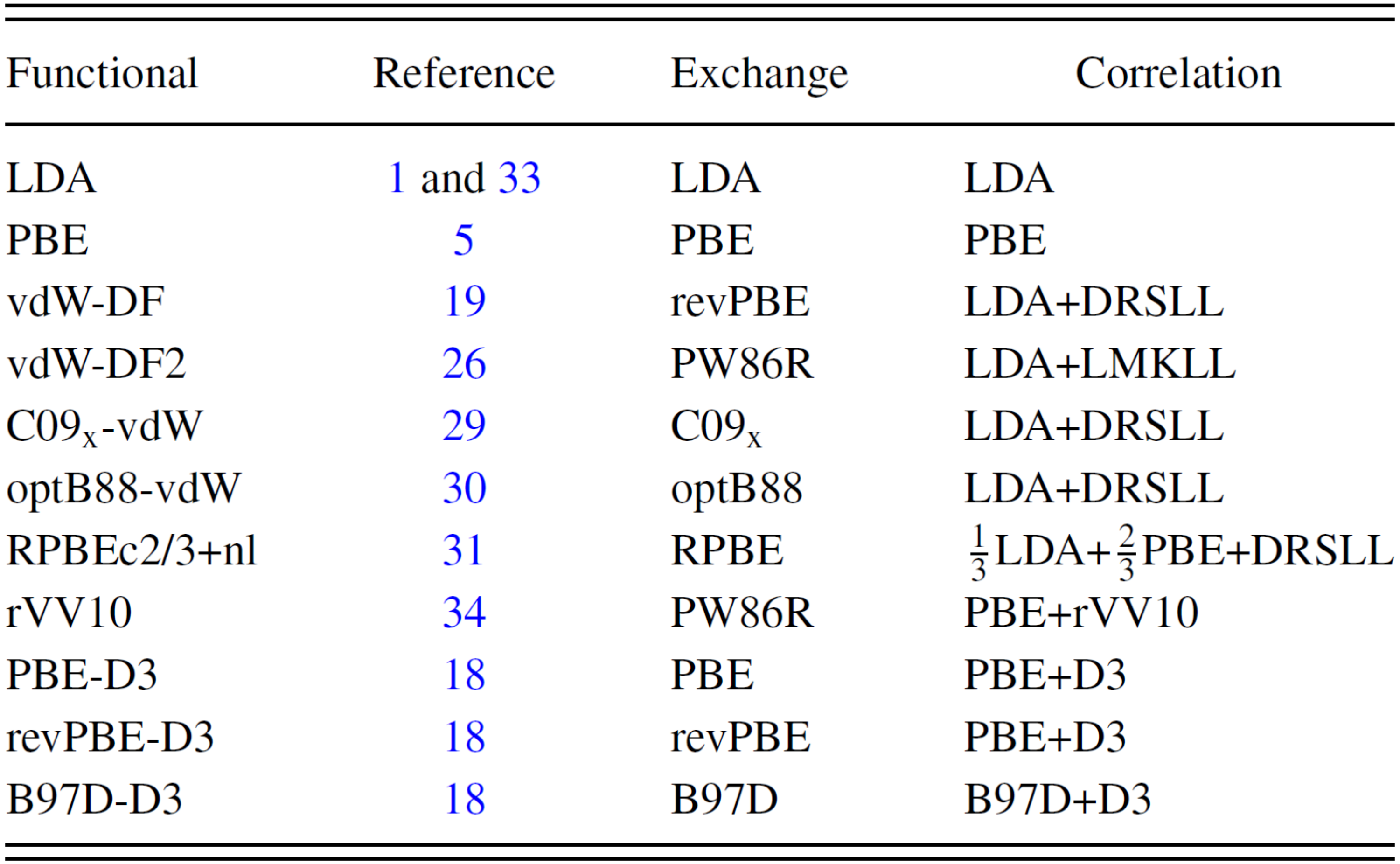
$$E_{\mathrm{xc}} = E_{\mathrm{x}}^{\mathrm{GGA}} + E_{\mathrm{c}}^{\mathrm{LDA}} + E_{\mathrm{c}}^{\mathrm{nl}}$$

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

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

Michaelides et al., J. Chem. Phys., 137, 120901 (2012)
Hutter et al., J. Chem. Phys., 138, 204103 (2013)

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

Hutter et al., J. Chem. Phys., 138, 204103 (2013)

vdW-DF

```
&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
          KERNEL_FILE_NAME vdW_kernel_table.dat
          CUTOFF  ???
        &END NON_LOCAL
     &END vdW_POTENTIAL
&END XC
```

revPBE exchange

LDA correlation

type of non-local vdW correlation functional

cutoff of FFT grid used to calculate E_c^{nl}

(see more examples in $CP2K/cp2k/tests/QS/regtest-dft-vdw-corr-3)

rVV10

```
&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
          PARAMETERS 6.3 0.0093
          KERNEL_FILE_NAME rVV10_kernel_table.dat
          CUTOFF  ???
        &END NON_LOCAL
     &END vdW_POTENTIAL
&END XC
```

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

← **parameters relevant to rVV10**

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

(see more examples in $CP2K/cp2k/tests/QS/regtest-dft-vdw-corr-3)

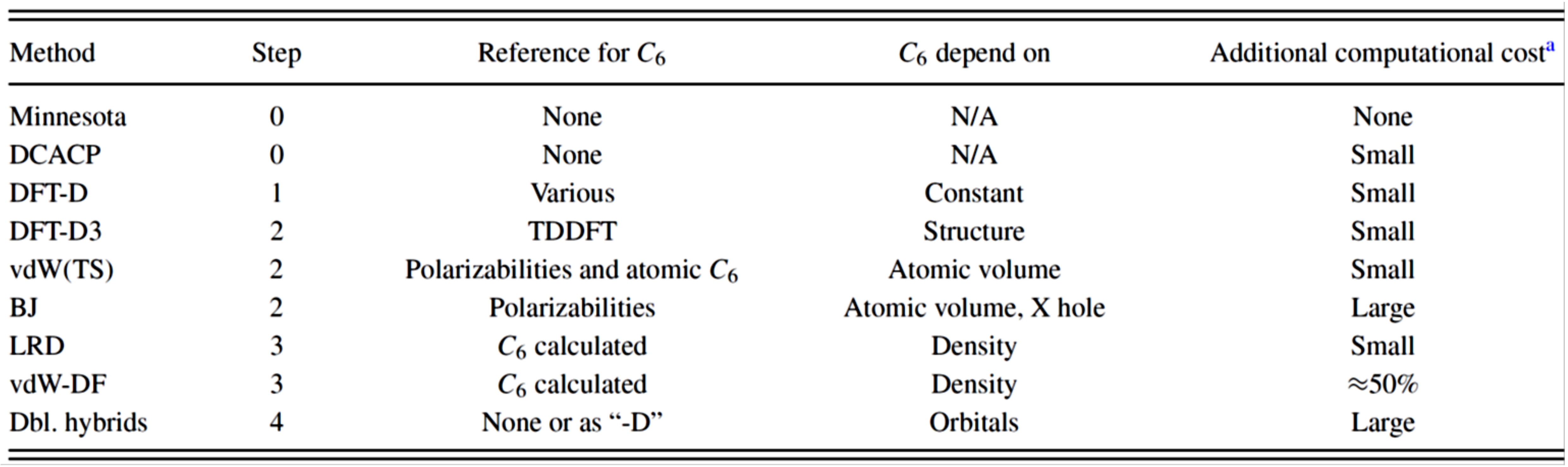
meta-GGA: M06-L

```
&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

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

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**

Methods beyond DFT

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

Further Reading

Self-Interaction Energy and Dispersion (by Prof Juerg Hutter)
http://www.cecam.org/upload/talk/presentation_2988.pdf

Van der Waals Corrections to DFT (by Dr Ari Paavo Seitsonen)
http://www.cecam.org/upload/talk/presentation_5738.pdf

Post HF: MP2 and RPA in CP2K (by Jan Wilhelm)
https://www.cp2k.org/_media/events:2015_cecam_tutorial:wilhelm_posthf.pdf

Van der Waals corrected DFT (by myself)
https://www.cp2k.org/_media/events:2015_cecam_tutorial:ling_vdw.pdf