Exchange and Correlations Functionals

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Exchange-correlation functional

- **Write down total kinetic energy functional as the sum of non-interacting particle density (n) and the one that represents rest of the kinetic energy functional**

$$T[n] = T_s[n] + T_c[n]$$

where,

$$T_s[n] = -\frac{\hbar^2}{2m} \sum_i^N \int d^3r \, \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r})$$
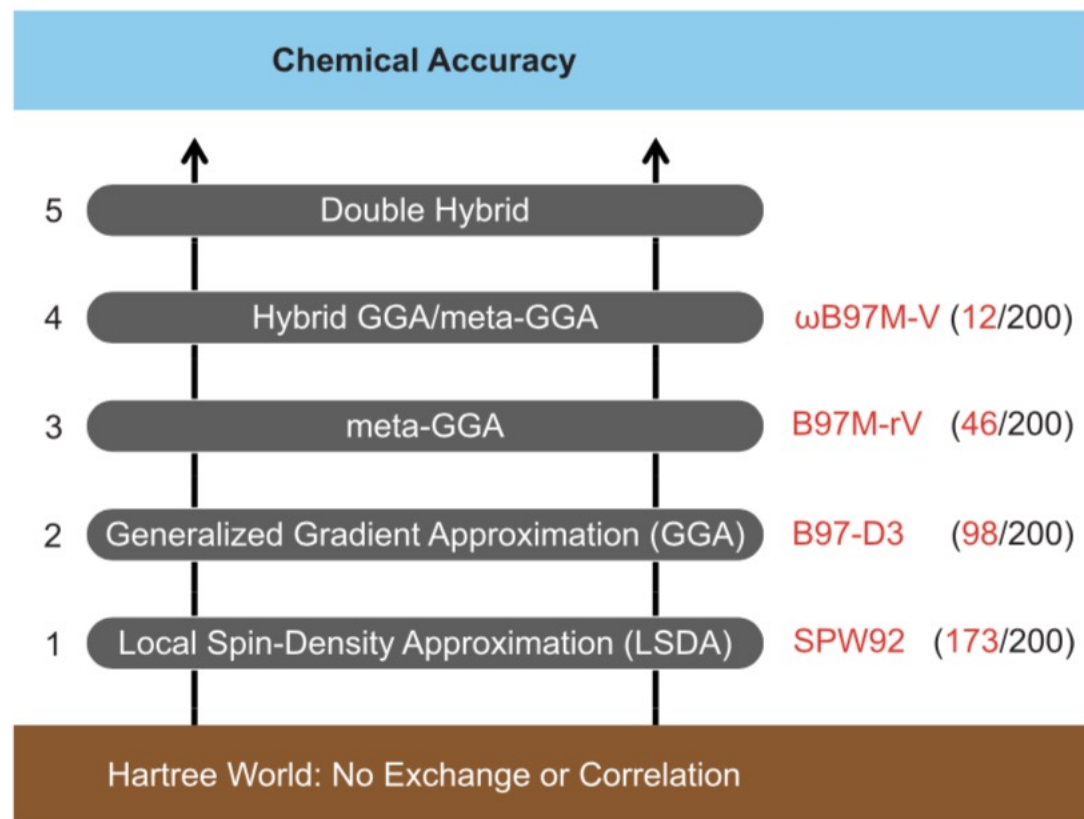
We rewrite the exact energy functional as:

$$E[n] = T[n] + U[n] + V[n] = T_s[\{\phi_i[n]\}] + U_H[n] + E_{xc}[n] + V[n]$$

Capelle, *Brazilian Journal of Physics*, **36, 1318-1343, 2006**

Perdew's Jacob's ladder

Mardirossian and Head-Gordon, *Mol. Phys.***, 115, 2315-2372, 2017**

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Local density approximation (LDA)

Exchange Functional (based on the exact exchange energy of homogeneous electron system):

$$E_x^{LDA}[n] = -\frac{3q^2}{4}\left(\frac{3}{\pi}\right)^{1/3} \int d^3r\, n(\mathbf{r})^{4/3}$$

The correlation functionals are parameterized against quantum Monte Carlo results for uniform electron gas. The overall exchange-correlation functional is of the form:

$$E_{xc}[n] \approx E_{xc}^{LDA}[n] = \int d^3r\, e_{xc}^{hom}(n)|_{n \to n(\mathbf{r})} = \int d^3r\, e_{xc}^{hom}(n(\mathbf{r}))$$

Success of LDA is primarily due to the cancellation of errors (E_X is overestimated while the E_C is underestimated]

Capelle, *Brazilian Journal of Physics*, 36, 1318-1343, 2006

Semilocal functionals

Gradient expansion approximations (GEA, $|\nabla n(r)|$, $|\nabla n(r)|^2$, $\nabla^2(n(r))$)

$$T_s[n] \approx T_s^W[n] = T_s^{LDA}[n] + \frac{\hbar^2}{8m} \int d^3r \, \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}$$

$$E_x[n] \approx E_x^{GEA(2)}[n] = E_x^{LDA}[n] - \frac{10q^2}{432\pi(3\pi^2)^{1/3}} \int d^3r \, \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})^{4/3}}$$

Generalized gradient approximation (GGA)

$$E_{xc}^{GGA}[n] = \int d^3r \, f(n(\mathbf{r}), \nabla n(\mathbf{r}))$$

Different choices for $f(n(r), \nabla n(r))$ lead to different GGA density functionals such as PBE (used extensively in physics community) and LYP (used extensively in chemistry community)

GGA: improved molecular structure and energetics; can not account for weak interactions such as van der Waals.

Capelle, *Brazilian Journal of Physics*, 36, 1318-1343, 2006

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Comparison of different LDA and GGA functions

method	$-E$/a.u.
Thomas-Fermi	625.7
Hartree-Fock	526.818
OEP (exchange only)	526.812
LDA (exchange only)	524.517
LDA (VWN)	525.946
LDA (PW92)	525.940
LDA-SIC(PZ)	528.393
ADA	527.322
WDA	528.957
GGA (B88LYP)	527.551
experiment	527.6

Ground state energy of the argon atom in atomic units (Hartree)

Capelle, *Brazilian Journal of Physics*, 36, 1318-1343, 2006

Meta-GGA functionals

Exchange-correlation functional depends not only on the density, gradient of the density but also on the Kohn-Sham kinetic energy density

$$\tau(\mathbf{r}) = \frac{\hbar^2}{2m} \sum_i |\nabla \phi_i(\mathbf{r})|^2$$

$$E_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r}), \tau(\mathbf{r})]$$

The additional degree of freedom is used to satisfy:
- **self-interaction corrected correlation functional**
- **recovery of fourth order gradient expansion for the exchange**
- **finite exchange potential at the nucleus**

Capelle, *Brazilian Journal of Physics*, 36, 1318-1343, 2006

Hybrid GGA, meta GGA

General form of global hybrid functionals is:

$$E_{xc}^{GH} = c_x E_x^{HF} + (1 - c_x) E_x^{DFT} + E_c^{DFT}$$

$$E_{xc}^{B3PW91} = c_x E_x^{HF} + (1 - c_x - a_x) E_x^S + a_x E_x^{B88}$$
$$+ (1 - a_c) E_c^{PW92} + a_c E_c^{PW91}$$

where $c_x = 0.20, a_x = 0.72, and\ a_c = 0.81$

Other common hybrid functionals are B3LYP, PBE0, etc.
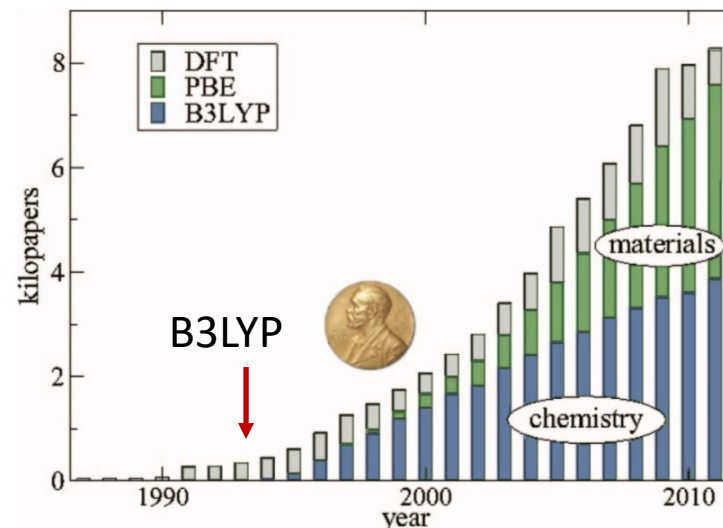
Burke, *J. Chem. Phys.*, **136**, 150901, 2018

Mardirossian and Head-Gordon, *Mol. Phys.*, **115**, 2315-2372, 2017

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Range separated functionals

Range separated functionals attempt to address self-interaction error and are given by the following form:

$$E_{xc}^{\mathrm{RSH}} = c_{x,\mathrm{sr}}E_{x,\mathrm{sr}}^{\mathrm{HF}} + c_{x,lr}E_{x,\mathrm{lr}}^{\mathrm{HF}} + \left(1 - c_{x,\mathrm{sr}}\right)E_{x,sr}^{\mathrm{DFT}}$$
$$+ \left(1 - c_{x,\mathrm{lr}}\right)E_{x,\mathrm{lr}}^{\mathrm{DFT}} + E_c^{\mathrm{DFT}}$$

Common examples include: ωB97, ωB97X, LRC-ωPBE, etc.
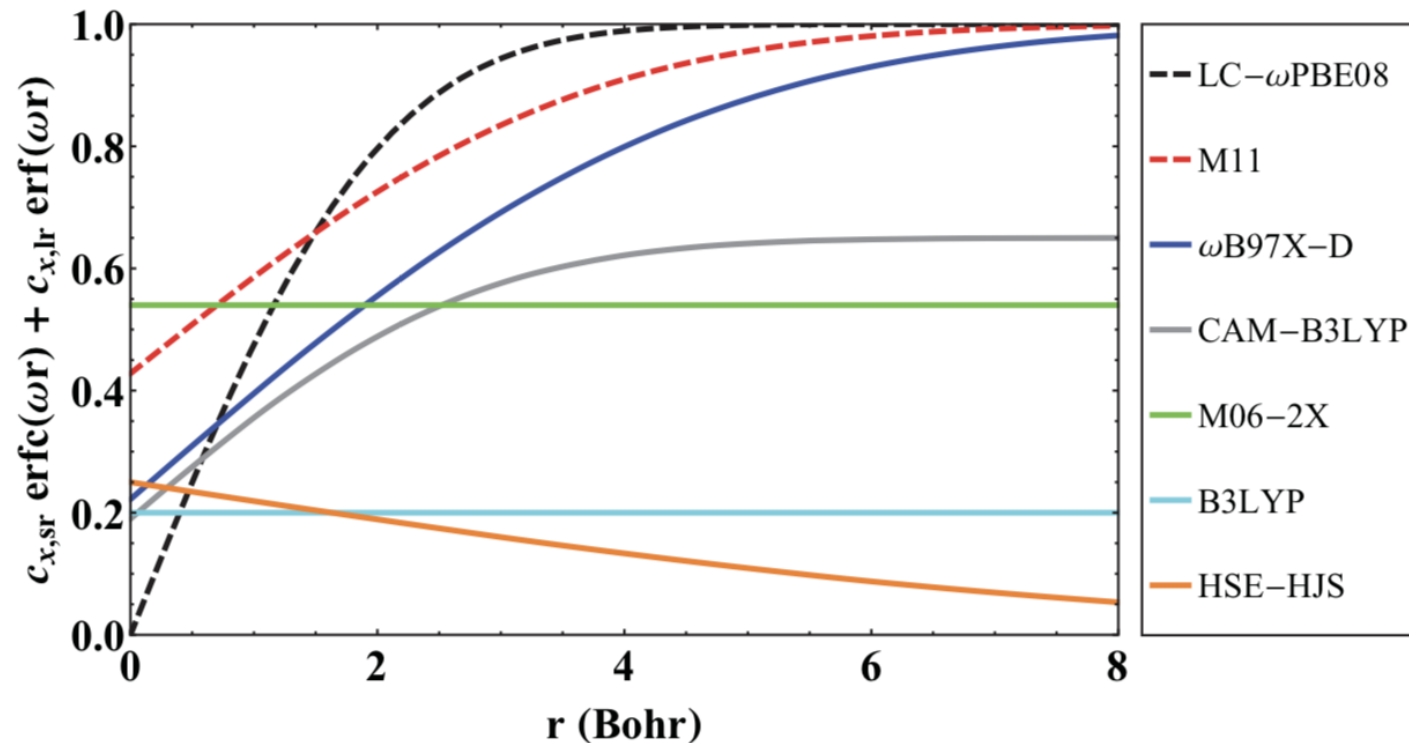
Mardirossian and Head-Gordon, *Mol. Phys.*, 115, 2315-2372, 2017

Another short coming of DFT functionals is the inability to capture vdW interactions
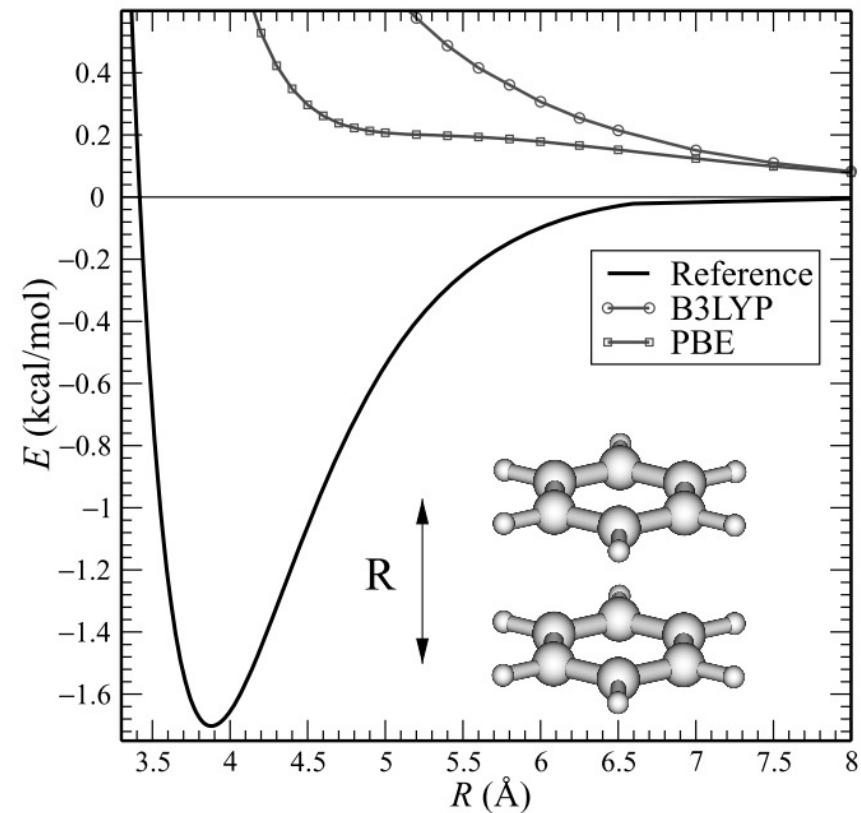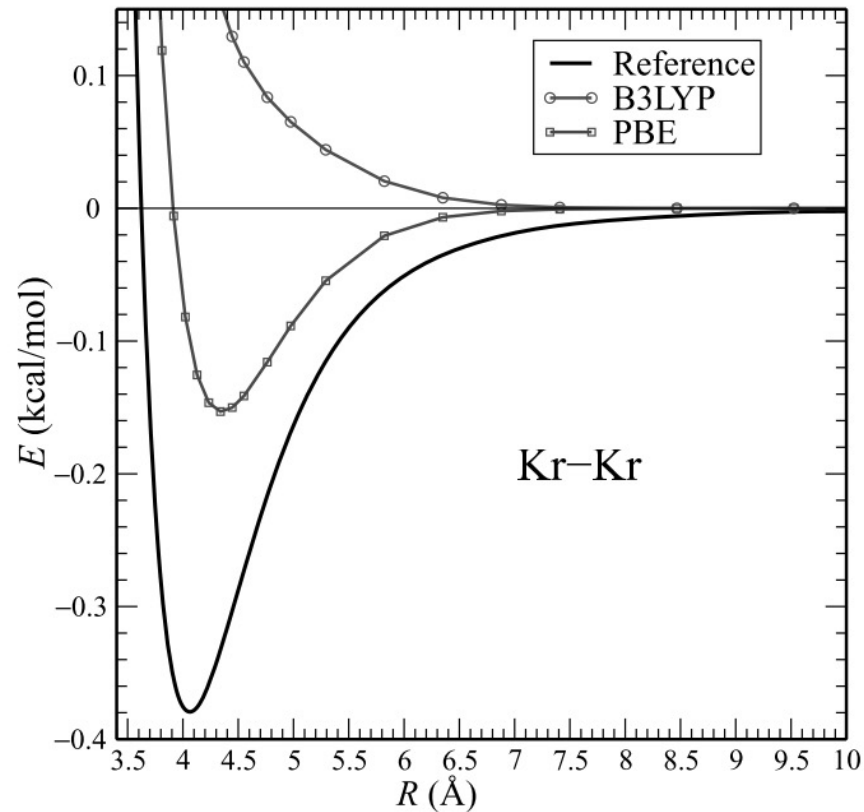
Grimme, *Comput. Mol. Sci.*, 1, 211-228, 2011

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Dispersion-corrected/nonlocal density functionals

Grimme's dispersion correction model:

$$E_{\text{disp}}^{\text{DFT}-D} = -\sum_{A<B} \sum_{n=6,8,\ldots} s_n \frac{C_n^{AB}}{R_{AB}^n} f_{\text{damp},n}\left(R_{AB}\right)$$

Nonlocal density functionals

$$E_{\text{disp}}^{\text{VV10}} = \int d\mathbf{r}\, \rho\left(\mathbf{r}\right) \left[\frac{1}{32} \left(\frac{3}{b^2} \right)^{\frac{3}{4}} + \frac{1}{2} \int d\mathbf{r}'\, \rho\left(\mathbf{r}'\right) \Phi\left(\mathbf{r}, \mathbf{r}'\right) \right]$$

Mardirossian and Head-Gordon, *Mol. Phys.*, 115, 2315-2372, 2017

Accuracy of different dispersion correction models
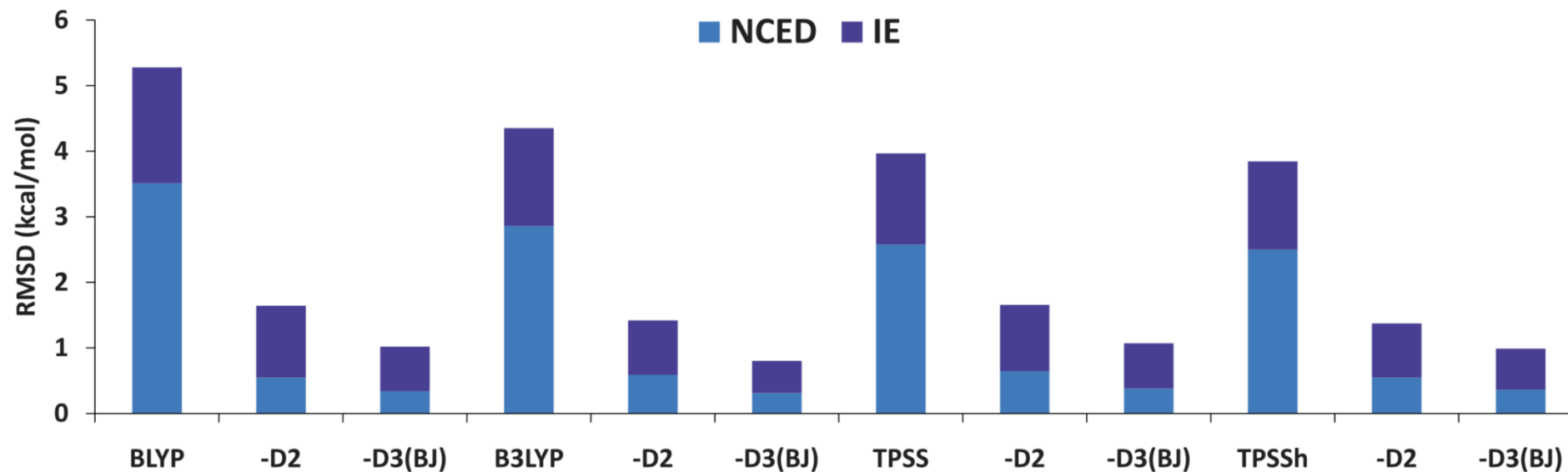
Mardirossian and Head-Gordon, *Mol. Phys.*, 115, 2315-2372, 2017

General accuracy for selected MN functionals for atomization energies bond dissociation

Mardirossian and Head-Gordon, *Mol. Phys.*, 115, 2315-2372, 2017

Number of parameters in different density functionals

Functional	Parameters
B97-D	9
B97-2	9
ωB97X-V	10
B97-K	10
B97-2-D2	10
B97-1	10
B97-D3(0)	11
B97-1-D2	11
ωB97M-V	12
B97M-V	12
B97M-rV	12
B97-D3M(BJ)	12
B97-D3(BJ)	12
B97	12
ωB97	13
B97-D2	13
ωB97X	14
ωB97X-D	15
HCTH/93	15
HCTH/407	15
HCTH/147	15
HCTH/120	15
ωB97X-D3	16
τ-HCTH	16
B97-3	16
τ-HCTHh	17
HCTH/120-D3(0)	17
BMK	17
B97-3-D2	17
HCTH/120-D3(BJ)	18
BMK-D2	18
M05-2X	19
BMK-D3(0)	19
M05-2X-D3(0)	20
BMK-D3(BJ)	20

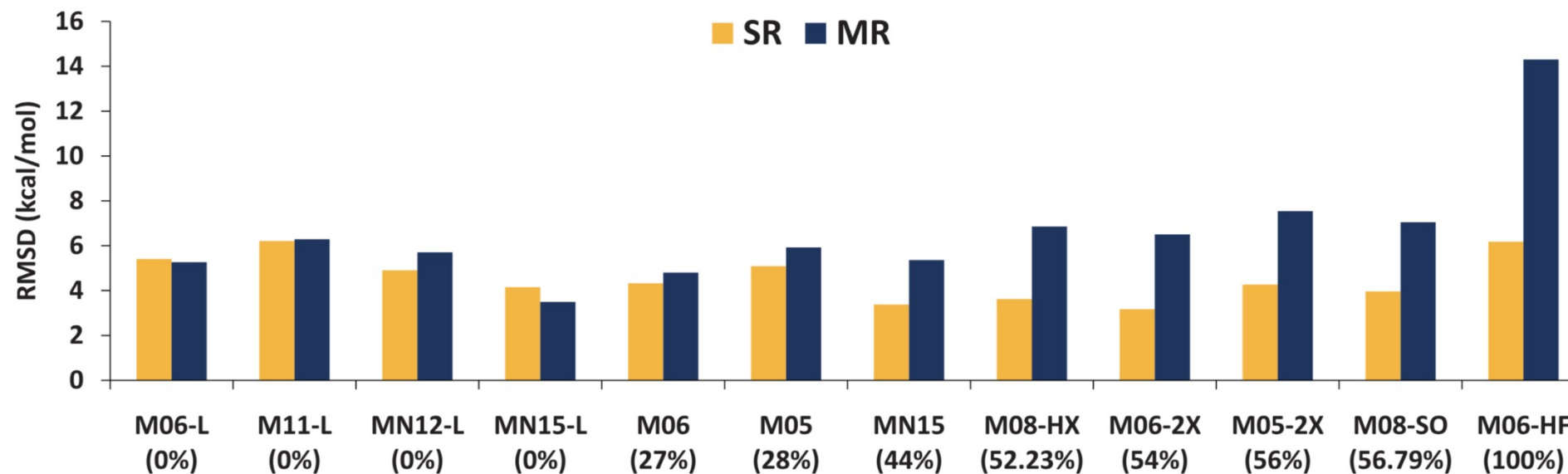| Functional	Parameters
ωM05-D	21
SOGGA11-X	21
N12	21
M05	22
N12-D3(0)	23
SOGGA11-X-D3(BJ)	24
M05-D3(0)	24
ωM06-D3	25
N12-SX	26
GAM	26
N12-SX-D3(BJ)	29
M06-2X	29
M06-2X-D3(0)	30
M06-2X-D2	30
M06-HF	32
M06-HF-D3(0)	33
M06	33
M06-L	34
M06-D3(0)	34
M06-D2	34
M06-L-D3(0)	35
M06-L-D2	35
M11	40
M11-D3(BJ)	42
M11-L	44
M08-SO	44
M11-L-D3(0)	46
M08-HX	47
MN15-L	58
MN12-SX	58
MN12-L	58
MN15	59
MN12-L-D3(BJ)	60
MN12-SX-D3(BJ)	61
mBEEF	64

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Accuracy of functionals for bond lengths and binding energies

Functional	NCED	NCEC	NCD	IE	ID	TCE	TCD	BH	EBL	EBE
SPW92	2.14	37.77	7.60	2.22	6.76	42.23	65.35	19.55	0.195	2.81
PBE	1.96	4.08	3.26	1.15	6.53	9.22	15.58	9.17	0.327	2.16
TPSS	2.58	8.90	2.63	1.39	8.44	5.94	10.45	8.03	0.398	2.80
B3LYP	2.86	8.91	1.77	1.49	11.10	5.24	11.97	5.96	0.643	3.04
PBE-D3(BJ)	0.46	5.78	3.67	0.71	5.19	9.67	17.20	9.99	0.049	0.42
revPBE-D3(BJ)	0.49	6.60	2.54	0.77	5.21	6.60	9.91	8.30	0.053	0.44
BLYP-D3(BJ)	0.34	2.18	2.82	0.68	11.40	6.63	11.11	9.91	0.031	0.25
B97-D3(BJ)	0.47	4.82	2.52	0.78	9.15	4.66	7.92	8.32	0.045	0.42
TPSS-D3(BJ)	0.38	2.28	3.06	0.69	6.47	5.88	8.86	8.72	0.070	0.33
SCAN-D3(BJ)	0.54	9.18	3.41	0.55	4.46	5.25	6.39	7.83	0.037	0.60
M06-L	0.55	2.20	1.87	0.71	10.16	5.44	12.97	6.85	0.043	0.60
B97M-rV	0.22	0.67	2.04	0.28	6.45	3.57	4.78	4.36	0.025	0.17
PBE0-D3(BJ)	0.44	4.45	2.28	0.58	3.47	4.76	8.72	4.91	0.043	0.46
B3LYP-D3(BJ)	0.31	3.02	1.88	0.49	8.51	3.72	5.97	5.65	0.022	0.37
ωB97X-D	0.37	1.01	1.46	0.67	3.11	3.44	5.79	2.34	0.038	0.42
ωB97X-V	0.24	0.64	1.23	0.27	2.72	3.41	5.01	2.44	0.042	0.15
TPSSh-D3(BJ)	0.36	1.73	2.49	0.62	5.29	5.55	5.92	6.63	0.068	0.33
M06-2X	0.43	2.52	0.99	0.50	5.56	3.29	7.23	2.57	0.077	0.33
MN15	0.47	1.83	0.96	0.71	4.06	3.76	6.44	1.98	0.042	0.60
ωB97M-V	0.18	0.48	1.13	0.28	2.05	2.48	4.30	1.68	0.014	0.15
Minimum	0.18	0.48	0.91	0.27	2.05	2.48	4.30	1.68	0.014	0.15
Best	ωB97M-V	ωB97M-V	M08-SO	B97M-V	ωB97M-V	ωB97M-V	ωB97M-V	ωB97M-V	ωB97M-V	ωB97X-V

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Open-shell non-covalent or dimers characterized by significant electron delocalization

Functional	TA13	XB18	Bauza30	CT20	XB51
SPW92	11.49	4.47	9.63	1.32	5.34
PBE	6.22	0.80	3.59	0.42	1.88
TPSS	5.06	0.80	2.76	0.64	1.65
B3LYP	3.37	1.26	1.66	0.70	1.28
PBE-D3(BJ)	6.54	1.36	4.20	0.49	2.43
revPBE-D3(BJ)	5.06	0.45	2.55	0.39	1.63
BLYP-D3(BJ)	6.10	0.87	2.32	0.43	1.86
B97-D3(BJ)	5.31	0.38	2.31	0.43	1.50
TPSS-D3(BJ)	5.46	1.02	3.49	0.34	2.13
SCAN-D3(BJ)	4.89	1.57	4.57	0.41	2.25
M06-L	3.78	0.39	1.95	0.40	0.89
B97M-rV	4.15	0.63	2.12	0.32	0.91
PBE0-D3(BJ)	3.31	0.38	3.19	0.25	1.12
B3LYP-D3(BJ)	3.85	0.37	1.87	0.28	1.04
ωB97X-D	2.91	0.98	1.34	0.50	0.89
ωB97X-V	2.88	0.51	0.81	0.11	0.63
TPSSh-D3(BJ)	4.20	0.62	3.06	0.28	1.59
M06-2X	1.38	0.58	1.30	0.23	0.69
MN15	2.12	0.28	0.81	0.19	0.52
ωB97M-V	2.75	0.42	0.60	0.11	0.54
Minimum	**1.38**	**0.09**	**0.60**	**0.10**	**0.44**
Best	M06-2X	ωB97X	ωB97M-V	PW6B95-D3(0)	M05-D3(0)

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Barrier heights

Functional	BHPERI26	CRBH20	DBH24	CR20	HTBH38	NHTBH38	PX13	WCPT27
SPW92	13.24	3.45	16.63	14.26	18.59	15.81	42.96	24.79
PBE	4.38	7.97	9.99	3.13	10.08	10.30	13.56	9.98
TPSS	2.88	10.14	9.21	5.69	8.38	10.06	8.37	5.75
B3LYP	5.10	8.49	4.79	10.83	4.89	5.52	3.38	1.78
PBE-D3(BJ)	6.87	7.91	10.36	1.83	10.63	10.62	15.77	11.56
revPBE-D3(BJ)	6.54	10.95	8.74	4.09	8.63	9.14	7.31	8.19
BLYP-D3(BJ)	4.29	16.62	9.56	9.77	9.42	10.61	9.12	7.20
B97-D3(BJ)	4.24	14.16	7.63	9.53	8.28	7.58	6.46	6.72
TPSS-D3(BJ)	5.70	10.08	9.67	2.68	8.99	10.46	10.95	7.70
SCAN-D3(BJ)	5.74	6.21	8.00	1.97	7.98	8.61	12.64	8.75
M06-L	2.18	13.73	5.24	12.70	4.66	4.86	1.66	2.24
B97M-rV	1.44	7.55	4.97	2.03	4.62	5.33	1.50	2.19
PBE0-D3(BJ)	3.49	1.29	4.68	2.53	5.03	4.68	9.00	6.42
B3LYP-D3(BJ)	1.55	8.29	5.39	6.48	5.62	6.00	6.40	4.29
ωB97X-D	2.40	1.66	2.03	3.68	2.69	1.86	1.62	2.05
ωB97X-V	2.75	3.16	1.75	2.90	2.36	1.69	3.38	2.12
TPSSh-D3(BJ)	4.21	6.44	7.60	1.90	7.21	8.11	8.42	5.82
M06-2X	1.81	1.58	1.08	2.07	1.29	1.67	6.94	3.42
MN15	1.77	1.09	1.82	1.72	1.38	2.55	2.87	2.24
ωB97M-V	1.44	1.23	1.46	0.56	1.72	1.98	2.55	1.82
Minimum	1.21	0.80	1.08	0.56	1.25	1.48	1.04	1.39
Best	PW6B95-D3(0)	ωM05-D	M06-2X	ωB97M-V	M08-HX	M11-D3(BJ)	M06-L-D2	M08-SO

Mardirossian and Head-Gordon, *Mol. Phys.*, 115, 2315-2372, 2017

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How does a beginning user decide what XC functionals to use – likely without understanding the underlying physics/math of why one might be better or worse for a given situation?

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How does a beginning user decide what XC functionals to use – likely without understanding the underlying physics/math of why one might be better or worse for a given situation?

-Ask a physicist/QM developer/expert what might work for your new system/material that no one has ever thought about modeling with QM before

-Look at empirical testing of what has been done on your system or something most similar (ie, has someone gotten the same types of values you want for a similar system and shown a functional that worked well enough)

-Look at what others have used (without perfect validation and possibly unknown error) and be conscious of lack of certainty in conclusions you are reaching…..

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Questions?