More efficient representations of compounds for machine learning models

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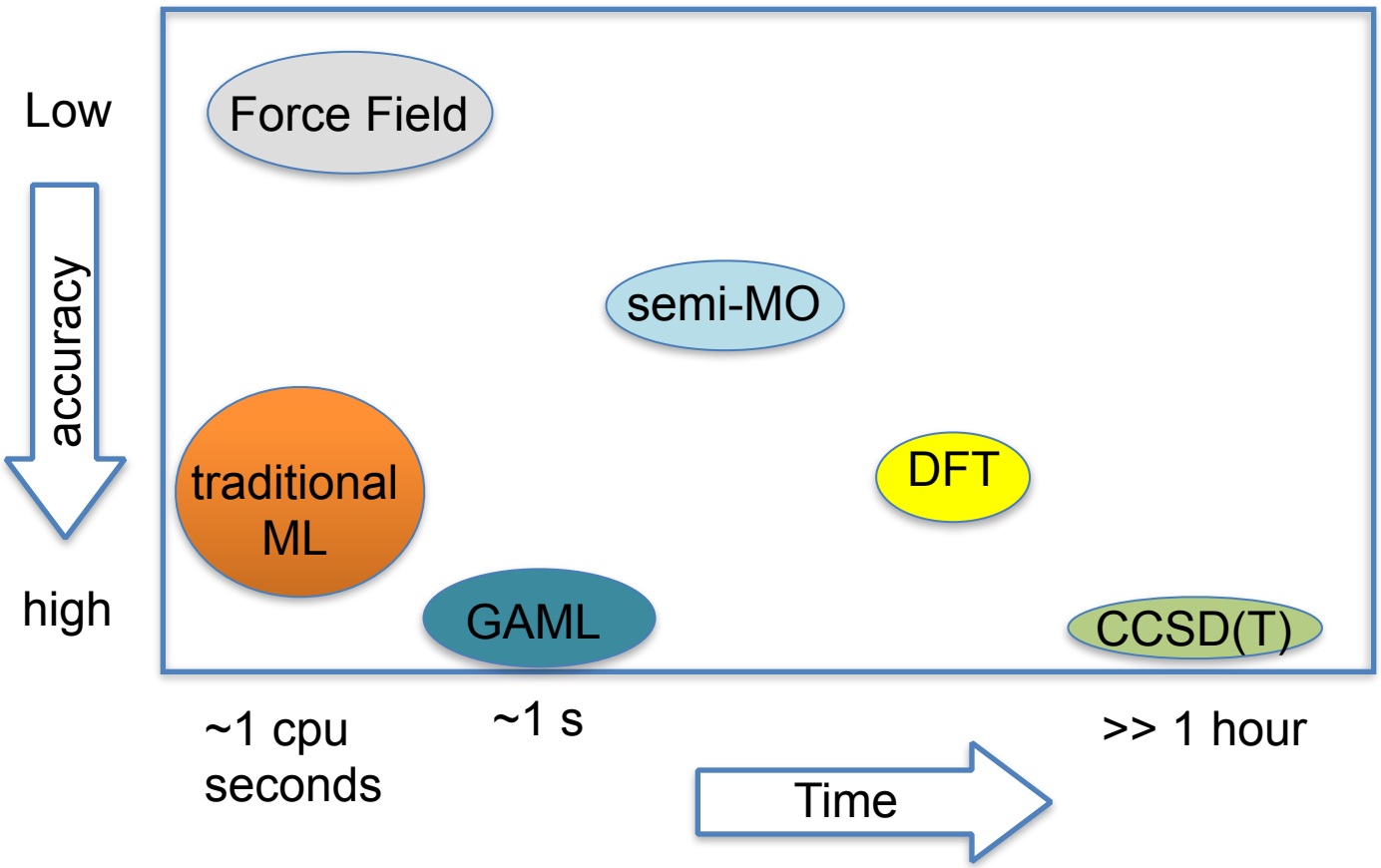
Breaking the hex!

$$\hat{H}\psi = E\psi$$



Machine Learning - basics

feature abstraction

- Given data set {$\mathbf{X}_0$; **Y**}, learn f: **X** -> **Y** and then infer for new $\mathbf{X}_0$'

training test

for molecules, $\mathbf{X}_0$: {Z, R}, **Y**: E

- **Kernel ridge regression**

$k(\mathbf{X}_i, \mathbf{X}_j)$ **covariance**

$$Y_i^{\text{est}}(\mathbf{X}_i) = \sum_j \alpha_j \boxed{\exp\left(-\frac{d(\mathbf{X}_j, \mathbf{X}_i)}{\sigma}\right)} + b$$

length-scale of the data set

$$\min_\alpha \sum_i (Y_i^{\text{est}}(\mathbf{X}_i) - Y_i)^2 + \lambda \sum_i \alpha_i^2$$

$$\Rightarrow \alpha = (\mathbf{K} + \lambda \mathbf{I})^{-1}$$

noise-level

N parameters to be regressed for N molecules
+ 2 global parameters

M. Rupp, *et al.*, *PRL*, 2012

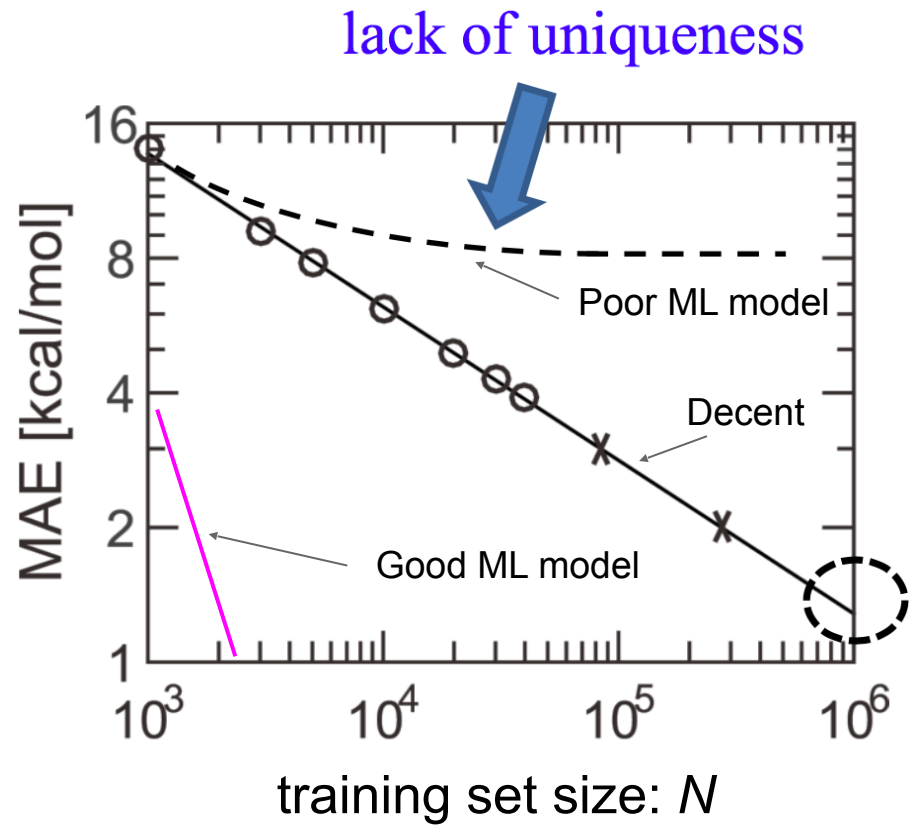
Machine Learning - basics

- More training data, better results for proper **X** (refer to **M** hereafter)

  at large *N*

  $$\log(\text{Error}) = a - b\log(N)$$

- representation (**M**) central to ML



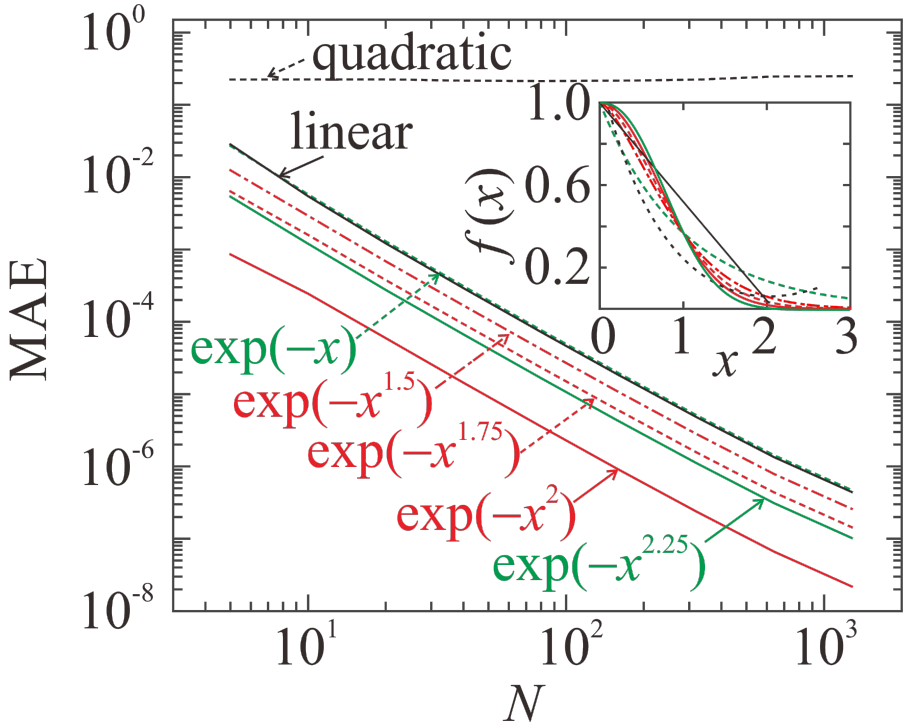
Huang, OAvL, *JCP Comm* (2016); arxiv.org/abs/1608.06194

Learning a simple 1-D function

$$f(x) = \exp(-x^2)$$

$$f^{\mathrm{est}}(x) = \sum \alpha_i k(\underbrace{ax_i + b}_{M_i}, \underbrace{ax + b}_{M})$$

For KRR, f & a*f + b
as rpsts are identical



$$\log(\mathrm{Error}) = a - b\log(N)$$

target similarity

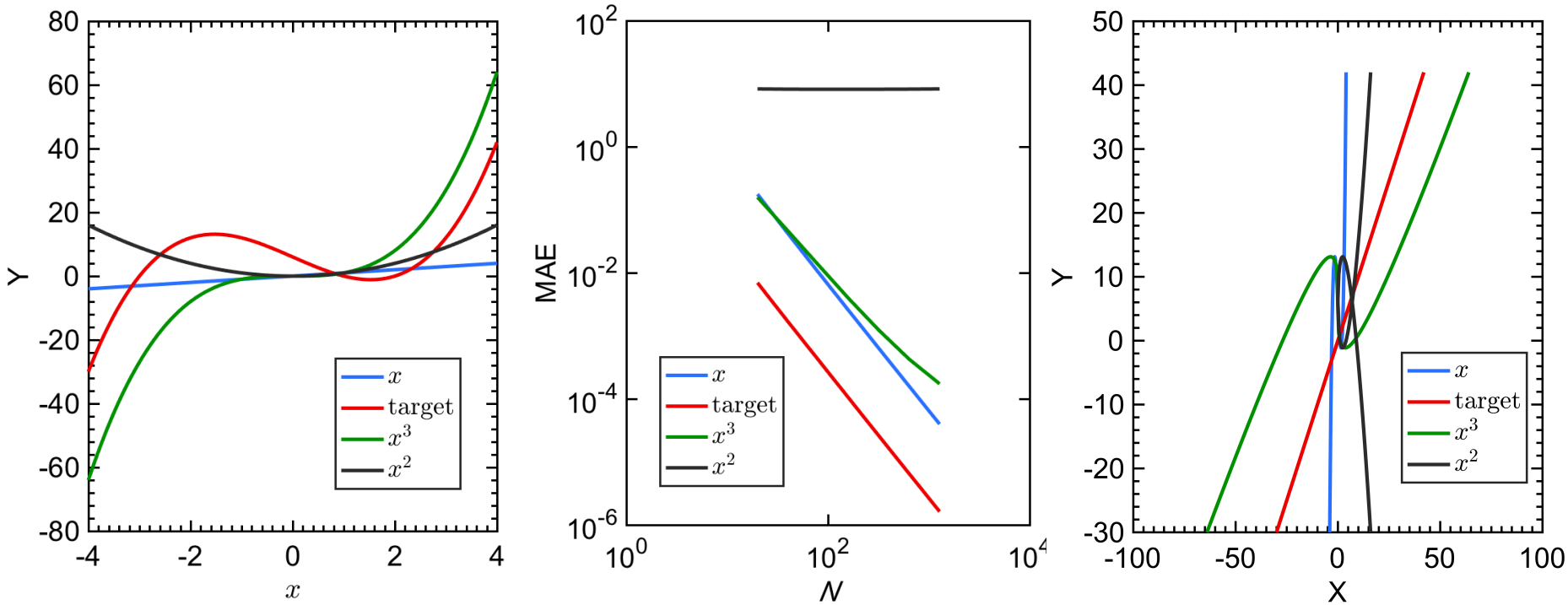
uniqueness

lack of uniqueness
→ absurd results
→ noise in training

OAvL *et al*, *IJQC* (2013)

Learning a "complicated 1-D function

target: Y = (*x*-1)(*x*-2)(*x*+3)

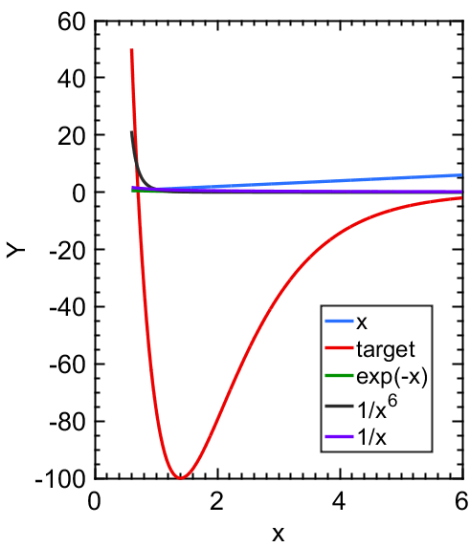


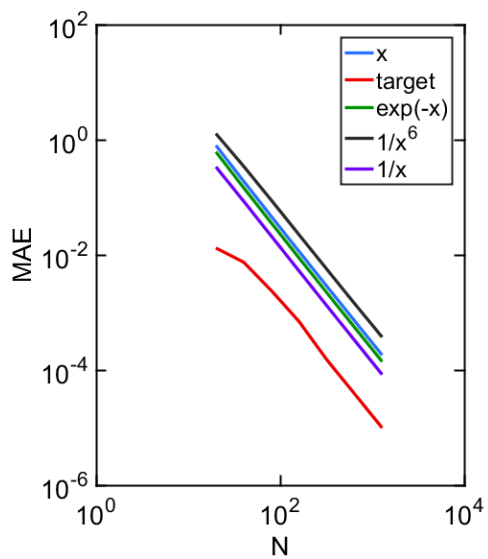
General guidelines for designing M

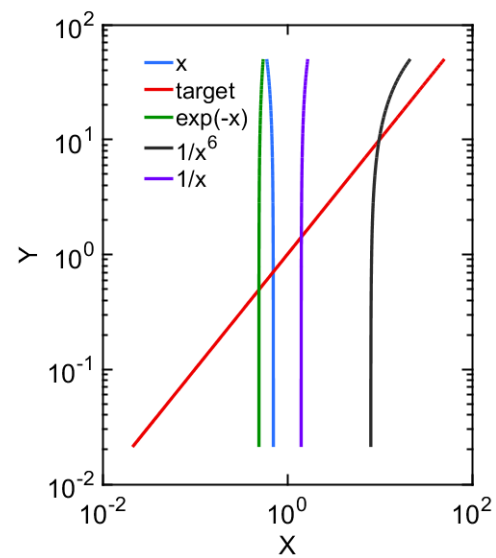
- in case you know *f* well (exact form unknown)
  use it as M
- otherwise you'd better know how *f* behaves
  use one monotonic part of *f*, refer it as *g*

best *g* minimizes $||g - f||_2$

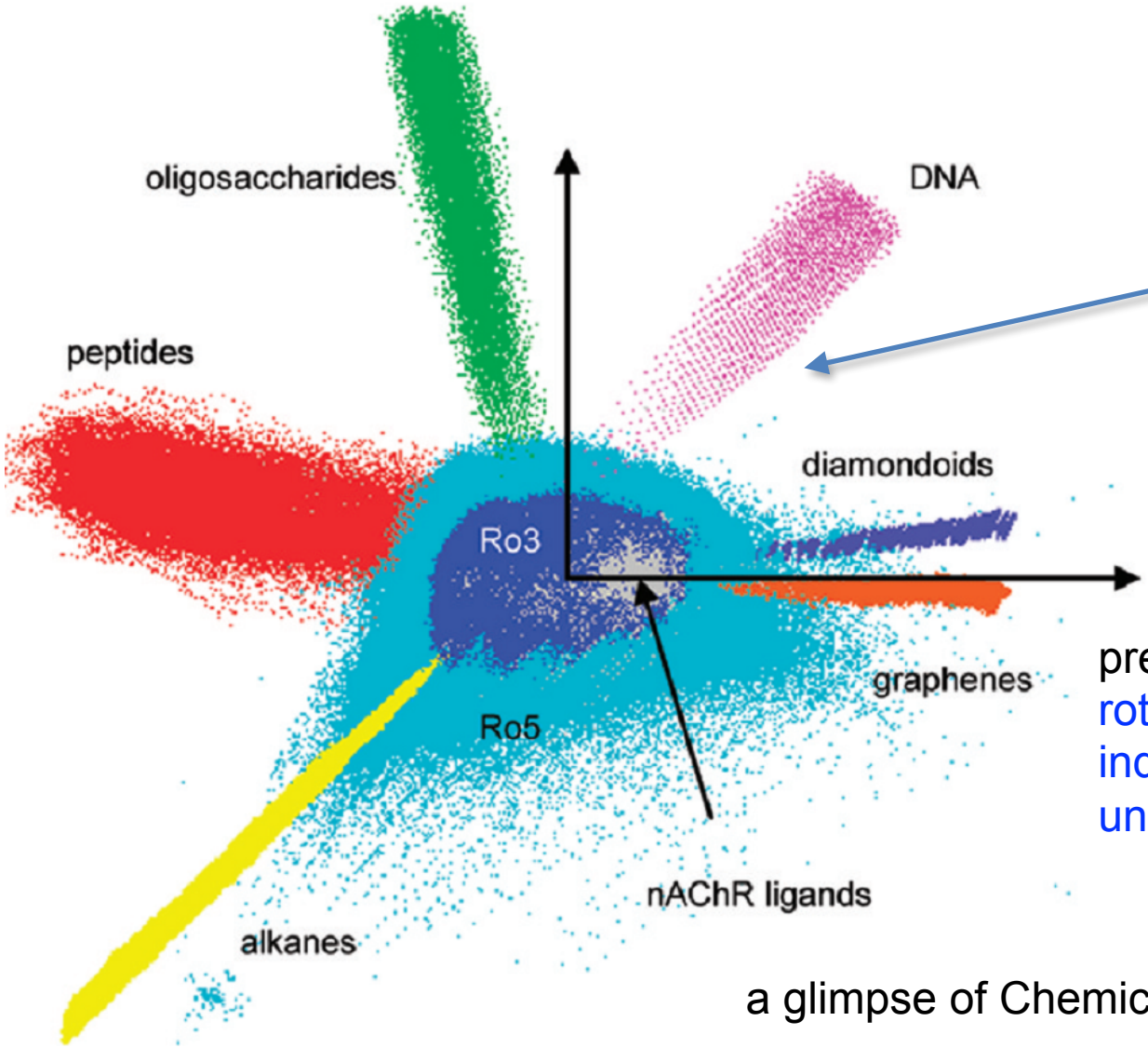
e.g., Morse potential $V(x) = -100*(2*\exp(-(x-1.4)) - \exp(-2(x-1.4)))$
Performance $V(x) > 1/x > \exp(-(x-1.4)) > x > 1/x^6 >> -(x-1.4)^2$

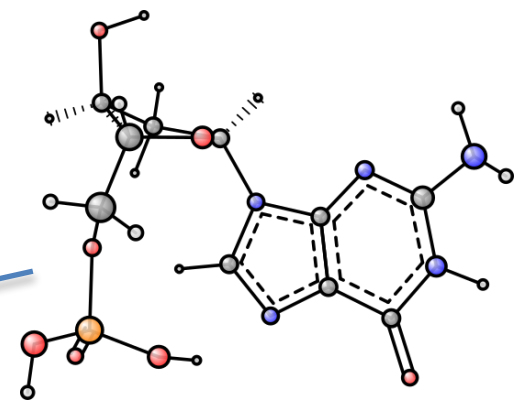






Representing molecules





X_0: $\{Z, R\}$

prerequisites:
rotation, translation invariant
index permutation invariant
unique (1 rpsts~2 molecule ⌫)

a glimpse of Chemical Compound Space (CCS)

J-L. Reymond *et al*, *ACS Chem. Neuro*. (2012)

Representing molecules

$\Psi/\rho/V$-based

atom/electron density

$\hat{H}\Psi = E\Psi$ straightforward !!

$E = E[\Psi] = E[\rho] = E[V\_ext]$

impractical

practical

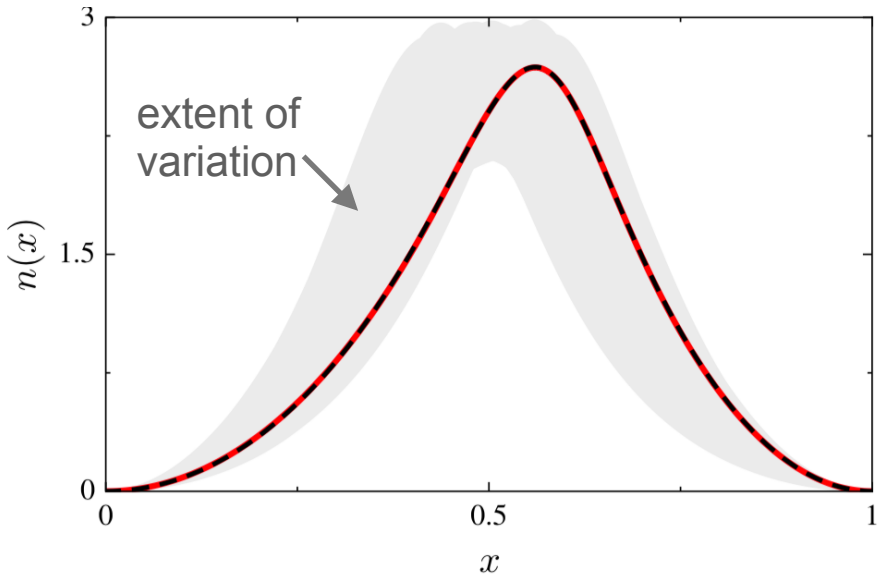
accessible

CCS: infinite dimension

projection to basis set

M: [c_1, c_2, ..., c_n]

Learning an 1-D functional

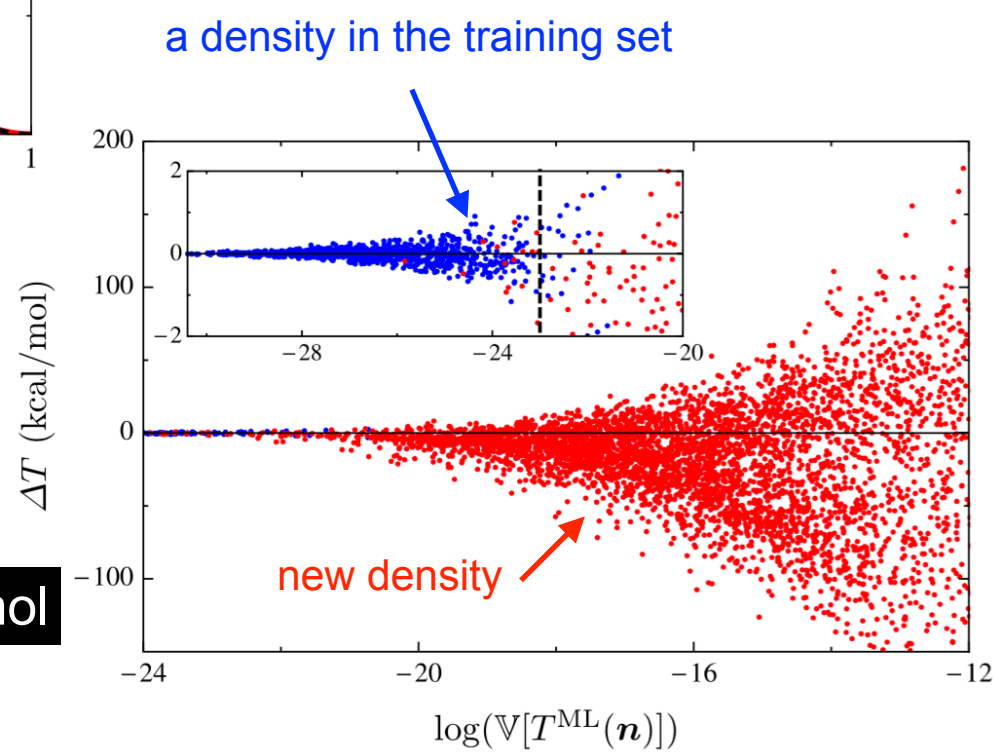


$$v(x) = -\sum_{i=1}^{3} a_i \exp[-(x-b_i)^2/(2c_i^2)].$$

noninteracting fermions in 1D

property: kinetic energy

MAE < 1.0 kcal/mol



J. C. Snyder, *et al*, *PRL* (2012)

fingerprint representations

$$P(\mathbf{r}) = \sum_I Z_I e^{-a|\mathbf{r}-\mathbf{R}_I|^2}$$

remove rotation dependence

projection to 1-D frequency domain & substitution

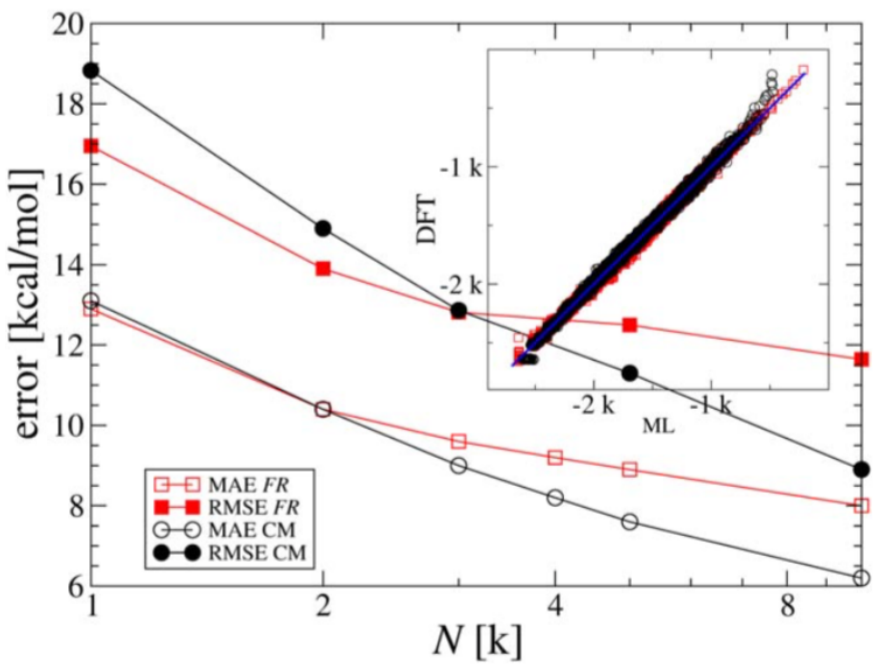
$$FR(r) = \sum_I Z_I^k \left(\cos\left[Z_I^m \sum_J Z_J^n e^{-b(r-r_{IJ})^2} \right] - 1 \right)$$

$$C(\eta) = \frac{1}{N} \sum_i^N \sum_{j \neq i} e^{-\left(\frac{r_{ij}}{\eta}\right)^2}$$

projection to 1-D η-grid

1-D discrete array

works good for Al_n systems



GDB-9 dataset

OAvL *et al*, *IJQC* (2015)

V. Botu, *et al*., *IJQC* (2015)

Representing molecules

why are fingerprint rpsts bad for molecules, but good for Al_n like systems?

$\Psi/\rho/V$-based

$||g - f||_2$ large for molecules, small for Al_n

Representing molecules

Ψ/ρ/*V*-based

many body expansion (MBE) of total energy

E-based

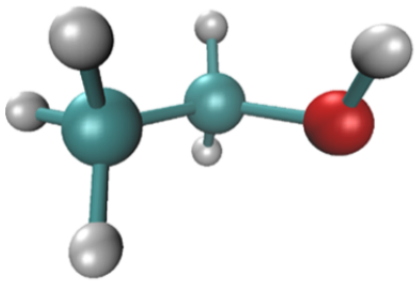
$$E(\{\mathbf{R}_I\}) = \sum_{I}^{[Z]} E^{(1)}(R_I) + \sum_{J>I}^{[Z]} E^{(2)}(R_{IJ}) + \sum_{K>J>I}^{[Z]} E^{(3)}(R_{IJ}, R_{IK}, R_{JK}) + \cdots$$

CCS: dimension is significantly reduced!!!

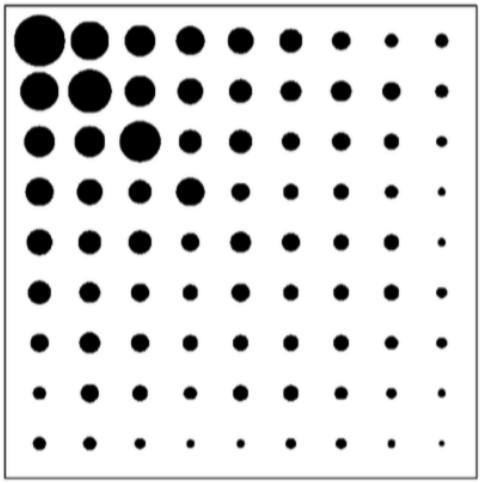
M: [{*E*(1)}, {*E*(12)}, {*E*(123)}, …]

BH, OAvL, *JCP comm.*, 2016

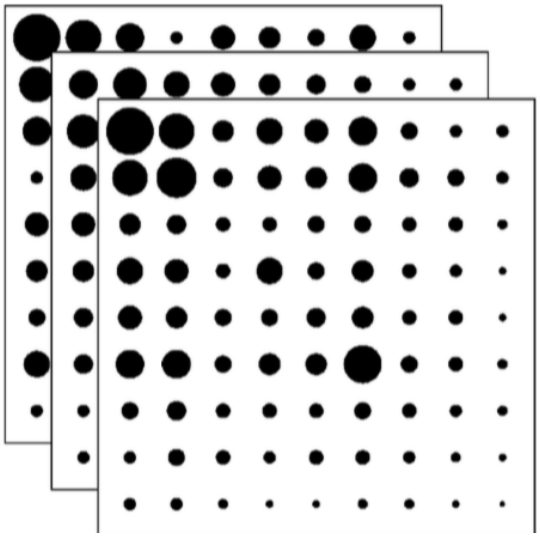
Coulomb matrix (CM)



$$C_{ij} = \begin{cases} 0.5\, Z_i^{2.4} & \forall i = j \\ \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} & \forall i \neq j. \end{cases}$$



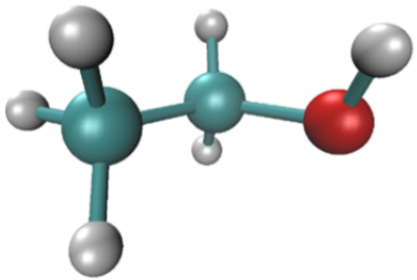
sorted CM



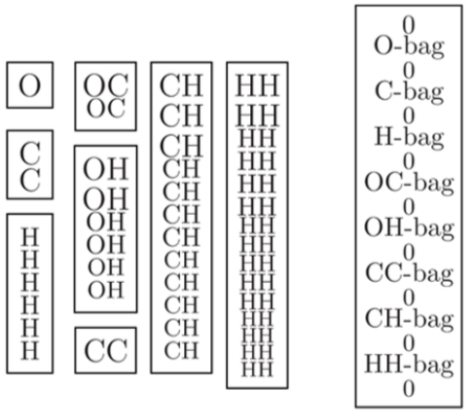
random CM

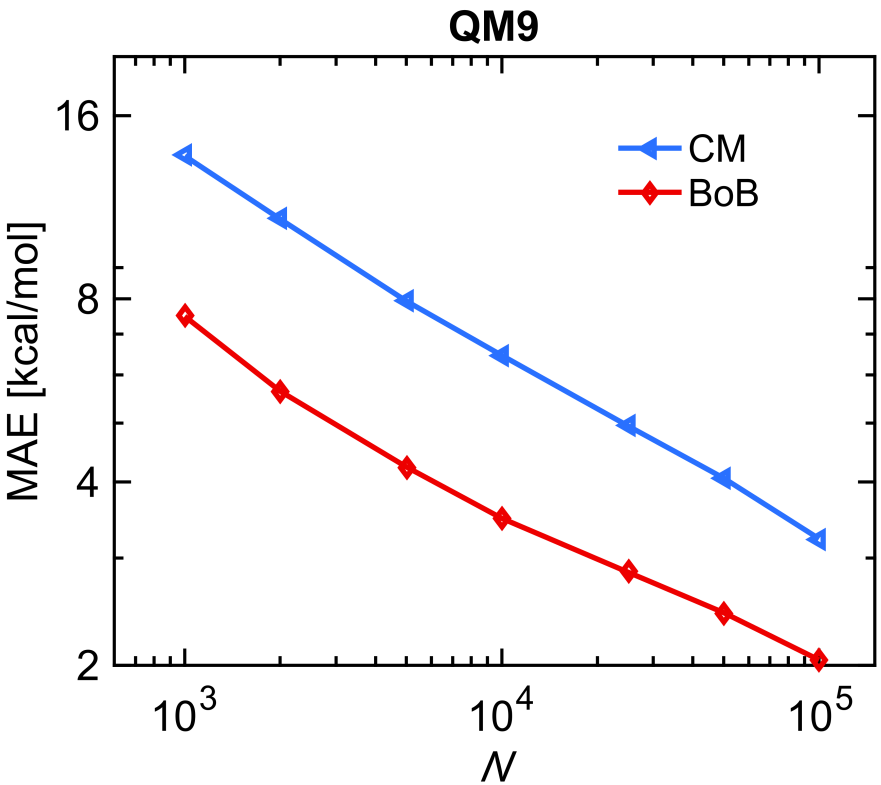
"CM", M. Rupp, *et al.*, PRL, 2012

Bag of Bonds (BoB)



	O	C	C	H	H	H	H	H	H
O	O	OC	OC	OH	OH	OH	OH	OH	OH
C	OC	C	CC	CH	CH	CH	CH	CH	CH
C	OC	CC	C	CH	CH	CH	CH	CH	CH
H	OH	CH	CH	H	HH	HH	HH	HH	HH
H	OH	CH	CH	HH	H	HH	HH	HH	HH
H	OH	CH	CH	HH	HH	H	HH	HH	HH
H	OH	CH	CH	HH	HH	HH	H	HH	HH
H	OH	CH	CH	HH	HH	HH	HH	H	HH
H	OH	CH	CH	HH	HH	HH	HH	HH	H

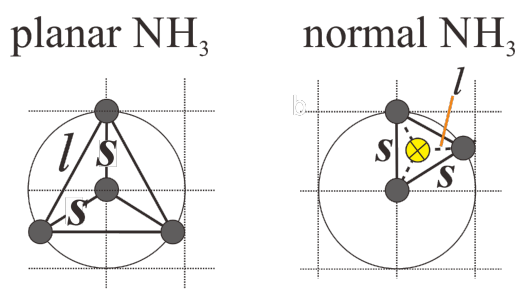




much better than CM, why??

K. Hansen, *et al.*, *JPCL*, 2015

non-uniqueness issue



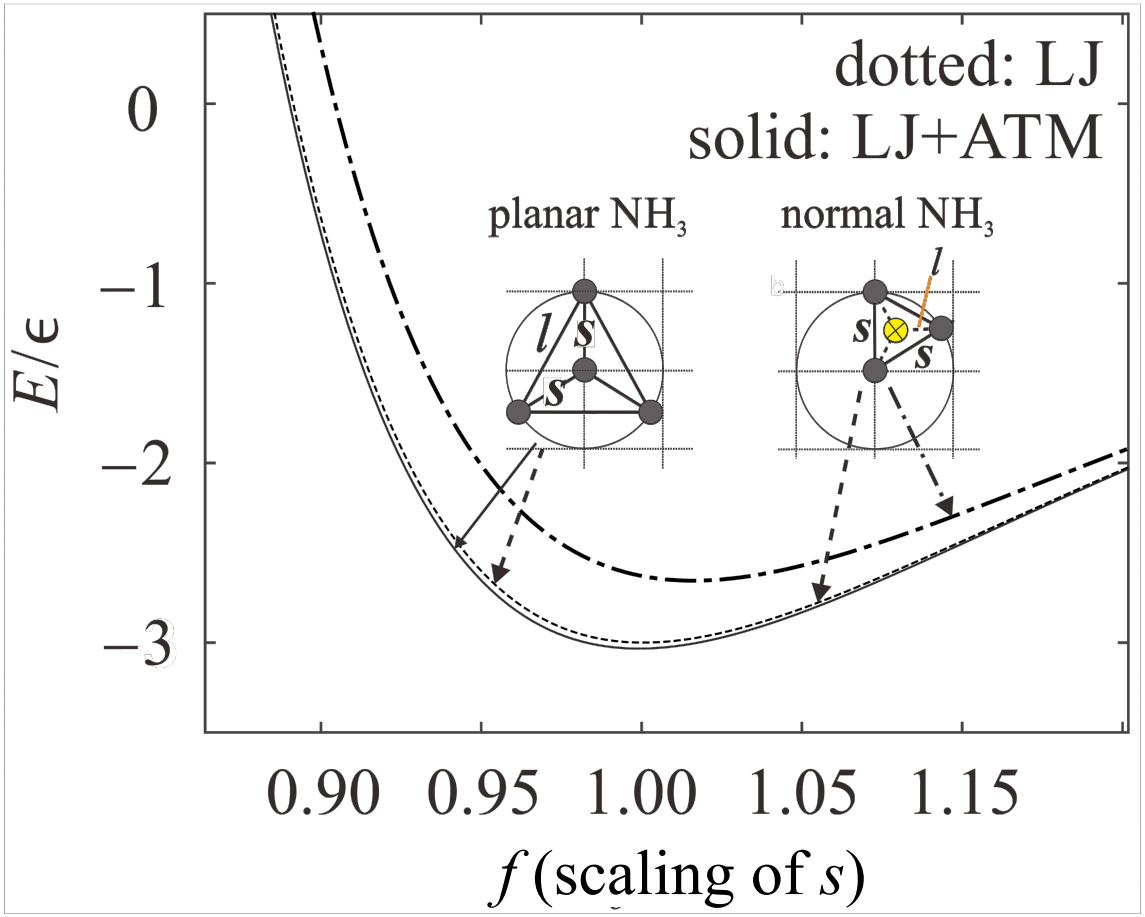
homometric molecules

same set of interatomic distance pairs

OAvL, *et al.*, IJQC, 2015

non-uniqueness issue

LJ: Lennard-Jones 2-body vdW potential
ATM: Axilrod-Teller-Muto 3-body vdW potential



homometric molecules

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BH, OAvL, *JCP comm.*, 2016

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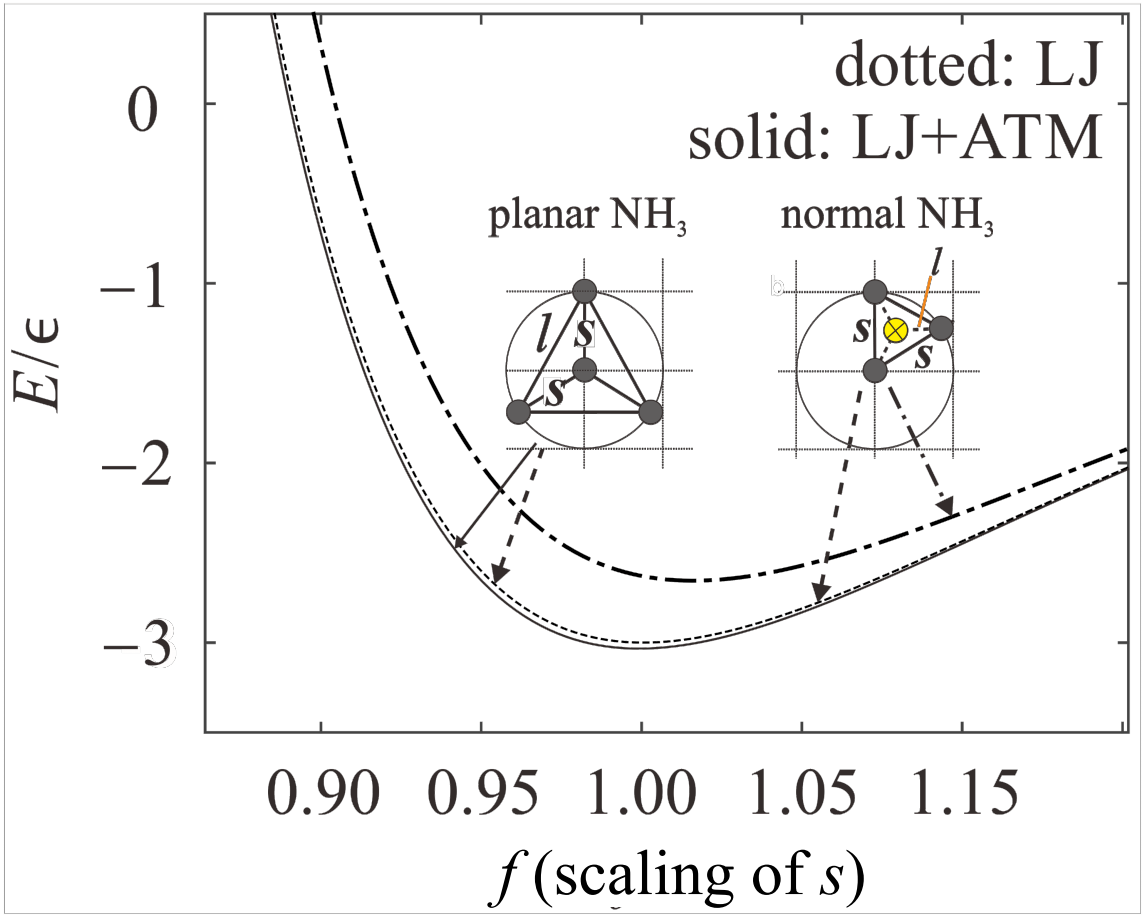


homometric molecules

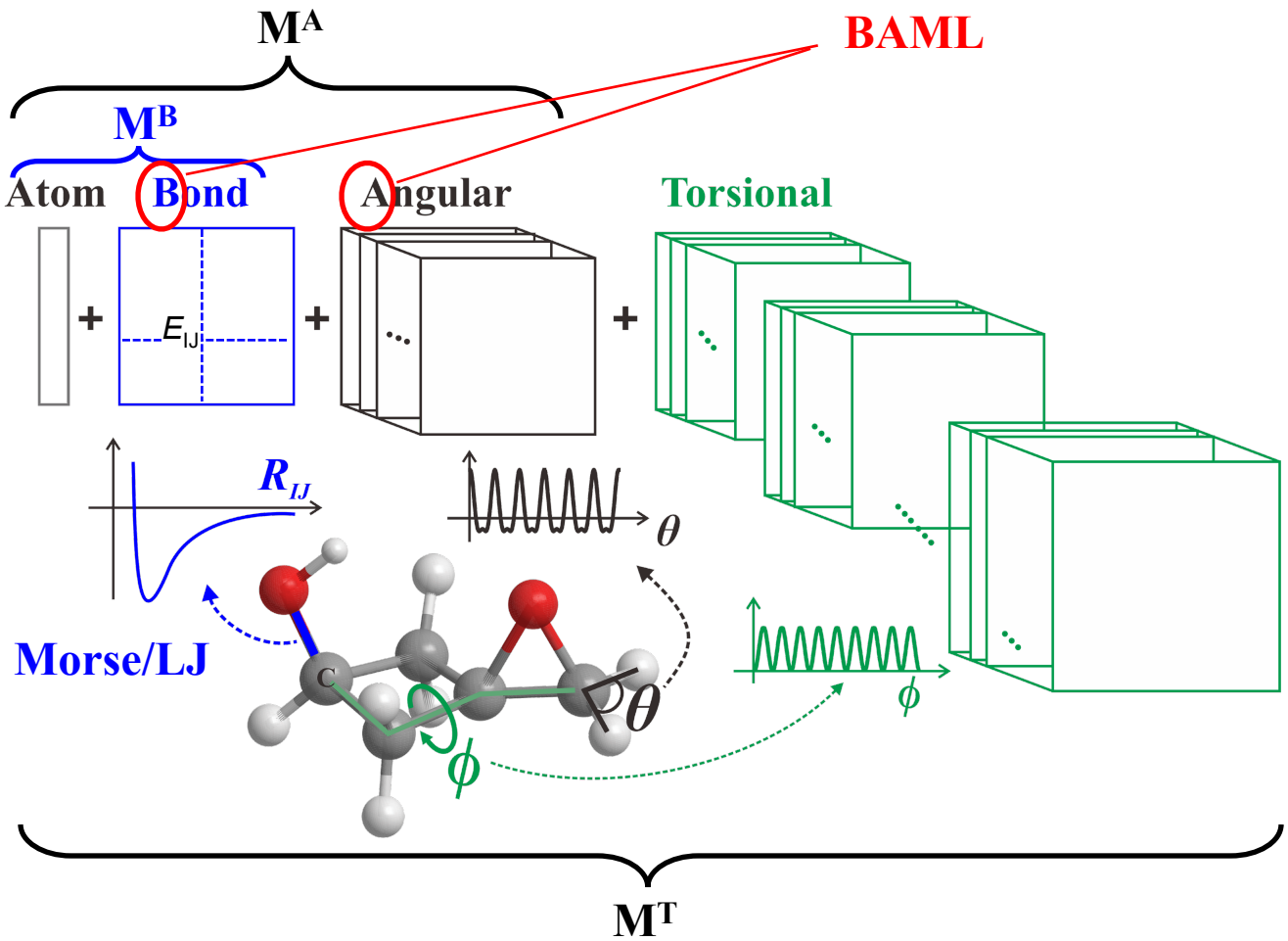
same set of interatomic distance pairs

2-body interaction is not enough!

BH, OAvL, *JCP comm.*, 2016

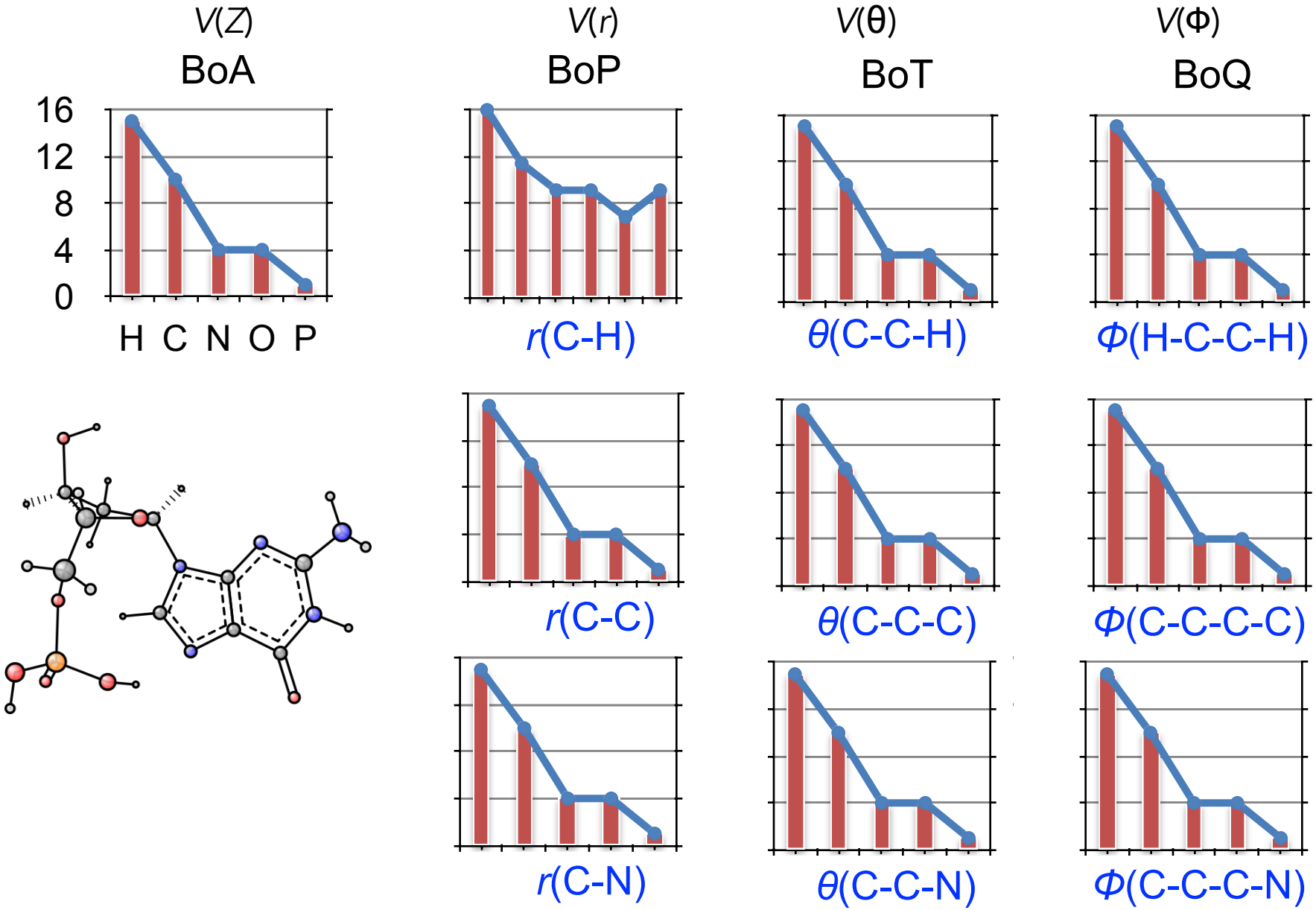
BAML

bags of Universal force field (UFF) contributions

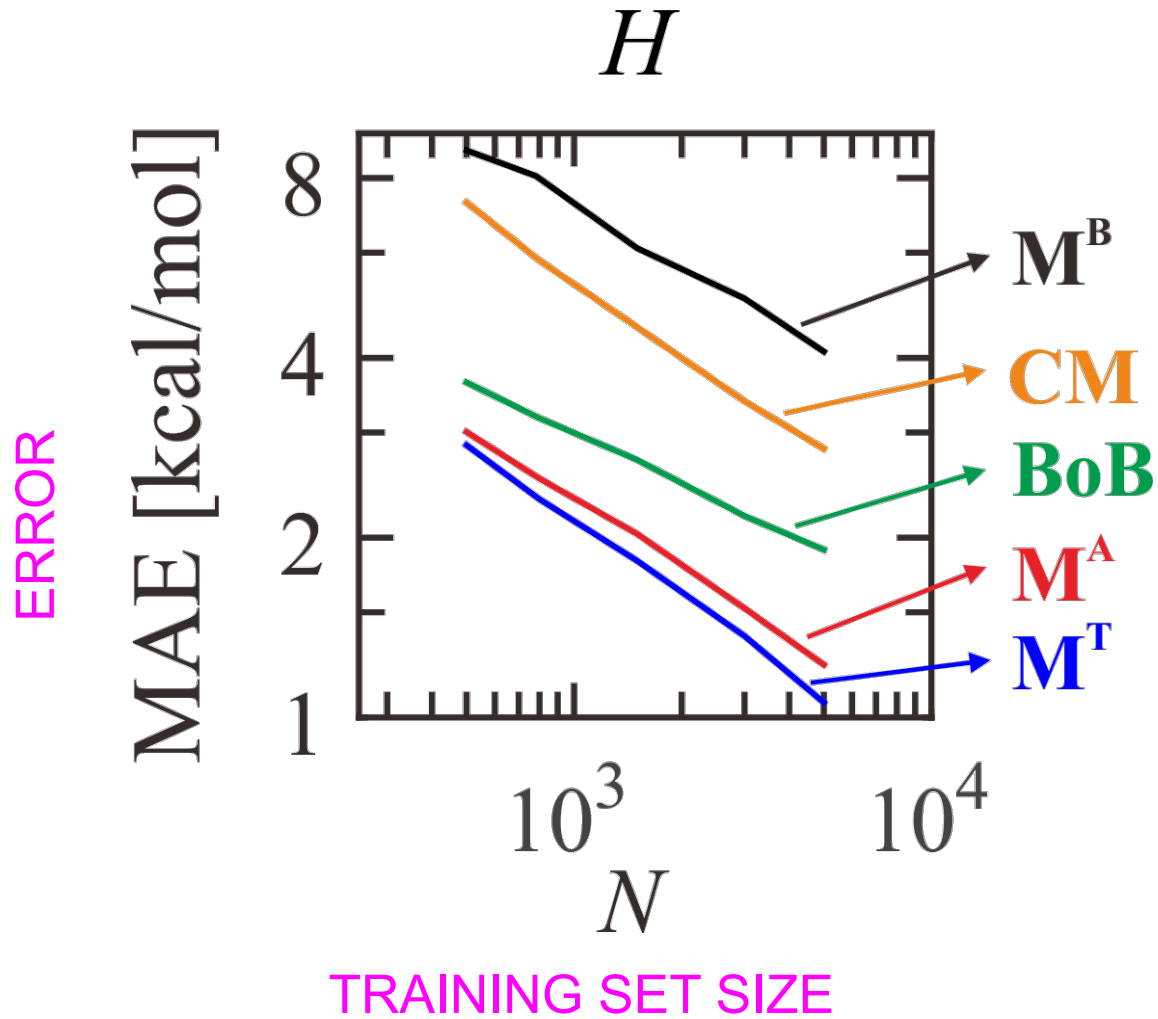


BH, OAvL, *JCP comm.*, 2016

BAML


V(Z)
BoA
16
12
8
4
0
H C N O P
V(r)
BoP
r(C-H)
V(θ)
BoT
θ(C-C-H)
V(Φ)
BoQ
Φ(H-C-C-H)
r(C-C)
θ(C-C-C)
Φ(C-C-C-C)
r(C-N)
θ(C-C-N)
Φ(C-C-C-N)

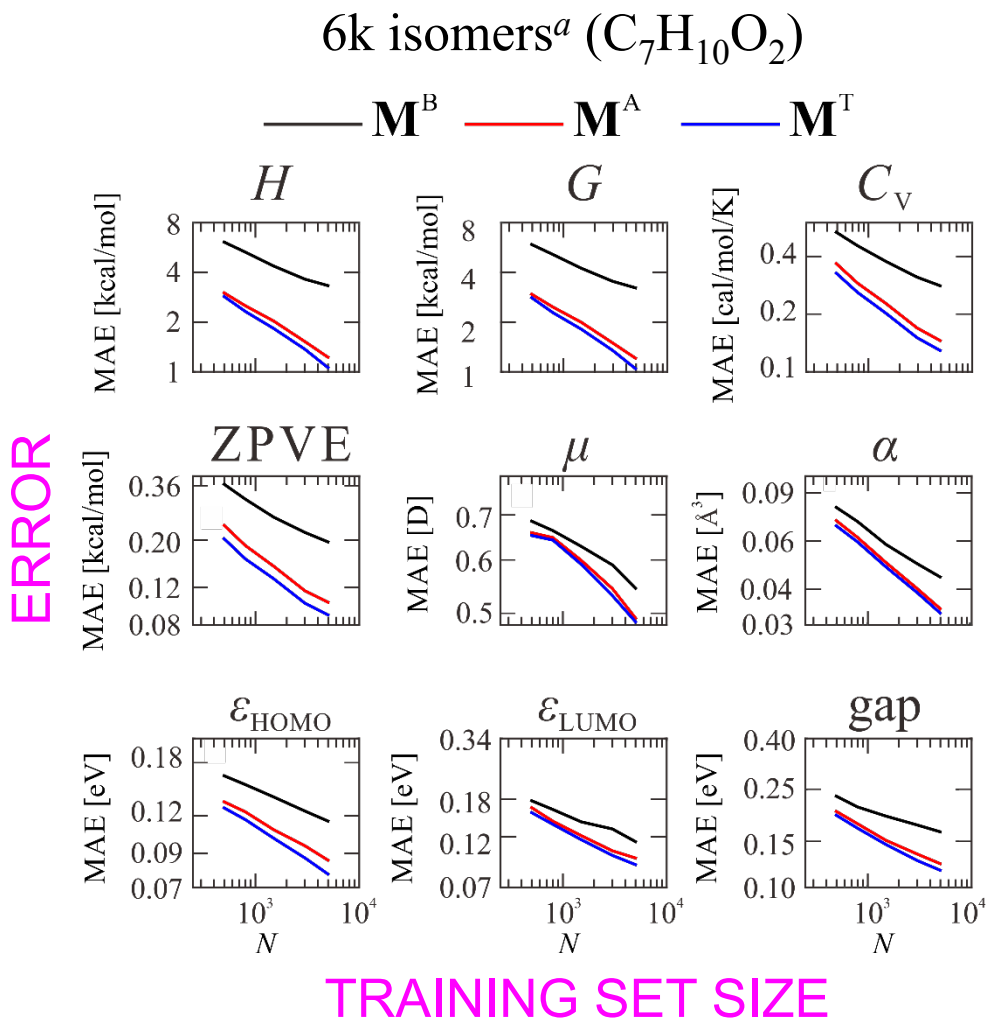
BAML



database: 6k isomers
($C_7H_{10}O_2$)

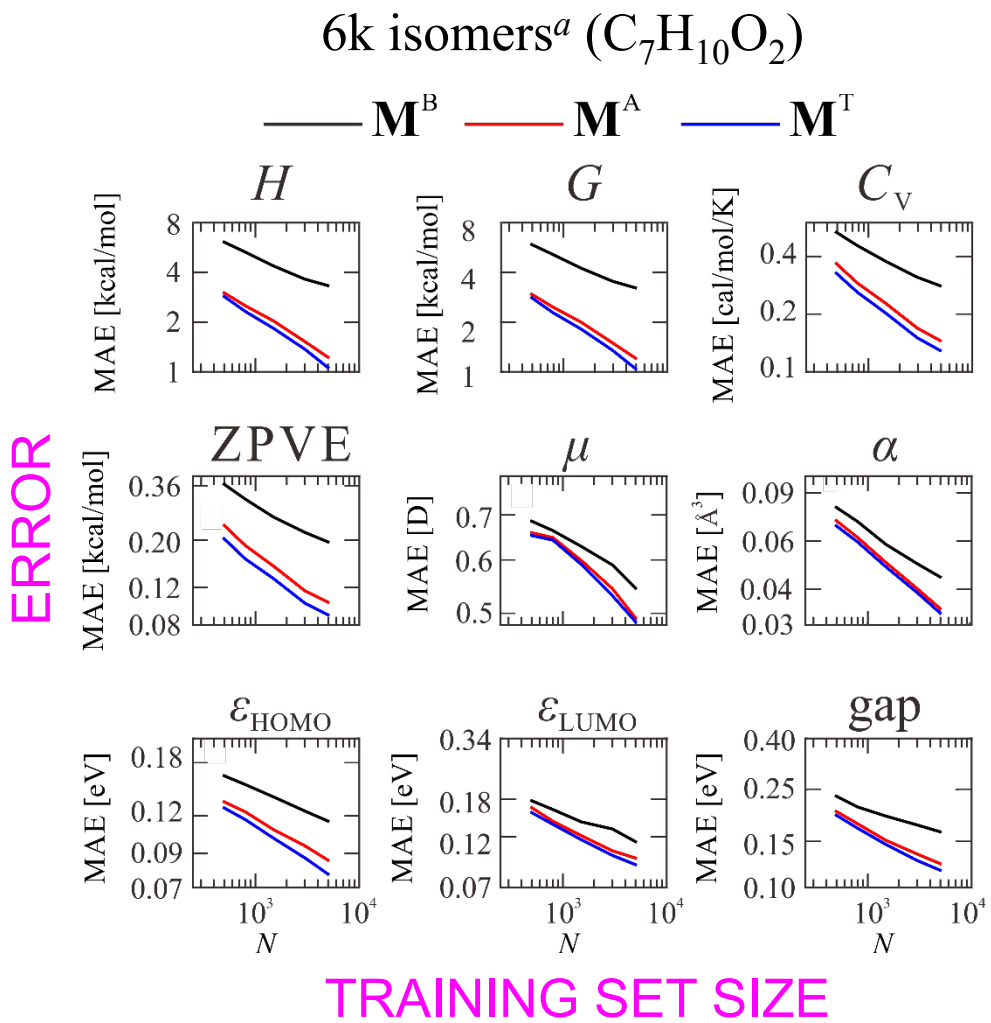
BH, OAvL, *JCP comm.*, 2016

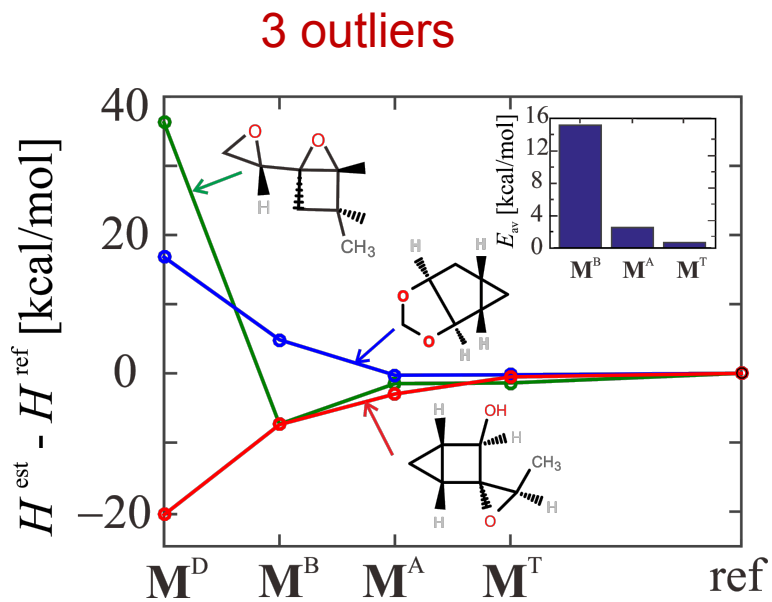
BAML



BH, OAvL, *JCP comm.*, 2016

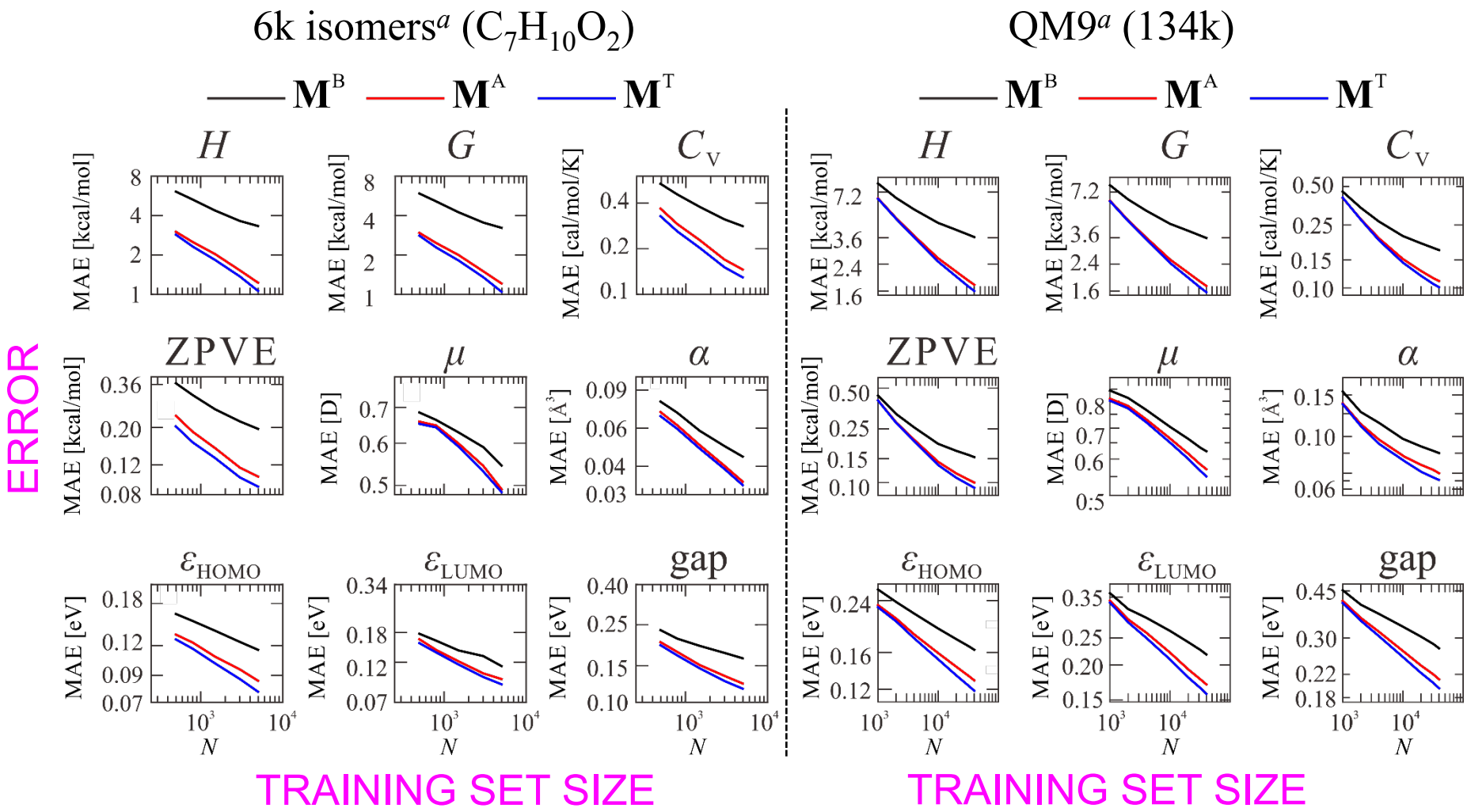
BAML





BH, OAvL, *JCP comm.*, 2016

BAML



BH, OAvL, *JCP comm.*, 2016

BAML

Comparison QM7b database (size: 7211)

MAE (5k out-of-sample)

	BAML	BoB	SOAP[a]	CM[b]	accuracy[b]
E (PBE0)/eV	0.05	0.08	0.04	0.16	0.15, 0.23, 0.09-0.22
α (PBE0)/ Å^3	0.07	0.09	0.05	0.11	0.05-0.27, 0.04-0.14
HOMO (GW)/eV	0.10	0.15	0.12	0.16	-
LUMO (GW)/eV	0.11	0.16	0.12	0.16	-
IP (ZINDO)/eV	0.15	0.20	0.19	0.17	0.20, 0.15
EA (ZINDO)/eV	0.07	0.17	0.13	0.11	0.16, 0.11
E_{1st}* (ZINDO)/eV	0.13	0.21	0.18	0.13	0.18, 0.21

[a] S. De, *et al.*, *PCCP*, 2016
[b] G. Montavon, *et al.*, *NJP,* 2013

BH, OAvL, *JCP comm.*, 2016

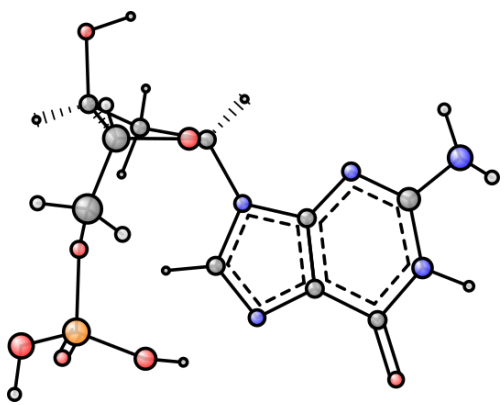
HDAD

$V(r) = r$

$V(\theta) = \theta$

$V(\Phi) = \Phi$

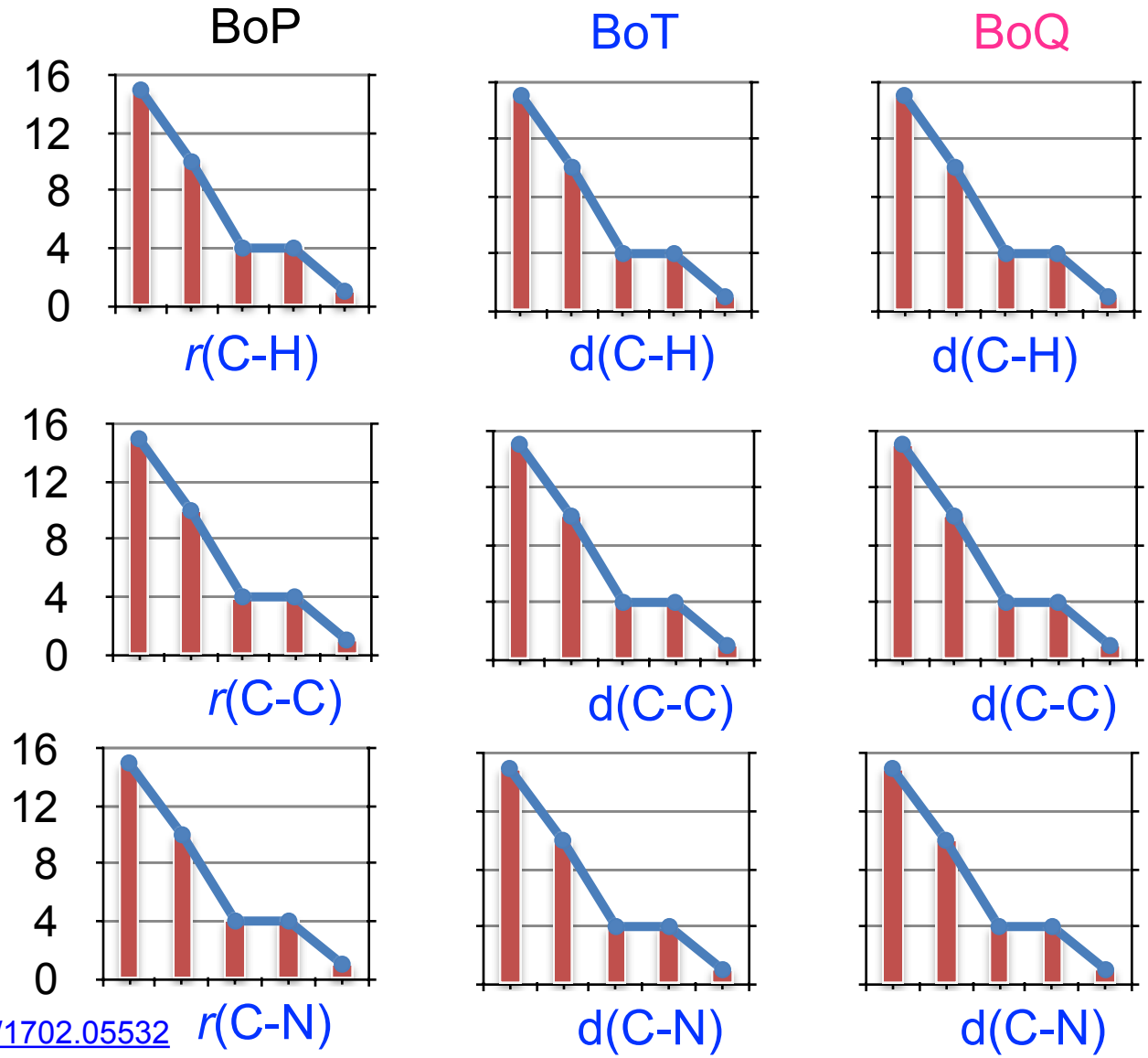
shortcoming:
force prediction



Histogram of Distance

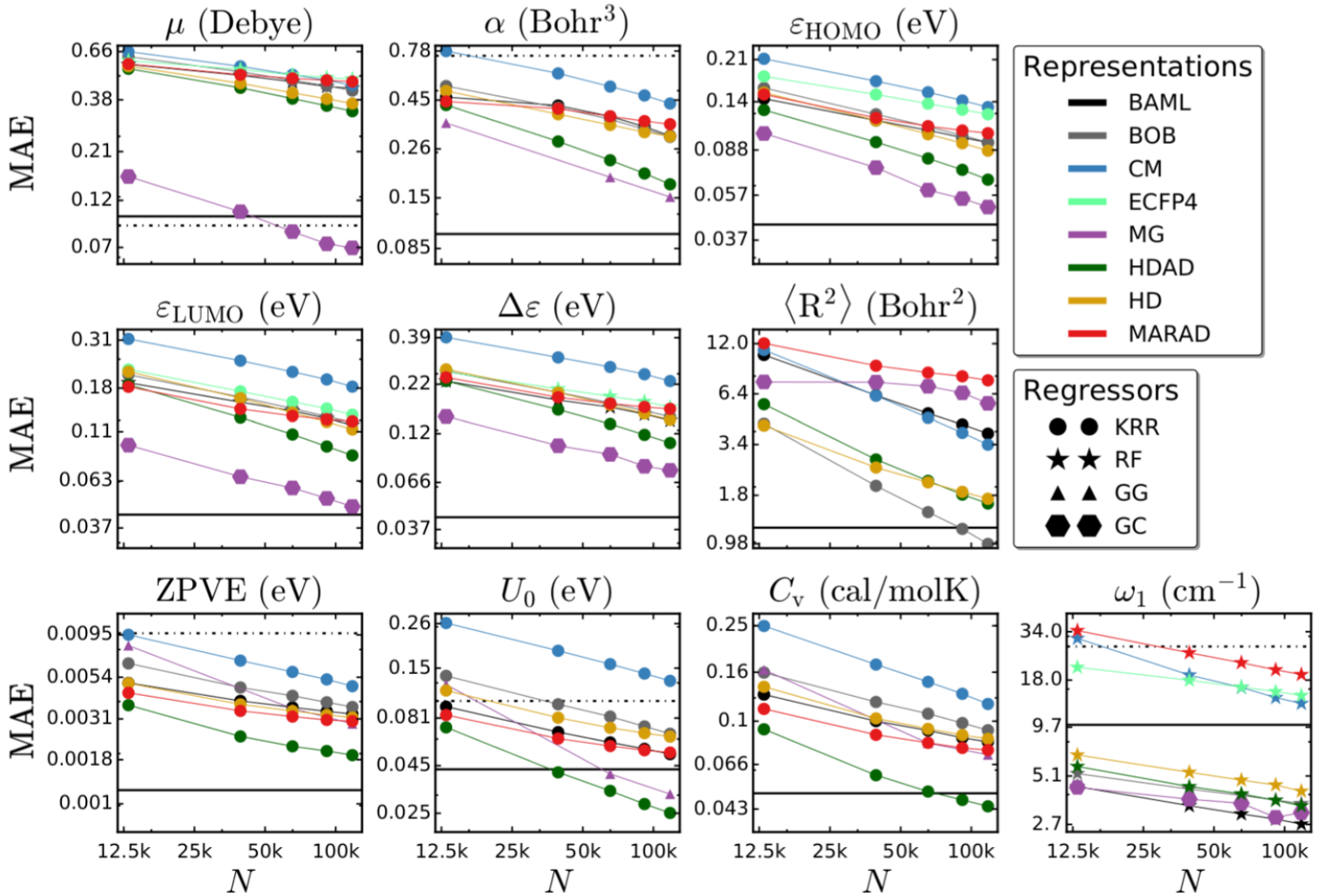
Histogram of Angles

Histogram of Dihedral angles



F. Faber, *et al.*, 2017, arxiv.org/abs/1702.05532

HDAD



F. Faber, *et al.*, 2017, arxiv.org/abs/1702.05532

Why is BAML worse than HDAD?

* empirical force field terms fails to describe reality in many cases

* uniqueness might also be an issue
    * e.g., a slighted deviated Morse potential may cause uniqueness issue

Bear in mind once again:

* be cautious to use the target function as representations!

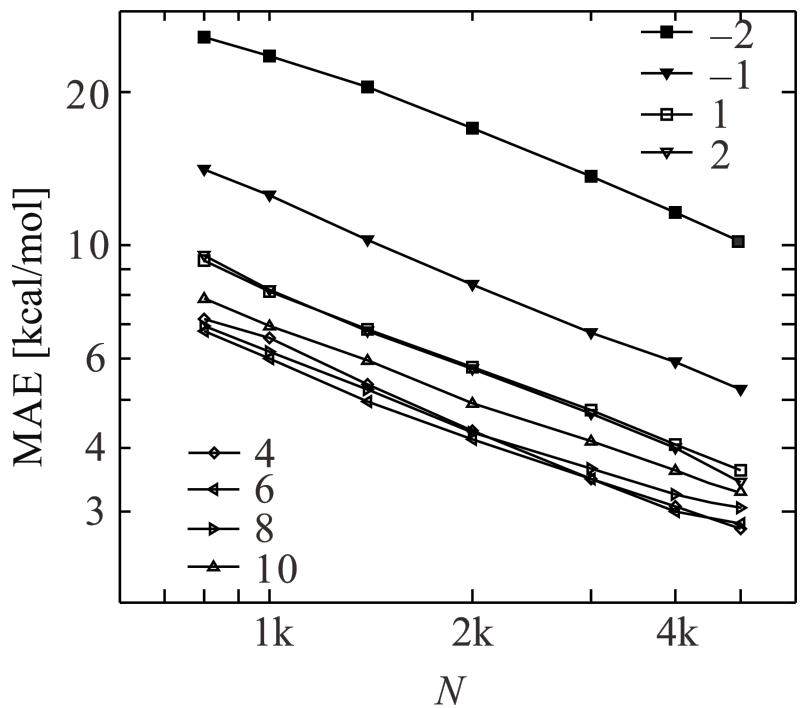
Improving the physics

E(2) = $Z_i Z_j$/R^n

QM7b dataset (size:7211)
property: enthalpy (H)

$$H^{\text{est}}(\text{CM}^{(n)}) = \sum \alpha_i k(\text{CM}^{(n)}, \text{CM}_i^{(n)})$$

Coulomb force: good as a rpst for bonding, bad for dispersion



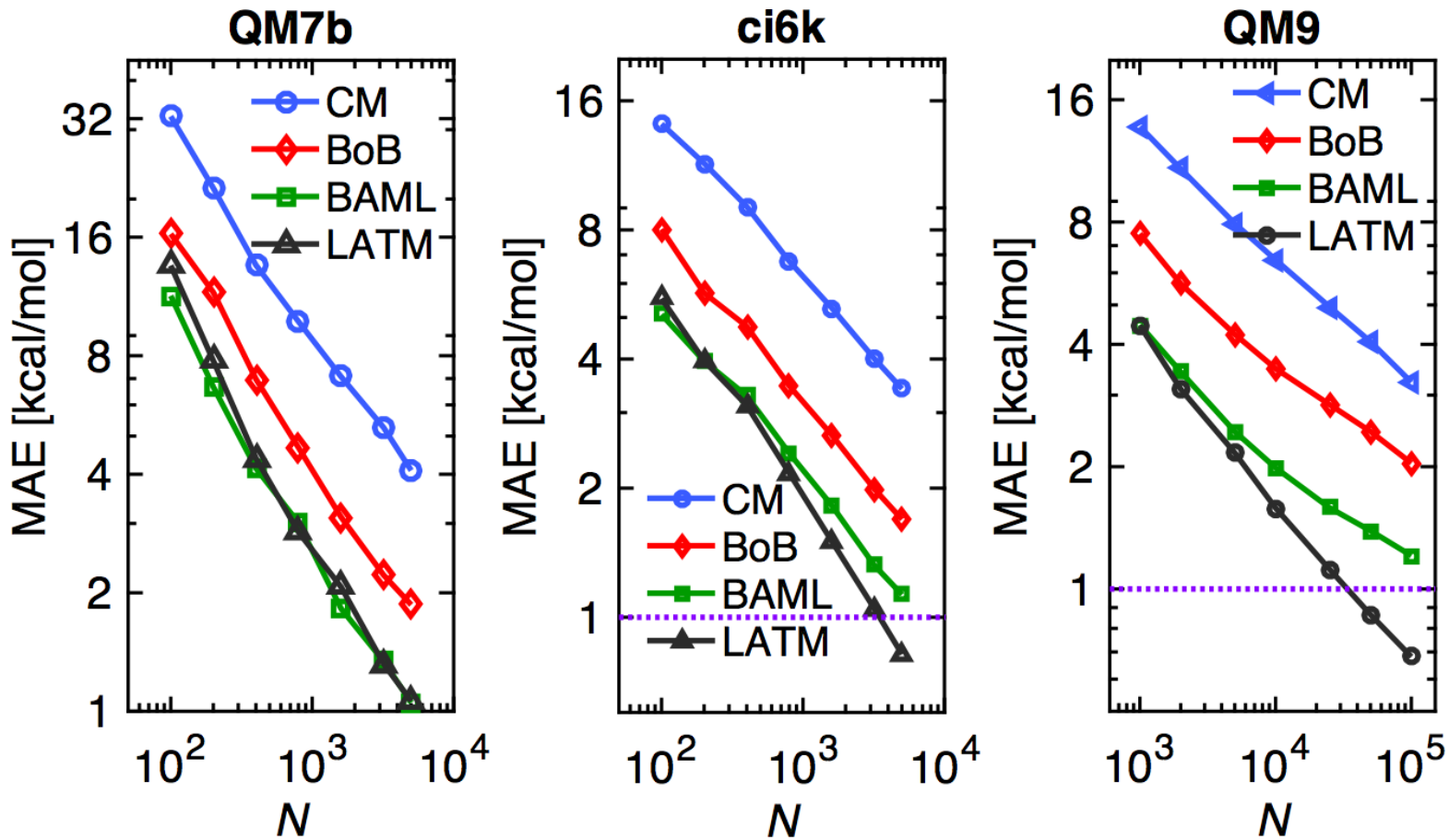
London force: good for dispersion, decent for bond

as a comprise, London wins!!

Improving the physics

Atoms + **L**ondon + **A**xilrod-**T**eller-**M**uto **(LATM)**

$$E^{(2)}(\mathbf{R_I}, \mathbf{R_J}) = -\frac{C_{6_{IJ}}}{R_{IJ}^6} \qquad E^{(3)}(\mathbf{R_I}, \mathbf{R_J}, \mathbf{R_K}) = C_{9_{IJK}} \frac{3\cos[\phi_I]\cos[\phi_J]\cos[\phi_K] + 1}{R_{IJ}^3 R_{IK}^3 R_{JK}^3}$$



HB, OAvL, *to be submitted* (2017)

extending *E*-based approach

build rpst based on decomposition of any extensive property:

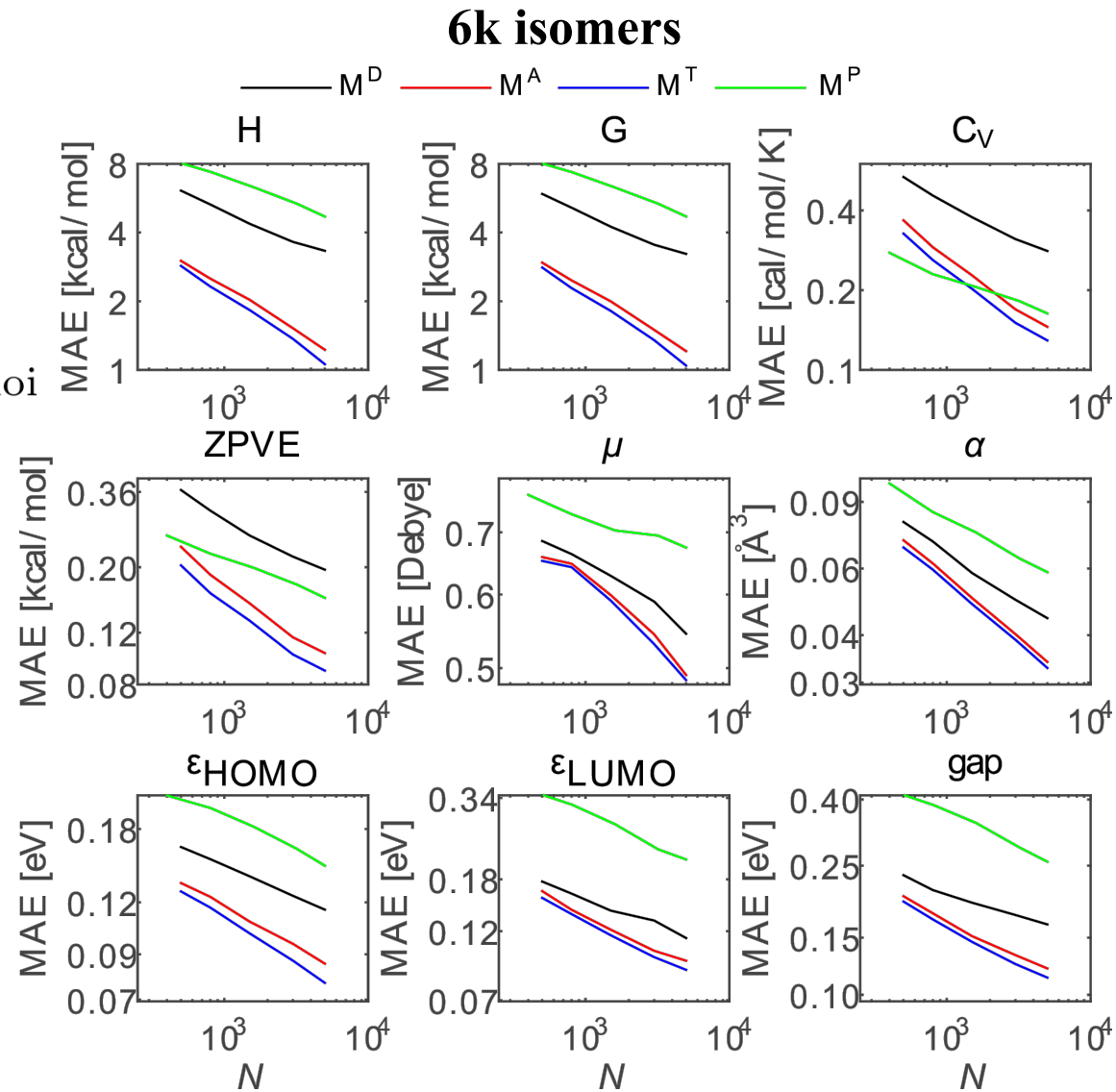
e.g., polarizability model

$$\alpha = \sum_I \alpha_I = \sum_I c_I V_I^{\text{voronoi}}$$

$$\mathbf{M}^{\mathrm{P}} = \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \vdots \\ \alpha_n \end{bmatrix}$$

Only ONE-body!!

BH, OAvL, *JCP comm.*, 2016



Categorizing M

I

II

III

global representations

$\Psi/\rho/V$-based

continuous

discrete

E-based

atomic representations

Go Atomic

$$\varepsilon_i = \varepsilon(\mathbf{d}_i, \mathbf{w}) = \sum_h w_h \phi_h(\mathbf{d}_i);$$

$$\langle \varepsilon_i \varepsilon_j \rangle = \left\langle \sum_{hh'} w_h w_{h'} \phi_h(\mathbf{d}_i) \phi_{h'}(\mathbf{d}_j) \right\rangle = \sum_{hh'} \langle w_h w_{h'} \rangle \phi_h(\mathbf{d}_i) \phi_{h'}(\mathbf{d}_j)$$
$$= \sigma_w^2 \sum_h \phi_h(\mathbf{d}_i) \phi_h(\mathbf{d}_j)$$

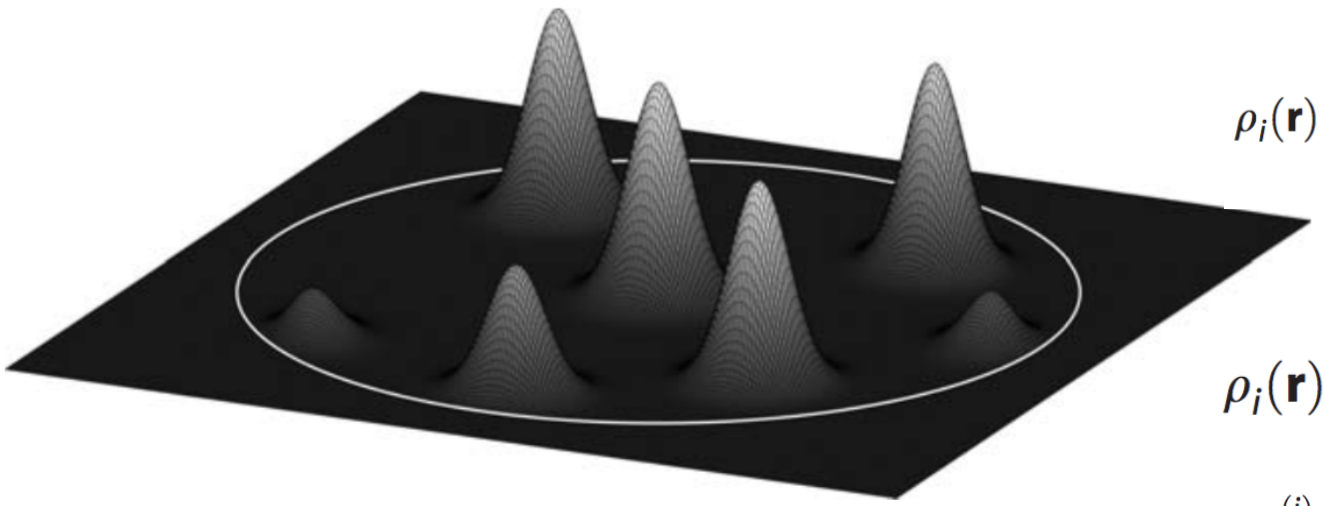
covariance

$$\langle E_N E_M \rangle = \left\langle \sum_{i \in N} \varepsilon(\mathbf{d}_i) \sum_{j \in M} \varepsilon(\mathbf{d}_j) \right\rangle = \left\langle \sum_{i \in N} \sum_{j \in M} \sum_{hh'} w_h w_{h'} \phi_h(\mathbf{d}_i) \phi_{h'}(\mathbf{d}_j) \right\rangle$$
$$= \sum_{i \in N} \sum_{j \in M} \sum_{hh'} \langle w_h w_{h'} \rangle \phi_h(\mathbf{d}_i) \phi_{h'}(\mathbf{d}_j) = \sigma_w^2 \sum_{i \in N} \sum_{j \in M} \sum_h \phi_h(\mathbf{d}_i) \phi_h(\mathbf{d}_j)$$
$$= \sigma_w^2 \sum_{i \in N} \sum_{j \in M} C(\mathbf{d}_i, \mathbf{d}_j)$$

$$Y_i^{\text{est}}(\mathbf{X}_i) = \sum_j \alpha_j \boxed{\exp\left(-\frac{d(\mathbf{X}_j, \mathbf{X}_i)}{\sigma}\right)} + b$$

P. R. Bartok *et al*, *IJQC* (2015)

Smooth Overlap of Atomic Positions (SOAP)



$$\rho_i(\mathbf{r}) \equiv \sum_j^{\text{neigh.}} \exp\left(-\frac{|\mathbf{r}-\mathbf{r}_{ij}|^2}{2\sigma_{\text{atom}}^2}\right)$$

projection to basis set

$$\rho_i(\mathbf{r}) = \sum_{nlm} c_{nlm}^{(i)} g_n(r) Y_{lm}(\hat{\mathbf{r}})$$

$$p_{nn'l}^{(i)} \equiv \frac{1}{\sqrt{2l+1}} \sum_m c_{nlm}^{(i)} (c_{n'lm}^{(i)})^*$$

$$C'(\rho_i, \rho_j) = \sum_{n,n',l} p_{nn'l}^{(i)} p_{nn'l}^{(j)}$$

A serious problem of SOAP:
for large r_cutoff, how to distinguish
two very different atoms around centre?

application: simple crystals so far

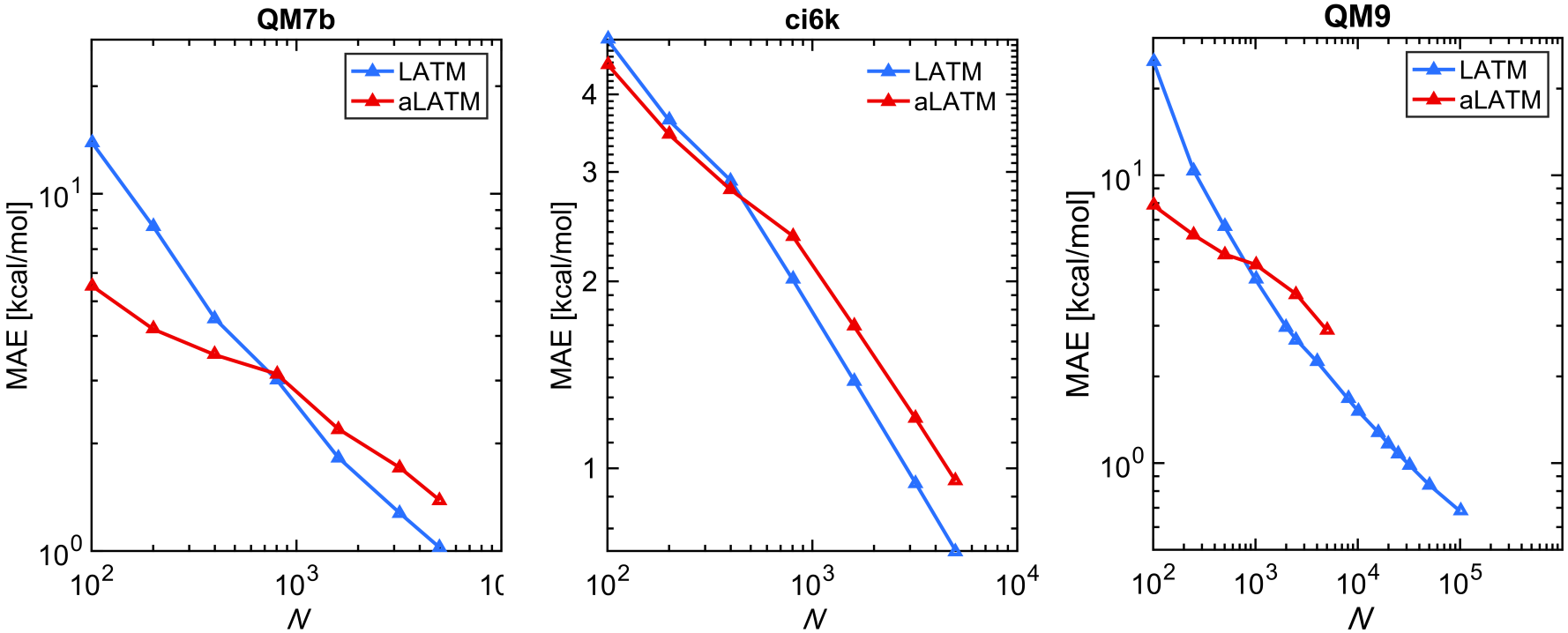
Fix SOAP for molecules by RE-Match, glory lost as an atomic rpst

works best with a small r_cutoff !!

P. R. Bartok *et al*, *PRB* (2013) S. De, *et al.*, *PCCP*, 2016

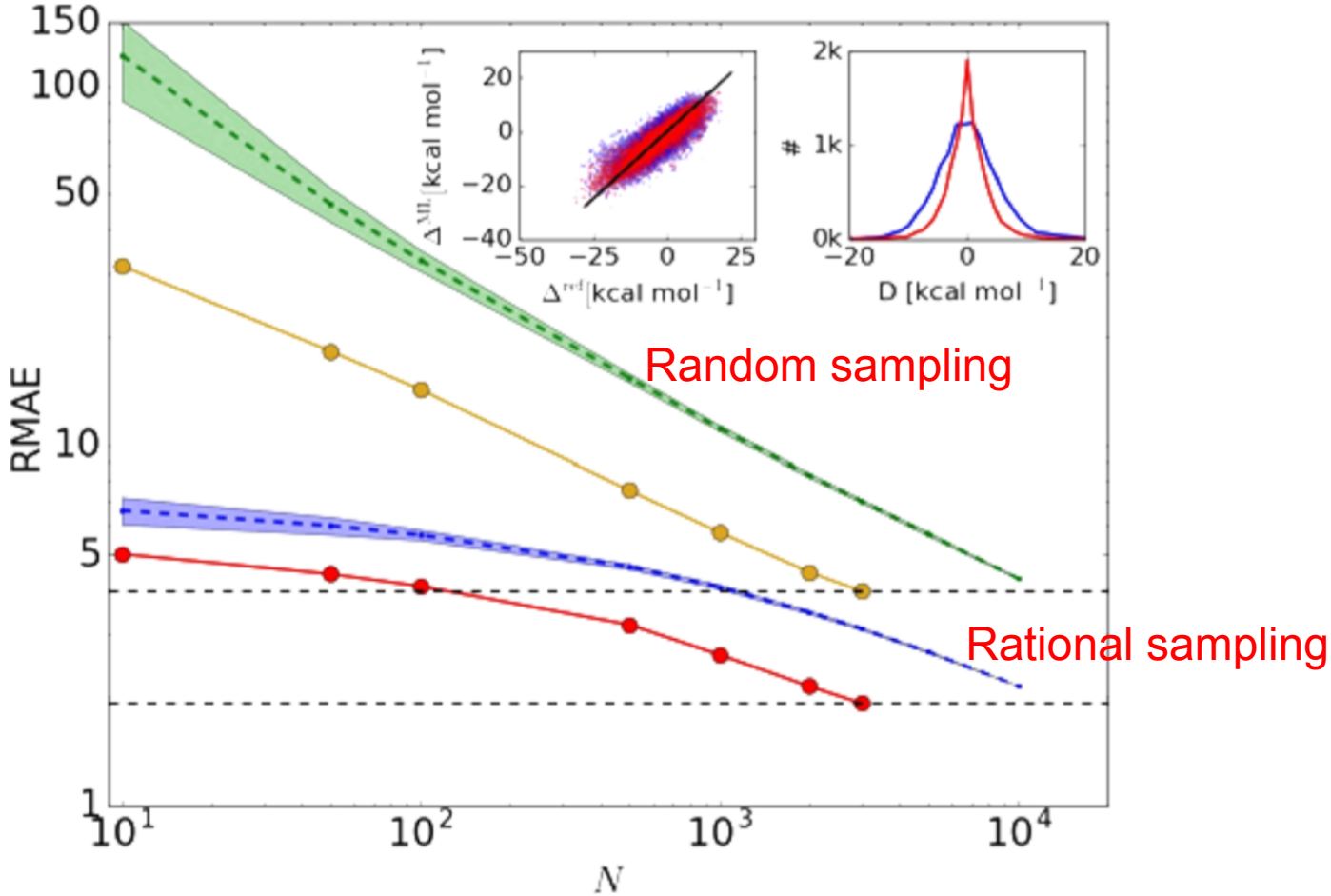
aLATM

MBE-based approach: more natural to define atomic rpst
1. includes 2-, 3-body interactions
2. both decay with r



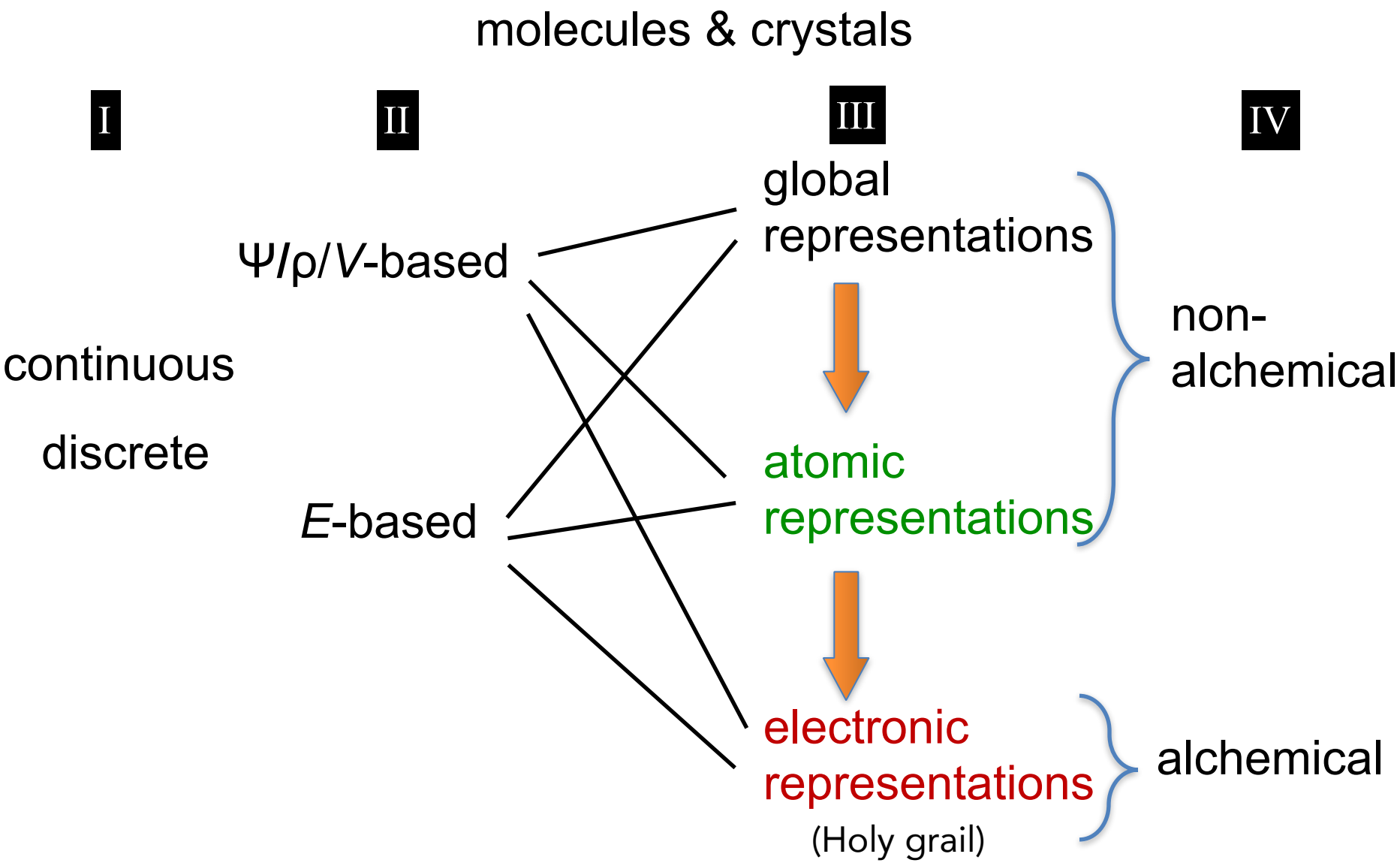
HB, OAvL, *to be submitted* (2017)

why aLATM is bad at larger *N*?



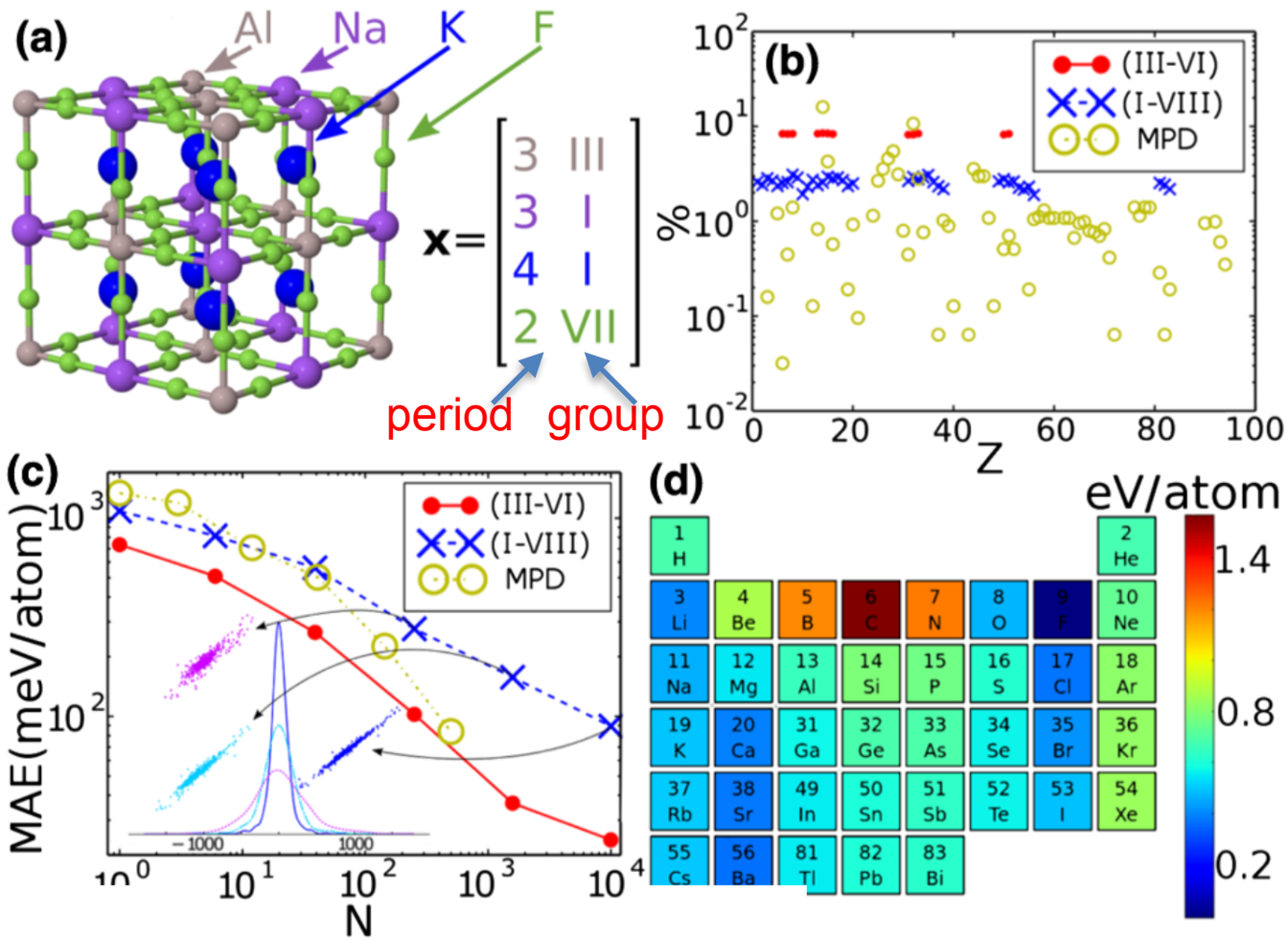
N. J. Browning, *et al.,* JPCL (2017)

Categorizing M



Go Electronic

overall 2*M* Elpasolite ABC_2D_6 Crystals



F. Faber, *et al*, *PRL* (2016)

Conclusions and Outlook

1. Almost all rpsts in literature were categorised

2. Two general approaches for rational design of rpst
    a. Schrödinger equation: ρ/Ψ/V_ext
    b. many-body expansion

3. Two general principles for rational design of rpst
    a. uniqueness (necessary for convergence)
    b. similarity to target reduces off-set of LC

4. MBE based rpst (e.g., BAML, LATM, HDAD) offer
    a. Meaning
    b. Simplicity
    c. Accuracy

5. and is generally better than ρ/Ψ/V_ext based approach

6. There is great potential for electronic rpst to beat everything else

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