Q-CHEM™
A Quantum Leap Into the Future of Chemistry

Quantum Chemistry Winterschool, February 9, 2023

Modern Density Functional Theory

Martin Head-Gordon

Department of Chemistry,
University of California, and,
Chemical Sciences Division
Lawrence Berkeley National Laboratory

BERKELEY LAB
Lawrence Berkeley National Laboratory

Outline

1. Introduction

2. Combinatorial design of density functionals

3. Performance of density functionals

A brief overview of density functional theory

- First Hohenberg-Kohn theorem:

  An exact density functional exists

  E is given in terms of $\rho(\mathbf{r})$:

$$E = \min_{\rho(\mathbf{r})} \left\{ E_{ext}\left[\rho\right] + E^{\text{exact}}_{T+V_{ee}}\left[\rho\right] \right\}$$

$$E_{ext} = \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r}$$

- Variational principle gives the constrained search picture.

$$E = \min_{|\Psi\rangle} \left[\left\langle \Psi \middle| \hat{T}_e + \hat{V}_{ee} + \hat{V}_{ext} \middle| \Psi \right\rangle \right]$$

$$= \min_{\rho(\mathbf{r})} \left\{ E_{ext}\left[\rho\right] + \min_{|\Psi\rangle \to \rho(\mathbf{r})} \left[\left\langle \Psi \middle| \hat{T}_e + \hat{V}_{ee} \middle| \Psi \right\rangle \right] \right\}$$

- So the functional must be modeled:

  Accuracy vs feasibility?

$$E^{\text{model}}_{T+V_{ee}}\left[\rho(\mathbf{r})\right] \cong E^{\text{exact}}_{T+V_{ee}}\left[\rho(\mathbf{r})\right]$$

- Given a functional, & an external potential ($V_{ext}(\mathbf{r})$)....

  Minimize over $\rho(\mathbf{r})$:

$$E = \min_{\rho(\mathbf{r})} \left\{ E_{ext}\left[\rho\right] + E^{\text{model}}_{T+V_{ee}}\left[\rho\right] \right\}$$

Kohn-Sham density functional theory

$$E_{T+V_{ee}}^{\text{model}}\left[\rho(\mathbf{r})\right] = E_T\left[\rho\right] + E_J\left[\rho\right] + E_{XC}\left[\rho\right] \qquad E_J = \frac{1}{2}\int \rho(\mathbf{r})\int \rho(\mathbf{r}')\left|\mathbf{r}-\mathbf{r}'\right|^{-1} d\mathbf{r}\, d\mathbf{r}'$$

- Must model kinetic energy (T) & exchange-correlation (XC)

  Largest (inexact) energy contribution is the kinetic energy.

  No satisfactory kinetic energy functional yet exists.

- Kohn-Sham framework: a beautiful sidestep….

  Use KE of non-interacting (NI) electrons with the same $\rho(r)$

  NI-wavefunction is a single determinant.

  Solves n-representability problem for $\rho(r)$: $\rho(\mathbf{r}) = \sum_{i=1}^{n} \left|\phi_i(\mathbf{r})\right|^2$

  Leaves exchange and electron correlation (XC) to specify.

$$E_{T+V_{ee}}^{KS}\left[\rho(\mathbf{r})\right] = E_T^{NI}\left[\rho\right] + E_J\left[\rho\right] + E_{XC}\left[\rho\right] \qquad E_T^{NI} = \sum_{i=1}^{n} \left\langle \phi_i \middle| -\nabla^2/2 \middle| \phi_i \right\rangle$$

- The functional design problem is modeling E_{XC}

Group functionals onto rungs of "Jacob's Ladder"

Rung 4: Hybrid density functionals

1993

Wave function exchange,

Eg.: B3LYP, M06-2X, ωB97X-D

Rung 3: Meta-GGA

1985

$$E_{XC} = \int d\mathbf{r}\ \varepsilon_{XC}\left\{\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \tau(\mathbf{r})\right\}$$

$$\tau(\mathbf{r}) = \sum_i \left|\nabla\phi_i\right|^2$$

Examples: B98, TPSS, M06-L

Rung 2: Generalized gradient approx. (GGA)

1985

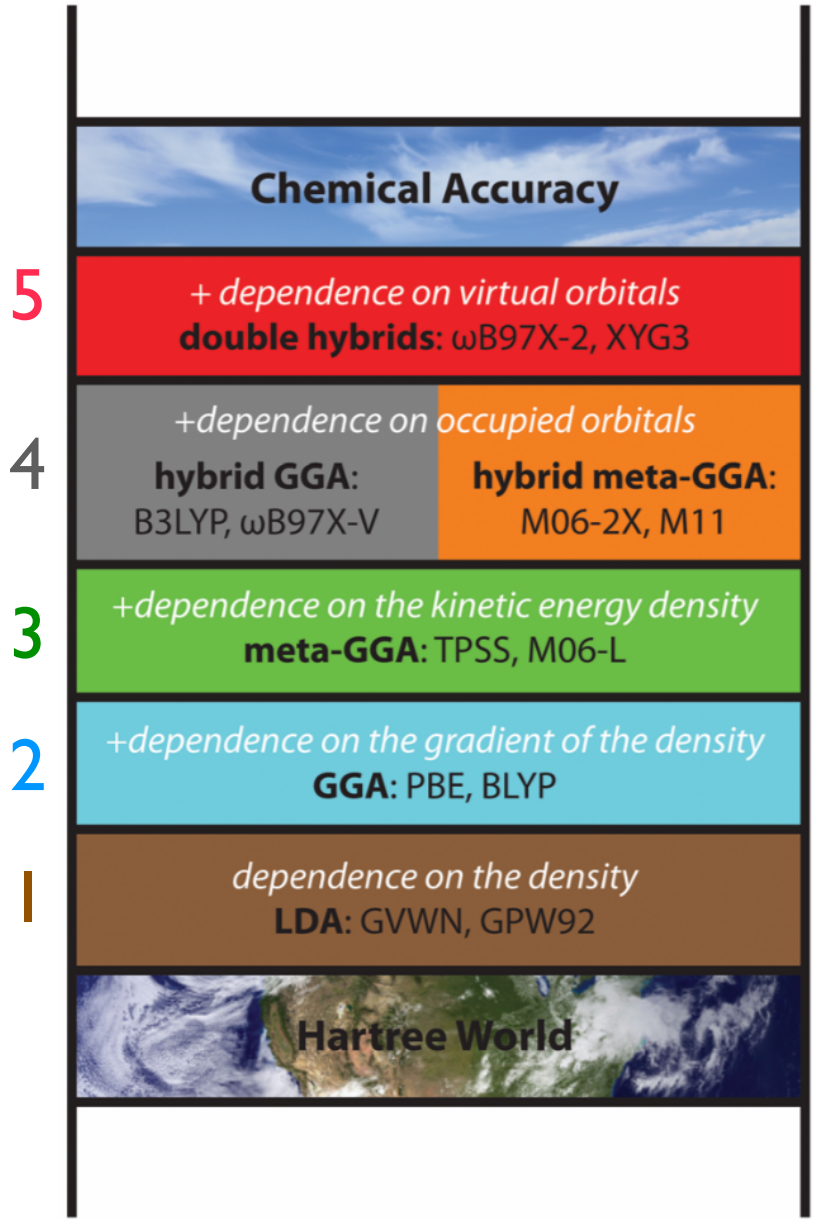
$$E_{XC} = \int d\mathbf{r}\ \varepsilon_{XC}\left\{\rho(\mathbf{r}), \nabla\rho(\mathbf{r})\right\}$$

Examples: BLYP, PBE

Rung 1: Local spin density approx. (LSDA)

1966

$$E_{XC} = \int d\mathbf{r}\ \varepsilon_{XC}\left\{\rho(\mathbf{r})\right\}$$



Group functionals onto rungs of "Jacob's Ladder"

Rung 4: Hybrid density functionals

1993

Wave function exchange,

Eg.: B3LYP, M06-2X, ωB97X-D

Rung 3: Meta-GGA

1985

$$E_{XC} = \int d\mathbf{r}\ \varepsilon_{XC}\left\{\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \tau(\mathbf{r})\right\}$$

$$\tau(\mathbf{r}) = \sum_i \left|\nabla\phi_i\right|^2$$

Examples: B98, TPSS, M06-L

Rung 2: GGAs

1985

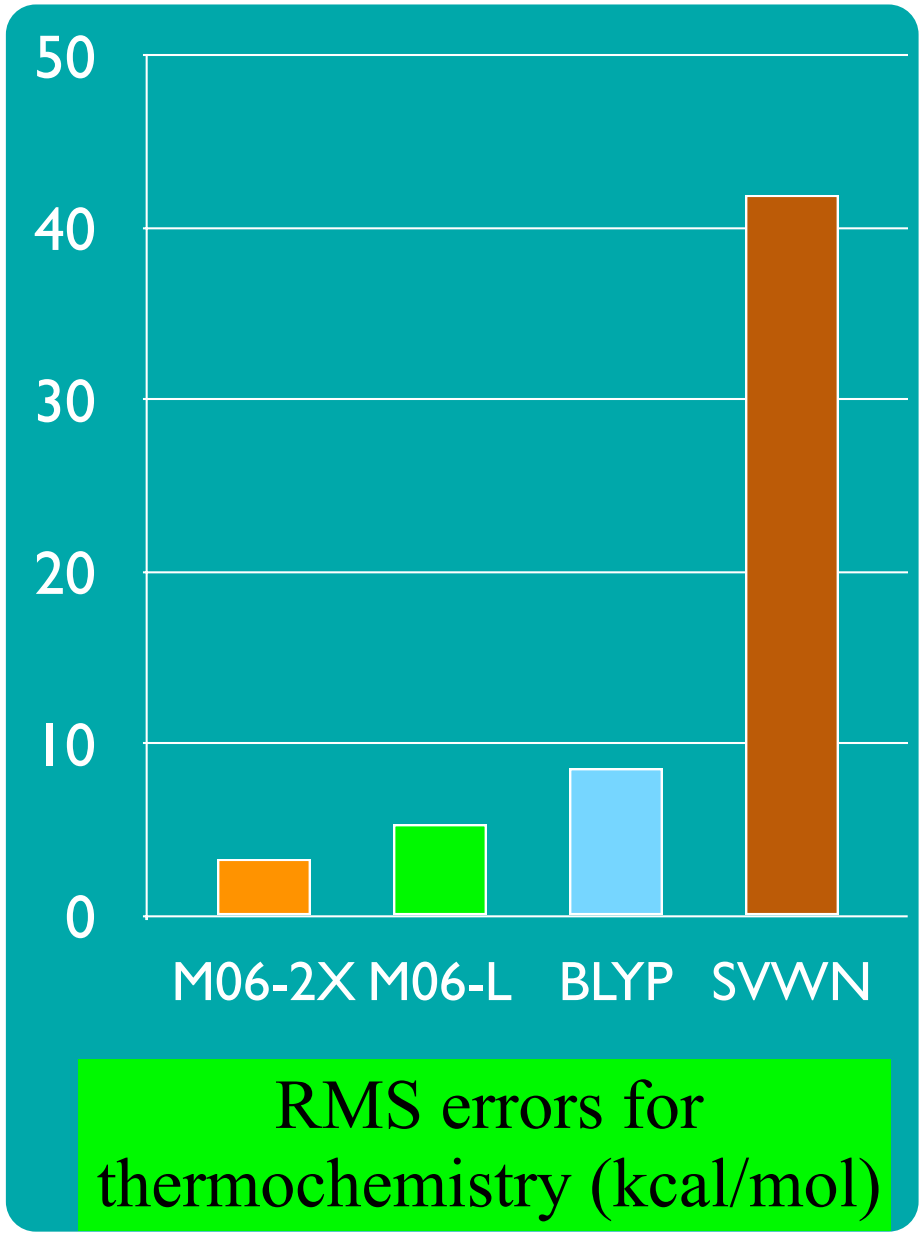
$$E_{XC} = \int d\mathbf{r}\ \varepsilon_{XC}\left\{\rho(\mathbf{r}), \nabla\rho(\mathbf{r})\right\}$$

Examples: BLYP, PBE

Rung 1: LSDA

1966

$$E_{XC} = \int d\mathbf{r}\ \varepsilon_{XC}\left\{\rho(\mathbf{r})\right\}$$



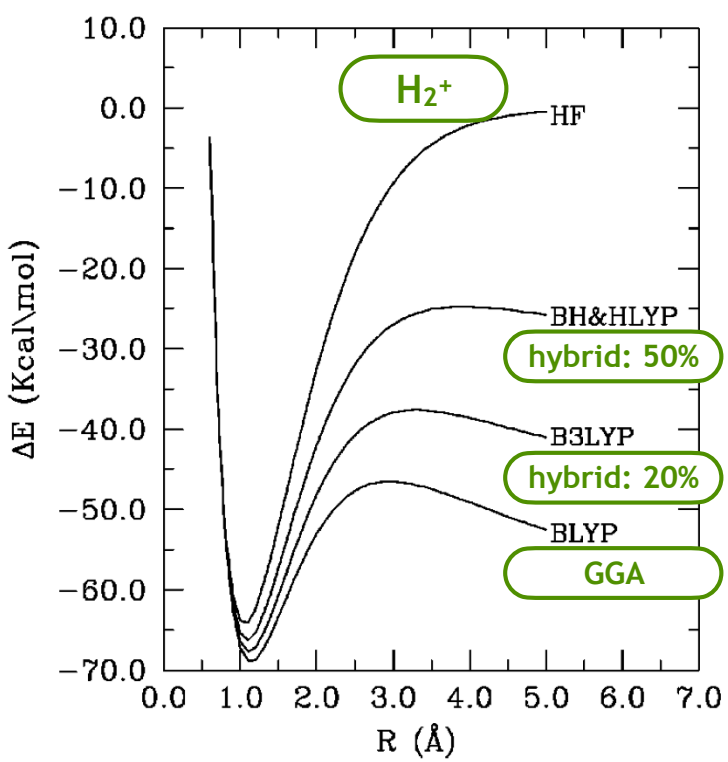
Rung 4 of Jacob's Ladder: exact exchange

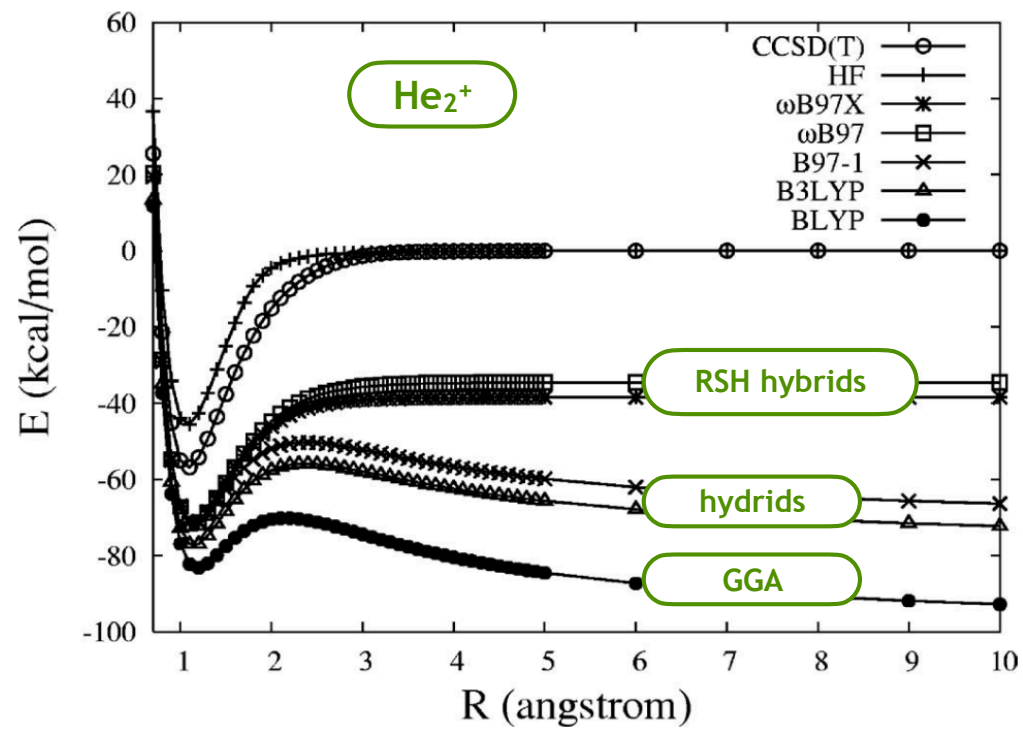
Exact functional includes exact exchange (adiabatic connection)

Exact exchange cancels self-interaction error (delocalization error)

Range-separation improves on a fixed fraction of exact exchange

$$E_X^{RS} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 P(\mathbf{r}_1,\mathbf{r}_2)\left[c_X \frac{s(r_{12})}{r_{12}} + \frac{l(r_{12})}{r_{12}}\right] P(\mathbf{r}_1,\mathbf{r}_2) \qquad s(r)+l(r)=1$$





Q-CHEM™
A Quantum Leap Into the Future of Chemistry

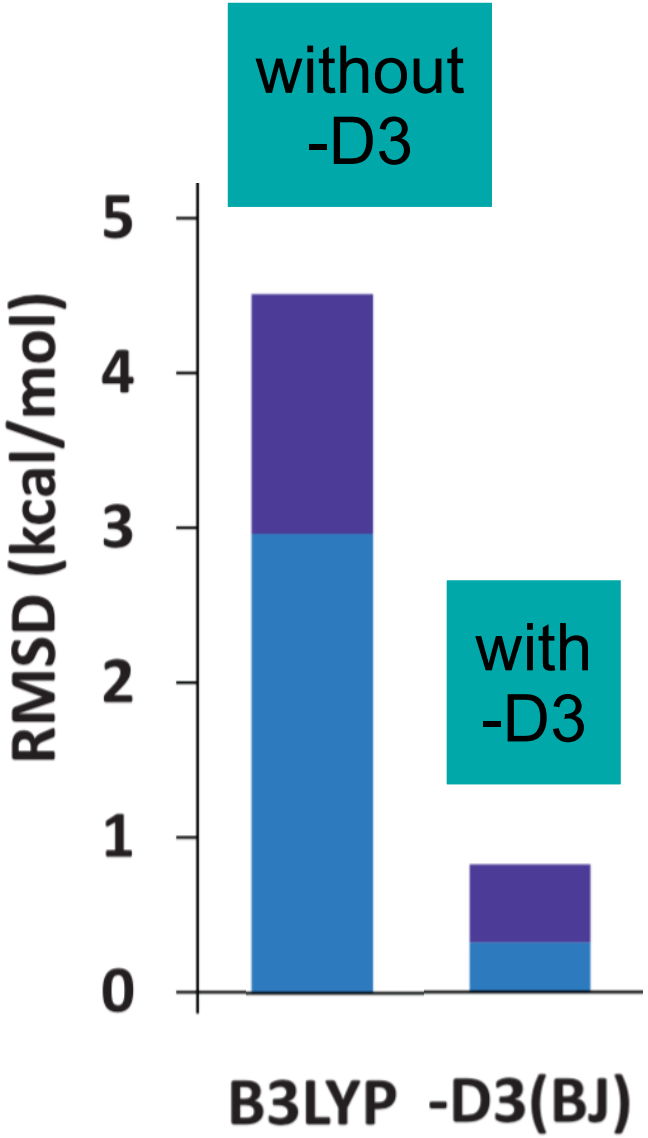
Jacob's ladder leaves out an important advance from the last 15 years: non-local dispersion

Dispersion cannot be described as a functional of position of one electron!

It is now common for functionals to be "dispersion-corrected" by adding a:

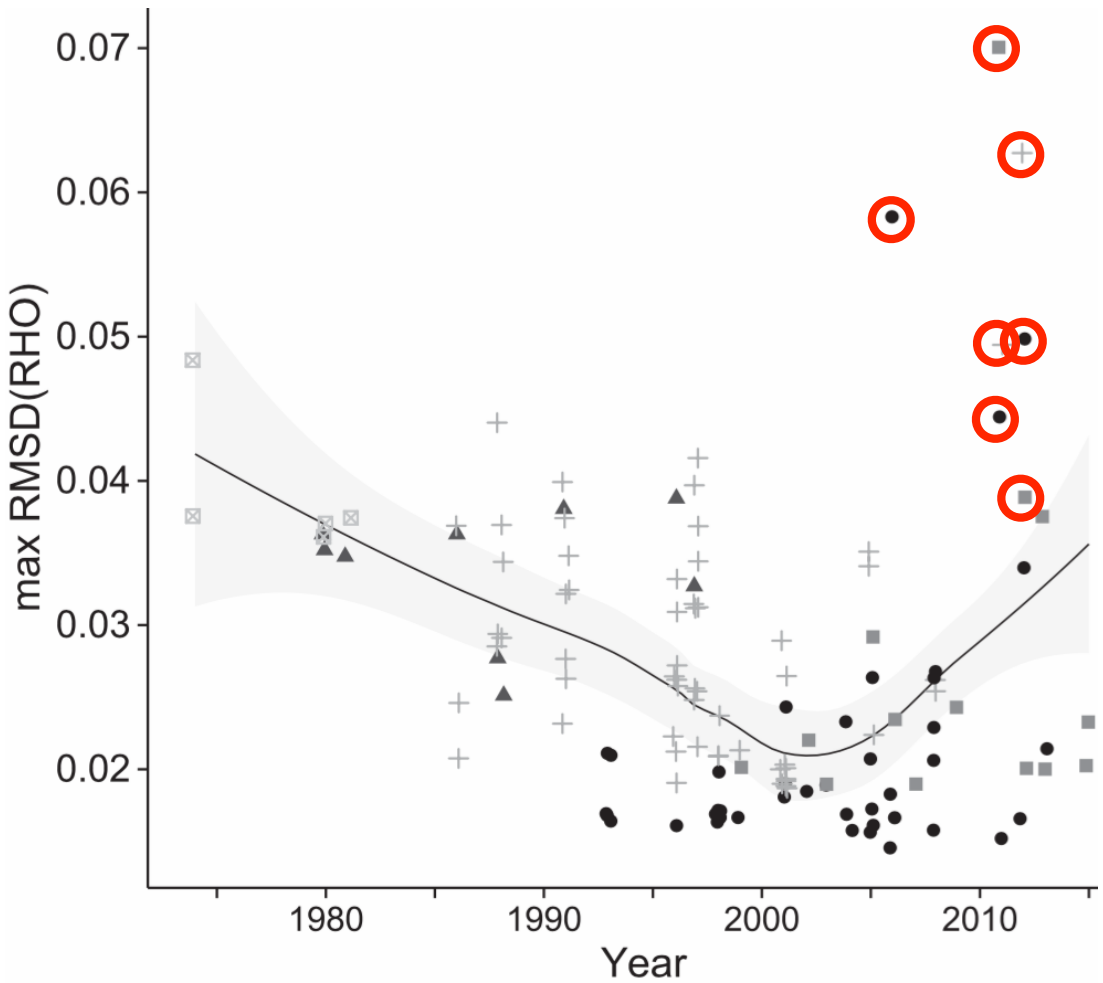
- damped C_6/R^6 atom-atom potential
  - (-D, -D3, -D4: Grimme)
- or a non-local Van der Waals functional (VV10, VdW-DF2)

Such corrections are needed to calculate accurate non-covalent interactions, as shown at right:



DFT is straying from the path toward the exact functional

M.G. Medvedev, I.S. Bushmarinov, J. Sun, J.P. Perdew, K.A. Lyssenko,
Science 355 (Issue 6320), pp. 49-52 (2017).



(Atomic) densities became closer to the exact ones, reflecting theoretical advances, until the early 2000s, when this trend was reversed by unconstrained functionals sacrificing physical rigor for the flexibility of empirical fitting.

Note: all 14 of the worst "post-2000" density functionals (Table 2) were developed by a single research group…

Overall, DFT is in need of new strategies for functional development.

Outline

1. Introduction

2. Combinatorial design of density functionals

3. Performance of density functionals

Q-CHEM™
A Quantum Leap Into the Future of Chemistry

Combinatorial design: "survival of the most transferable"

Define a (very large) space of density functionals.

Search this space to find the "most accurate" functional that is "least empirical". Use 4986 benchmark values.

"Most accurate" should mean most predictive!

Training data:	870 points
Primary test data:	2964 points
Secondary test data:	1152 points

Weights of individual test sets were a great challenge

Total RMS errors balance finite amounts of trusted data vs too much dependence on "training data".

Defining "least empirical":

Each extra parameter must reduce total error by > 0.05 kcal/mol.

Q-CHEM™
A Quantum Leap Into the Future of Chemistry

Training, Primary test, and Secondary test data: NC (Easy/Difficult), I (E/D), TC (E/D), BH

Name	Set	Datatype	#	Description	ΔE (kcal/mol)	References
A24	Train	NCED	24	Binding energies of small non-covalent complexes	2.65	55
DS14	Train	NCED	14	Binding energies of complexes containing divalent sulfur	3.70	56
HB15	Train	NCED	15	Binding energies of hydrogen-bonded dimers featuring ionic groups common in biomolecules	19.91	57
HSG	Train	NCED	21	Binding energies of small ligands interacting with protein receptors	6.63	58 and 59
NBC10	Train	NCED	184	PECs for BzBz (5), BzMe (1), MeMe (1), BzH_2S (1), and PyPy (2)	1.91	59–62
S22	Train	NCED	22	Binding energies of hydrogen-bonded and dispersion-bound non-covalent complexes	9.65	59 and 63
X40	Train	NCED	31	Binding energies of non-covalent interactions involving halogenated molecules	5.26	64
A21x12	PriTest	NCED	252	PECs for the 21 equilibrium complexes from A24	1.43	65
BzDC215	PriTest	NCED	215	PECs for benzene interacting with two rare-gas atoms and eight first- and second-row hydrides	1.81	66
HW30	PriTest	NCED	30	Binding energies of hydrocarbon-water dimers	2.34	67
NC15	PriTest	NCED	15	Binding energies of very small non-covalent complexes	0.95	68
S66	PriTest	NCED	66	Binding energies of non-covalent interactions found in organic molecules and biomolecules	6.88	69 and 70
S66x8	PriTest	NCED	528	PECs for the 66 complexes from S66x8	5.57	69
3B-69-DIM	SecTest	NCED	207	Binding energies of all relevant pairs of monomers from 3B-69-TRIM	5.87	71
AlkBind12	SecTest	NCED	12	Binding energies of saturated and unsaturated hydrocarbon dimers	3.14	72
CO2Nitrogen16	SecTest	NCED	16	Binding energies of CO_2 to molecular models of pyridinic N-doped graphene	3.84	73
HB49	SecTest	NCED	49	Binding energies of small- and medium-sized hydrogen-bonded systems	14.12	74–76
Ionic43	SecTest	NCED	43	Binding energies of anion-neutral, cation-neutral, and anion-cation dimers	69.94	77
H2O6Bind8	Train	NCEC	8	Binding energies of isomers of $(H_2O)_6$	46.96	78 and 79
HW6Cl	Train	NCEC	6	Binding energies of $Cl^-(H_2O)_n$ ($n = 1-6$)	57.71	78 and 79
HW6F	Train	NCEC	6	Binding energies of $F^-(H_2O)_n$ ($n = 1-6$)	81.42	78 and 79
FmH2O10	PriTest	NCEC	10	Binding energies of isomers of $F^-(H_2O)_{10}$	168.50	78 and 79
Shields38	PriTest	NCEC	38	Binding energies of $(H_2O)_n$ ($n = 2-10$)	51.54	80
SW49Bind345	PriTest	NCEC	31	Binding energies of isomers of $SO_4^{2-}(H_2O)_n$ ($n = 3-5$)	28.83	81
SW49Bind6	PriTest	NCEC	18	Binding energies of isomers of $SO_4^{2-}(H_2O)_6$	62.11	81
WATER27	PriTest	NCEC	23	Binding energies of neutral and charged water clusters	67.48	82 and 83
3B-69-TRIM	SecTest	NCEC	69	Binding energies of trimers, with three different orientations of 23 distinct molecular crystals	14.36	71
CE20	SecTest	NCEC	20	Binding energies of water, ammonia, and hydrogen fluoride clusters	30.21	84 and 85
H2O20Bind10	SecTest	NCEC	10	Binding energies of isomers of $(H_2O)_{20}$ (low-energy structures)	198.16	79
H2O20Bind4	SecTest	NCEC	4	Binding energies of isomers of $(H_2O)_{20}$ (dod, fc, fs, and es)	206.12	82, 83, 86, and 87
TA13	Train	NCD	13	Binding energies of dimers involving radicals	22.00	88
XB18	Train	NCD	8	Binding energies of small halogen-bonded dimers	5.23	89
Bauza30	PriTest	NCD	30	Binding energies of halogen-, chalcogen-, and pnicogen-bonded dimers	23.65	90 and 91
CT20	PriTest	NCD	20	Binding energies of charge-transfer complexes	1.07	92
XB51	PriTest	NCD	20	Binding energies of large halogen-bonded dimers	6.06	89
AlkIsomer11	Train	IE	11	Isomerization energies of $n = 4-8$ alkanes	1.81	93
Butanediol65	Train	IE	65	Isomerization energies of butane-1,4-diol	2.89	94
ACONF	PriTest	IE	15	Isomerization energies of alkane conformers	2.23	83 and 95
CYCONF	PriTest	IE	11	Isomerization energies of cysteine conformers	2.00	83 and 96
Pentane14	PriTest	IE	14	Isomerization energies of stationary points on the n-pentane torsional surface	6.53	97
SW49Rel345	PriTest	IE	31	Isomerization energies of $SO_4^{2-}(H_2O)_n$ ($n = 3-5$)	1.47	81
SW49Rel6	PriTest	IE	18	Isomerization energies of $SO_4^{2-}(H_2O)_6$	1.22	81
H2O16Rel5	SecTest	IE	5	Isomerization energies of $(H_2O)_{16}$ (boat and fused cube structures)	0.40	98
H2O20Rel10	SecTest	IE	10	Isomerization energies of $(H_2O)_{20}$ (low-energy structures)	2.62	79
H2O20Rel4	SecTest	IE	4	Isomerization energies of $(H_2O)_{20}$ (dod, fc, fs, and es)	5.68	82, 83, 86, and 87

Name	Set	Datatype	#	Description	ΔE (kcal/mol)	References
Melatonin52	SecTest	IE	52	Isomerization energies of melatonin	5.54	99
YMPJ519	SecTest	IE	519	Isomerization energies of the proteinogenic amino acids	8.33	100
EIE22	Train	ID	22	Isomerization energies of enecarbonyls	4.97	101
Styrene45	Train	ID	45	Isomerization energies of C_8H_8	68.69	102
DIE60	PriTest	ID	60	Isomerization energies of reactions involving double-bond migration in conjugated dienes	5.06	103
ISOMERIZATION20	PriTest	ID	20	Isomerization energies	44.05	104
C20C24	SecTest	ID	8	Isomerization energies of the ground state structures of C_{20} and C_{24}	36.12	105
AlkAtom19	Train	TCE	19	$n = 1-8$ alkane atomization energies	1829.31	93
BDE99nonMR	Train	TCE	83	Bond dissociation energies (SR)	114.98	104
G21EA	Train	TCE	25	Adiabatic electron affinities of atoms and small molecules	40.86	83 and 106
G21IP	Train	TCE	36	Adiabatic ionization potentials of atoms and small molecules	265.35	83 and 106
TAE140nonMR	Train	TCE	124	Total atomization energies (SR)	381.05	104
AlkIsod14	PriTest	TCE	14	$n = 3-8$ alkane isodesmic reaction energies	10.35	93
BH76RC	PriTest	TCE	30	Reaction energies from HTBH38 and NHTBH38	30.44	83, 107, and 108
EA13	PriTest	TCE	13	Adiabatic electron affinities	42.51	109
HAT707nonMR	PriTest	TCE	505	Heavy-atom transfer energies (SR)	74.79	104
IP13	PriTest	TCE	13	Adiabatic ionization potentials	256.24	109
NBPRC	PriTest	TCE	12	Reactions involving NH_3/BH_3 and PH_3/BH_3	30.52	83, 110, and 111
SN13	PriTest	TCE	13	Nucleophilic substitution energies	25.67	104
BSR36	SecTest	TCE	36	Hydrocarbon bond separation reaction energies	20.06	111 and 112
HNBrBDE18	SecTest	TCE	18	Homolytic N–Br bond dissociation energies	56.95	113
WCPT6	SecTest	TCE	6	Tautomerization energies for water-catalyzed proton-transfer reactions	7.53	114
BDE99MR	PriTest	TCD	16	Bond dissociation energies (MR)	54.51	104
HAT707MR	PriTest	TCD	202	Heavy-atom transfer energies (MR)	83.41	104
TAE140MR	PriTest	TCD	16	Total atomization energies (MR)	147.20	104
PlatonicHD6	SecTest	TCD	6	Homodesmotic reactions involving platonic hydrocarbon cages, C_nH_n ($n = 4, 6, 8, 10, 12, 20$)	136.71	115
PlatonicID6	SecTest	TCD	6	Isodesmic reactions involving platonic hydrocarbon cages, C_nH_n ($n = 4, 6, 8, 10, 12, 20$)	96.19	115
PlatonicIG6	SecTest	TCD	6	Isogyric reactions involving platonic hydrocarbon cages, C_nH_n ($n = 4, 6, 8, 10, 12, 20$)	356.33	115
PlatonicTAE6	SecTest	TCD	6	Total atomization energies of platonic hydrocarbon cages, C_nH_n ($n = 4, 6, 8, 10, 12, 20$)	2539.27	115
BHPERI26	Train	BH	26	Barrier heights of pericyclic reactions	23.15	83 and 116
CRBH20	Train	BH	20	Barrier heights for cycloreversion of heterocyclic rings	46.40	117
DBH24	Train	BH	24	Diverse barrier heights	28.34	118 and 119
CR20	PriTest	BH	20	Cycloreversion reaction energies	22.31	120
HTBH38	PriTest	BH	38	Hydrogen transfer barrier heights	16.05	108
NHTBH38	PriTest	BH	38	Non-hydrogen transfer barrier heights	33.48	107
PX13	SecTest	BH	13	Barrier heights for proton exchange in water, ammonia, and hydrogen fluoride clusters	28.83	84 and 85
WCPT27	SecTest	BH	27	Barrier heights of water-catalyzed proton-transfer reactions	38.73	114
AE18	Train	–	18	Absolute atomic energies of hydrogen through argon	148 739.00	121
RG10	PriTest	–	569	PECs for the 10 rare-gas dimers involving helium through krypton	1.21	122

Q-CHEM™
A Quantum Leap Into the Future of Chemistry

Under the hood: What's in the functional?

$$E_{XC} = E_X^{B97} + E_{Cos}^{B97} + E_{Css}^{B97} + E_X^{RS} + E_{VdW}^{VV10}$$

B97 GGA (Becke) or meta-B97 is used for X, C_{os}, C_{ss}

$$E^{B97} = \int d\mathbf{r}\ \varepsilon^{LSDA} \sum_{j=0}^{M} c_j u^j$$

$$u = u(\nabla\rho)$$

$$w = w(\tau)$$

$$E^{B97M} = \int d\mathbf{r}\ \varepsilon^{LSDA} \sum_{j=0}^{M} \sum_{k=0}^{M} c_{jk} w^j u^k$$

- Polynomial expansions -- truncate at M=4
- Each parameter can be included or excluded.
- GGA: ~ 2^{15} possible functionals. Fully searchable!
- metaGGA: ~ 2^{75} ~ 10^{23} functionals. A functional genome!!

$$E_X^{RS} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 P(\mathbf{r}_1,\mathbf{r}_2)\left[c_X \frac{s(r_{12})}{r_{12}} + \frac{l(r_{12})}{r_{12}}\right] P(\mathbf{r}_1,\mathbf{r}_2) \qquad s(r)+l(r)=1$$

$$E_{VdW}^{VV10} = \int d\mathbf{r}\ \rho(\mathbf{r}) \int d\mathbf{r}'\rho(\mathbf{r}')\Theta(\mathbf{r}-\mathbf{r}') \qquad \lim_{|\mathbf{r}_{12}|\to\infty} \Theta(\mathbf{r}_{12}) \propto |\mathbf{r}_{12}|^{-6}$$

Q-CHEM™
A Quantum Leap Into the Future of Chemistry

4 new semi-empirical functionals (Narbe Mardirossian)

	rung 3	rung 4a	rung 4b	rung 5
	B97M-rV	ωB97X-V	ωB97M-V	ωB97M(2)
semi-local	meta-GGA	GGA	meta-GGA	meta-GGA
NLX	none	range-separated	range-separated	range-separated
NLC	rVV10	VV10	VV10	VV10+PT2
search space	~ 10^{40}	~ 10^{5}	~ 10^{40}	~ 10^{23}
parameters	12 (of 144)	10 (of 16)	12 (of 144)	14 (of 76)
reference	JCP 142, 074111 (2015)	PCCP 16, 9904 (2014)	JCP 144, 214110 (2016)	JCP 148, 241736 (2018)

Partial search of the mGGA functional genome

Can search up to 7 free parameters

Start with LSDA + VV10 orbitals

Going further: Find a parameter that recurs in the top-performing fits and select it unconditionally.

Cx01, Cx10 emerged from first fits.

6 more parameters likewise selected.

Filter out unacceptable functionals.

Especially excessive grid sensitivity!

Re-evaluate orbitals with “best 8”

Search further

Over 1 trillion forms screened!

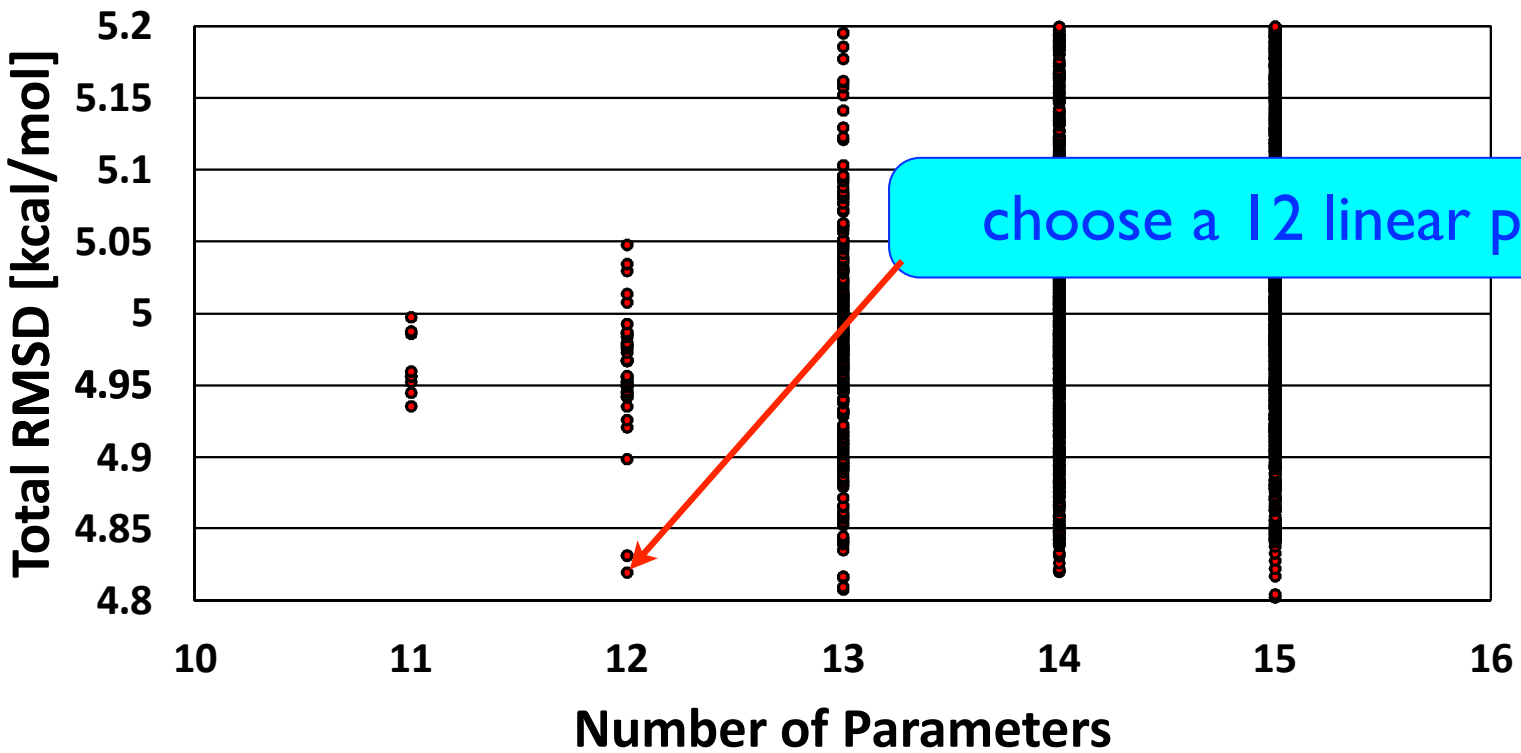
Frozen	No of initial fits	# (Fitted)
–	2 898 753 715	7
$c_{x,01}$	2 641 902 120	8
$c_{x,10}$	2 404 808 340	9
$c_{css,10}$	2 186 189 400	10
$c_{css,20}$	1 984 829 850	11
$c_{cos,20}$	1 799 579 064	12
$c_{css,00}$	1 629 348 612	13
$c_{cos,10}$	1 473 109 704	14
$c_{cos,21}$	1 329 890 705	15

Q-CHEM™
A Quantum Leap Into the Future of Chemistry

Sample results from the screening process: The (100 billion functional) search for B97M-V

We removed fits with:

- High quadrature grid sensitivity
- Negative exchange ICF's
- Above tolerance thermochemistry or non-covalent errors



choose a 12 linear parameter form

Outline

1. Introduction

2. Combinatorial design of density functionals

3. Performance of density functionals

Convergence on Jacob's ladder

N. Mardirossian and MHG, Mol. Phys. 115, 2315 (2017); J. Chem.Phys. 148, 241736 (2018).

RMS errors (kcal/mol) on 5000 data points. E=easy, D=difficult

NC=noncovalent, I=isomer, TC=thermochemistry, BH=barriers

Functional	Rung	NCED	NCEC	NCD	IE	ID	TCE	TCD	BH
ωB97M(2)	5	0.14	0.36	0.32	0.11	0.97	0.96	2.71	0.84
ωB97M-V	4	0.15	0.42	0.53	0.11	1.32	1.56	4.15	1.48
B97M-rV	3	0.18	0.57	1.10	0.24	4.24	1.88	5.47	3.12
B97-D3(BJ)	2	0.45	3.20	1.25	0.62	5.04	3.43	8.88	7.67
SPW92	1	1.91	27.76	5.11	1.26	5.58	10.13	32.20	15.53

More than 200 functionals tested: Our new designs fare well....

RMS error in each category decreases with each step up Jacob's Ladder, as represented by the best functional at each level.

In this statistical sense, DFT is systematically improvable!....

Q-CHEM™ A Quantum Leap Into the Future of Chemistry

N. Mardirossian and MHG, Mol. Phys. 115, 2315 (2017)

How good are other rung 3, 4 functionals?

Rung 4b: hybrid meta-GGAs

Functional	NCED	NCEC	NCD	IE	ID	TCE	TCD	BH
TPSSh-D3(BJ)	0.36	1.73	2.49	0.62	5.29	5.55	5.92	6.63
M06-2X	0.43	2.52	0.99	0.50	5.56	3.29	7.23	2.57
MN15	0.47	1.83	0.96	0.71	4.06	3.76	6.44	1.98
ωB97M-V	0.18	0.48	1.13	0.28	2.05	2.48	4.30	1.68

Rung 4a: hybrid-GGAs

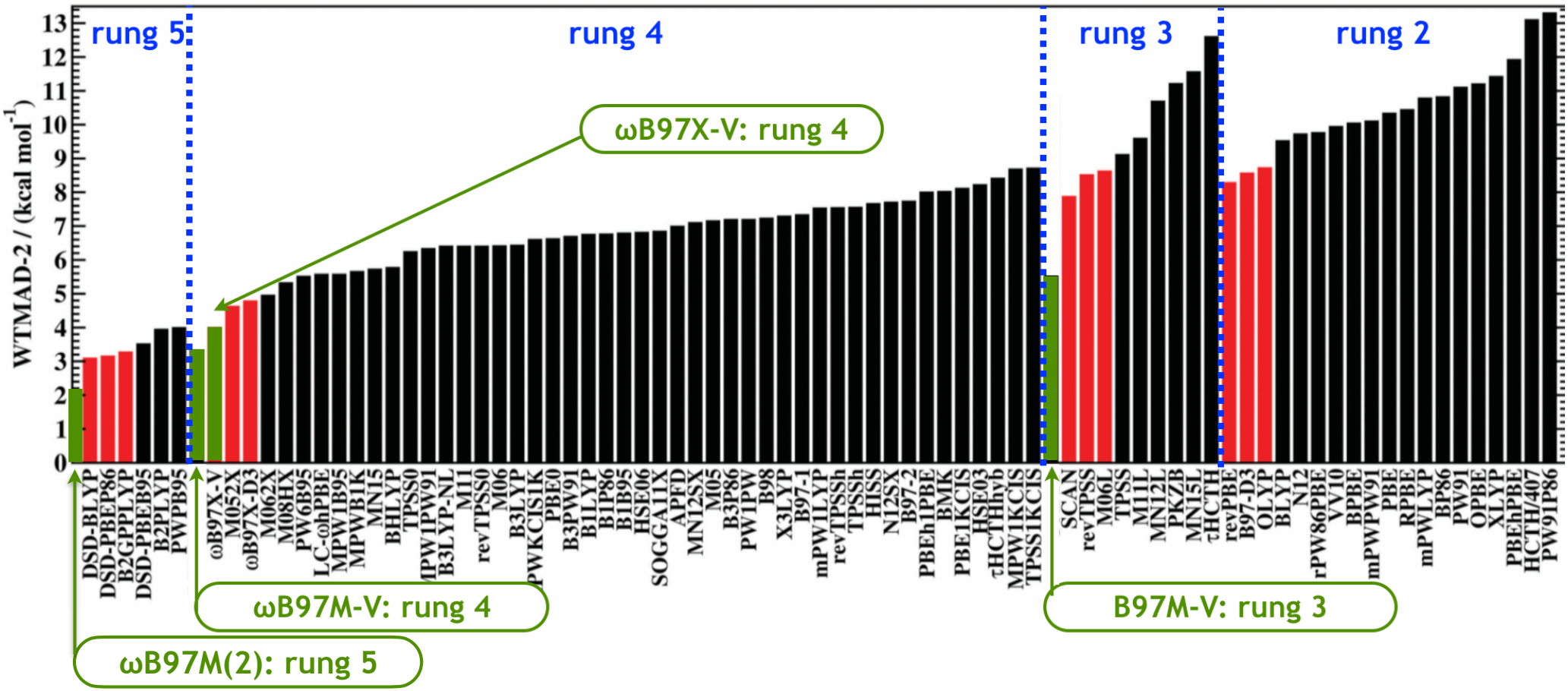
Functional	NCED	NCEC	NCD	IE	ID	TCE	TCD	BH
PBE0-D3(BJ)	0.44	4.45	2.28	0.58	3.47	4.76	8.72	4.91
B3LYP-D3(BJ)	0.31	3.02	1.88	0.49	8.51	3.72	5.97	5.65
ωB97X-D	0.37	1.01	1.46	0.67	3.11	3.44	5.79	2.34
ωB97X-V	0.24	0.64	1.23	0.27	2.72	3.41	5.01	2.44

Rung 3: meta-GGAs

Functional	NCED	NCEC	NCD	IE	ID	TCE	TCD	BH
TPSS-D3(BJ)	0.38	2.28	3.06	0.69	6.47	5.88	8.86	8.72
SCAN-D3(BJ)	0.54	9.18	3.41	0.55	4.46	5.25	6.39	7.83
M06-L	0.55	2.20	1.87	0.71	10.16	5.44	12.97	6.85
B97M-rV	0.22	0.67	2.04	0.28	6.45	3.57	4.78	4.36

Grimme's GMTKN55 dataset

PCCP 2017, 19, 32184



- B97M-rV is the best meta-GGA (rung 3).
- ωB97X-V & ωB97M-V are best hybrids (rung 4)
- ωB97M(2) is best functional at rung 5, and overall.

A. Najibi & L. Goerigk, JCTC 2018, 14, 5725.

G. Santra, M. Sylvetsky & J. Martin, JPCA, 2019, 123, 5129

Q-CHEM™
A Quantum Leap Into the Future of Chemistry

Basis set requirements: bond energies

Aim to be close to CBS limit

But not too close!

Cost grows fast with size….

Recommended basis sets for bonded interaction energies

QZ: aug-pc-3, aug-cc-pVQZ, pc-3, def2-QZVPPD, def2-QZVPP

TZ: aug-pc-2, and pc-2

At right: RMS errors for functionals vs basis set

(kcal/mol vs reference data)

Functional	Basis	TCE
PBE-D3(BJ)	6-31G*	13.00
	def2-SVPD	12.67
	def2-TZVPPD	9.76
	def2-QZVPPD	9.67
B3LYP-D3(BJ)	6-31G*	9.00
	def2-SVPD	7.66
	def2-TZVPPD	3.87
	def2-QZVPPD	3.72
ωB97M-V	6-31G*	9.00
	def2-SVPD	8.23
	def2-TZVPPD	2.65
	def2-QZVPPD	2.48

Q-CHEM™
A Quantum Leap Into the Future of Chemistry

Basis set requirements: non-bonded energies

Recommended basis sets for non-bonded interactions

No counterpoise correction

QZ: aug-pc-3, aug-cc-pVQZ, pc-3, def2-QZVPPD

With counterpoise correction

aTZ: aug-pc-2, def2-TZVPPD

At right: RMS errors for functionals vs basis set

(kcal/mol vs reference data)

Functional	Basis	NCED
PBE-D3(BJ)	6-31G*	2.52
	def2-SVPD	1.38
	def2-TZVPPD	0.49
	def2-QZVPPD	0.46
B3LYP-D3(BJ)	6-31G*	2.34
	def2-SVPD	1.32
	def2-TZVPPD	0.35
	def2-QZVPPD	0.31
ωB97M-V	6-31G*	2.12
	def2-SVPD	1.31
	def2-TZVPPD	0.20
	def2-QZVPPD	0.18

Summary and future work

Combinatorial functional design has been quite successful.

- Jacob's ladder concept is statistically true
- combinatorially designed functionals perform very well
- Tests on transition-metal systems are encouraging
  - (see MOR41 & ROST79: A. Hansen, TMC151: B. Chan, etc.)

Caveats: (i) need large basis sets

(ii) DFT breaks down

Delocalization (X) / Strong correlation (C) errors

Further problems: At the meta-GGA level, we are likely not yet completely constrained by data…