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Modeling many-body van der Waals interactions without electrons

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van der Waals

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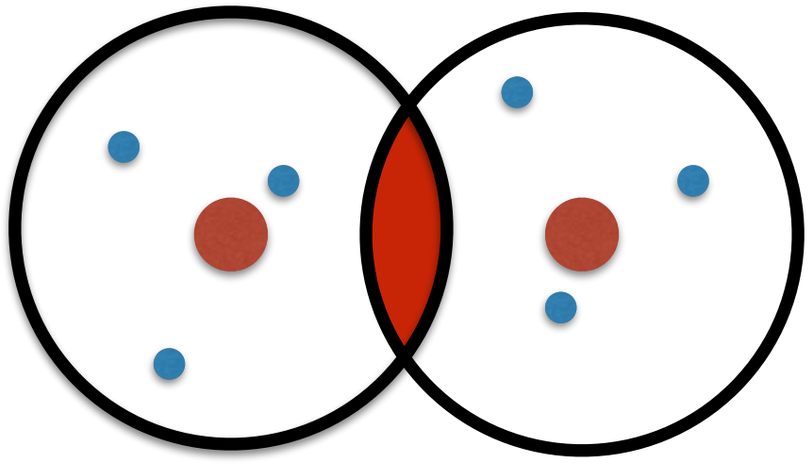
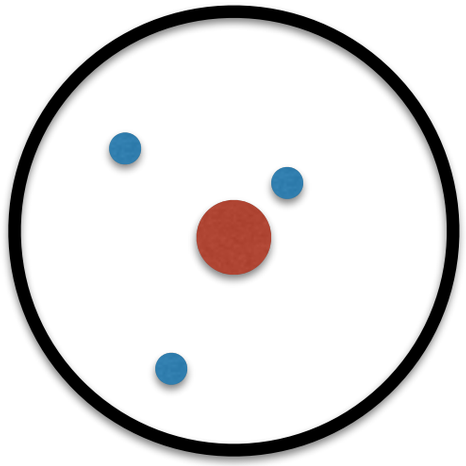
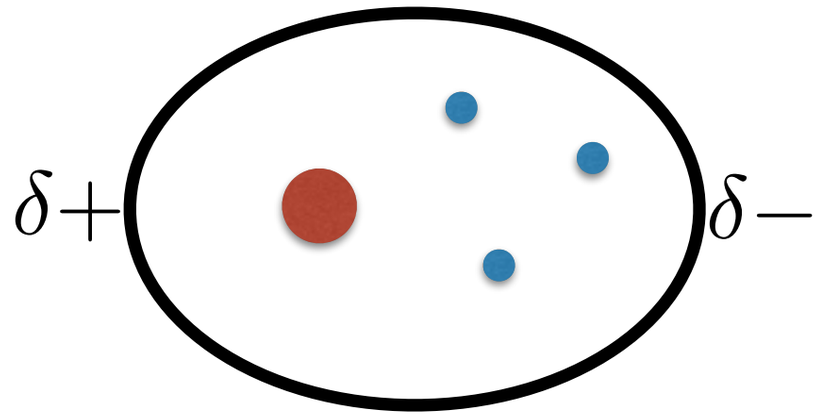
Repulsion



Dispersion





van der Waals

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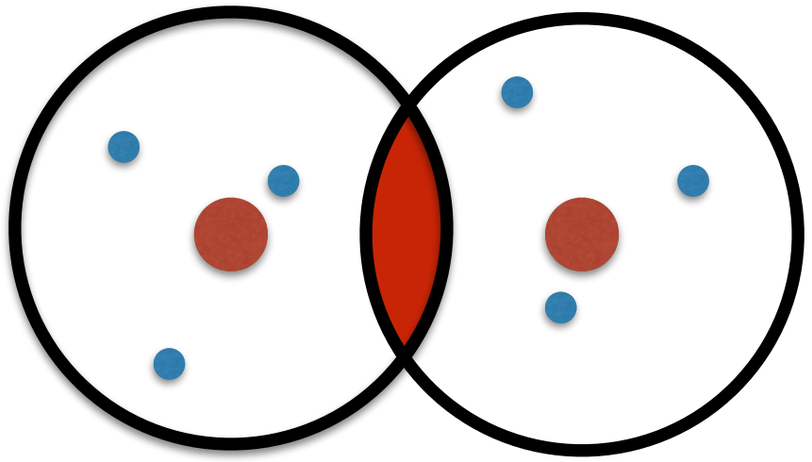
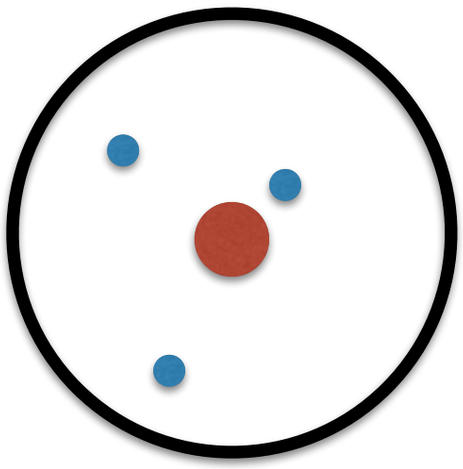
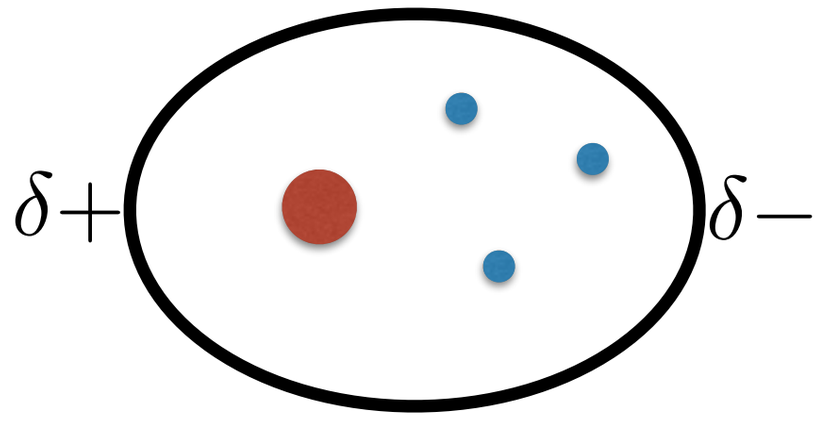
Repulsion



Dispersion





Pairwise assumption

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London dispersion: $$E_{AB} = -\frac{C_{6AB}}{R^6}$$

Casimir-Polder: $$C_{6AB} = \frac{3}{\pi}\int_0^\infty \mathrm{d}\omega \alpha_p(i\omega)\alpha_q(i\omega)$$

Pairwise assumption

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Pairwise approximation can be poor

$$E_{ABC} \neq E_{AB} + E_{BC} + E_{AC}$$

von Lilienfeld and Tkatchenko, J. Chem. Phys. **132** 234109 (2009).

Pairwise assumption

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London dispersion: $$E_{AB} = -\frac{C_{6AB}}{R^6}$$

Generalization?

Casimir-Polder: $$C_{6AB} = \frac{3}{\pi}\int_0^\infty \mathrm{d}\omega \alpha_p(i\omega)\alpha_q(i\omega)$$

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Many-body dispersion (MBD)

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PRL **108,** 236402 (2012) PHYSICAL REVIEW LETTERS week ending 8 JUNE 2012

Accurate and Efficient Method for Many-Body van der Waals Interactions

Alexandre Tkatchenko,[1] Robert A. DiStasio, Jr.,[2] Roberto Car,[2] and Matthias Scheffler[1]

[1]*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*

[2]*Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA*

(Received 4 August 2011; published 7 June 2012)

Dispersion-correction method for **DFT**

Many-body dispersion (MBD)

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PRL **108,** 236402 (2012) PHYSICAL REVIEW LETTERS week ending 8 JUNE 2012

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Dispersion-correction method for **DFT**

- Atomic polarizabilities
  - Scaled from local environment
  - long-range coupling (Thole model)
- MBD energy
  - Quantum harmonic oscillators

MBD model

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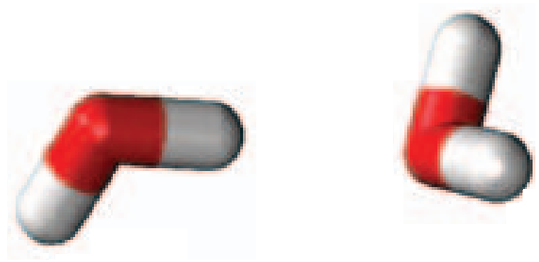
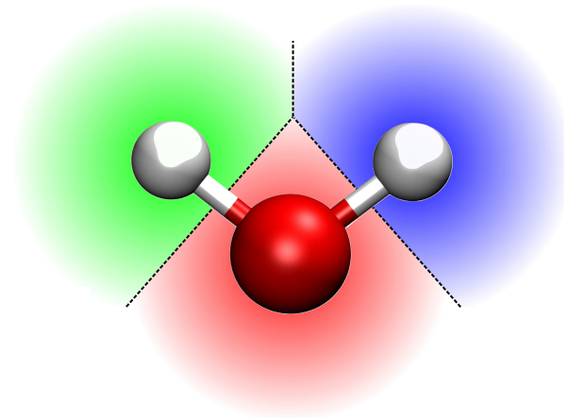
1

DFT



2

Polarizabilities



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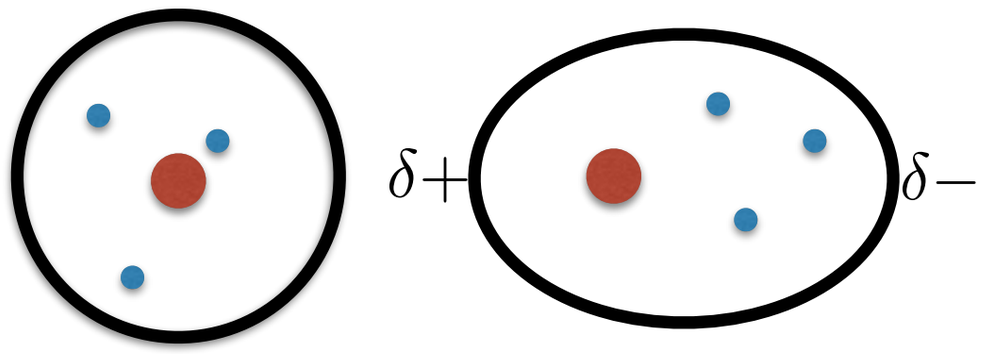
Dispersion energy



MBD model

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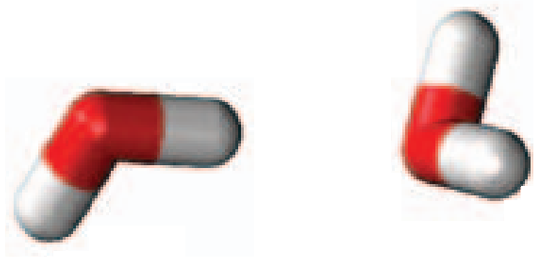
1

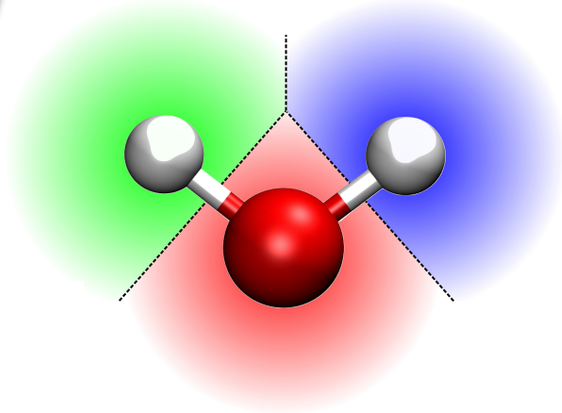
~~DFT~~



- too expensive
- force field

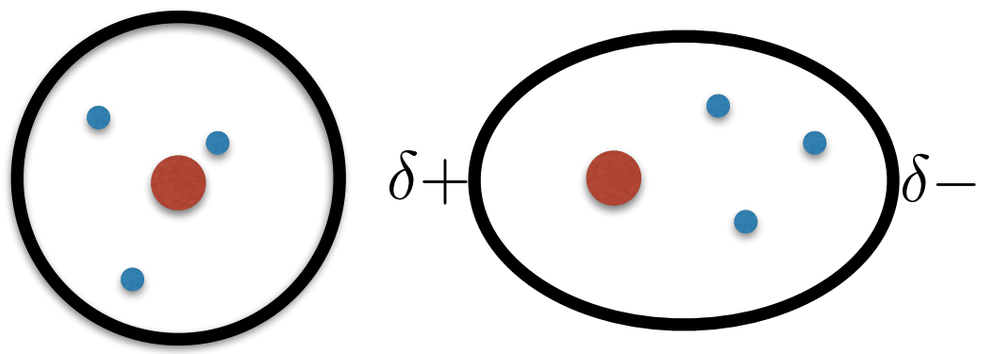
2

Polarizabilities



3

Dispersion
energy



Polarizabilities

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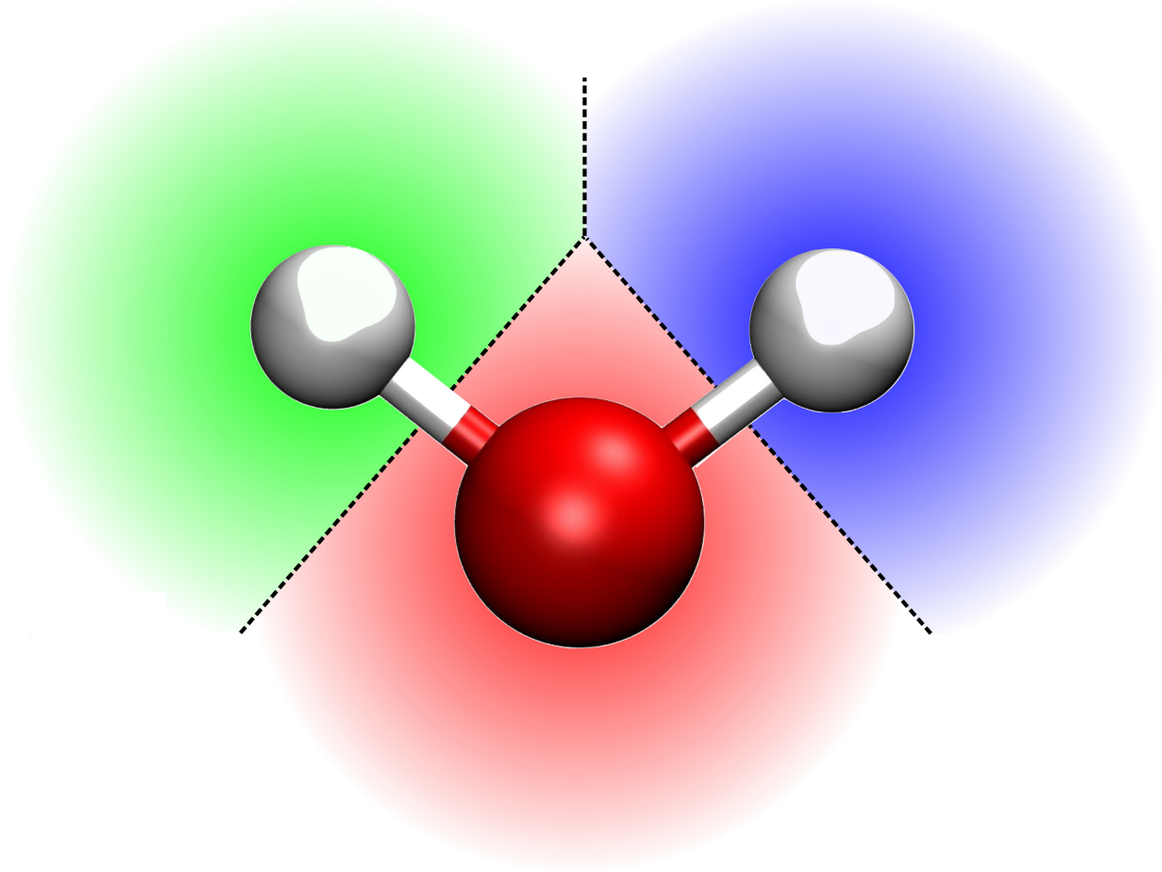
Atom squeezed in molecule lowers polarizability

$$\alpha_p^0 \approx \frac{V_p^{\text{eff}}}{V_p^{\text{free}}}\alpha_p^{\text{free}} = \frac{\int \mathrm{d}\mathbf{r} r^3 w_p(\mathbf{r}) n(\mathbf{r})}{\int \mathrm{d}\mathbf{r} r^3 n_p^{\text{free}}}\alpha_p^{\text{free}}$$

$n(\mathbf{r})$: electron density



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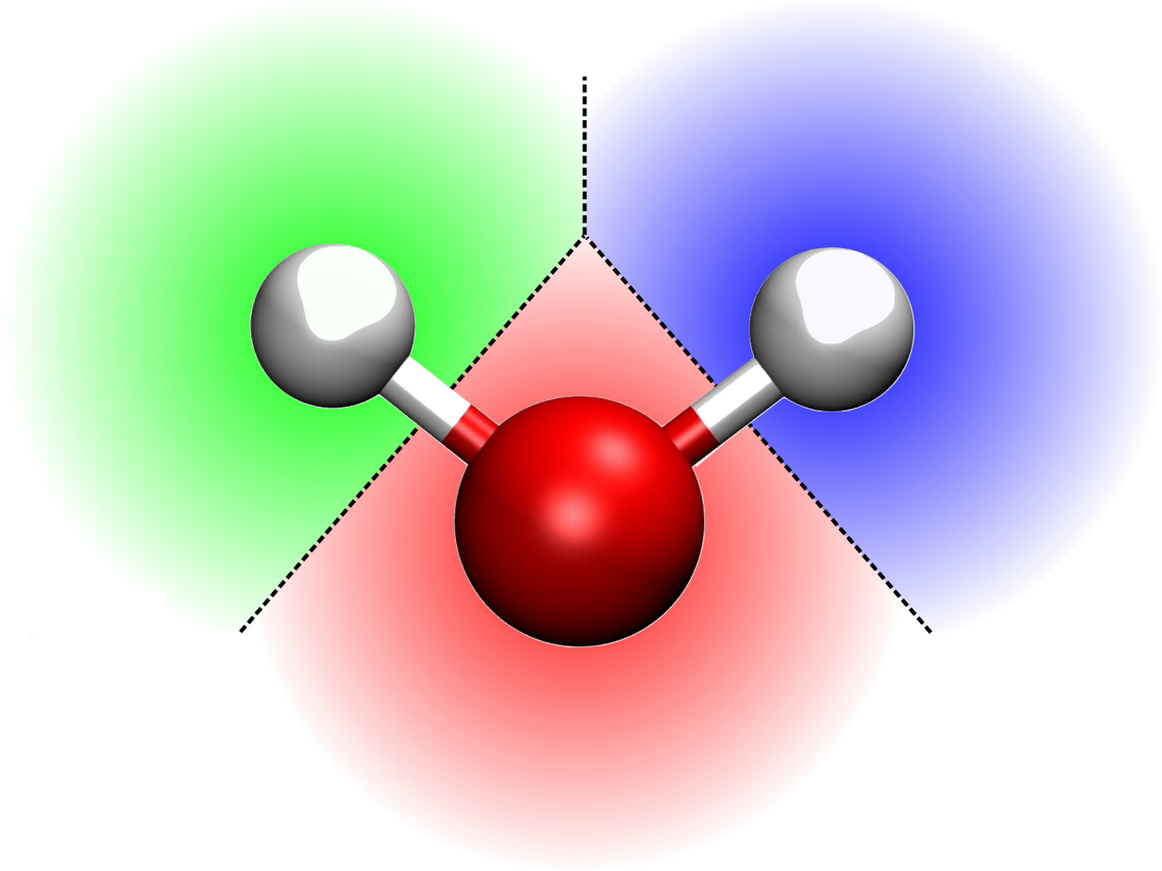
DFT



Polarizabilities

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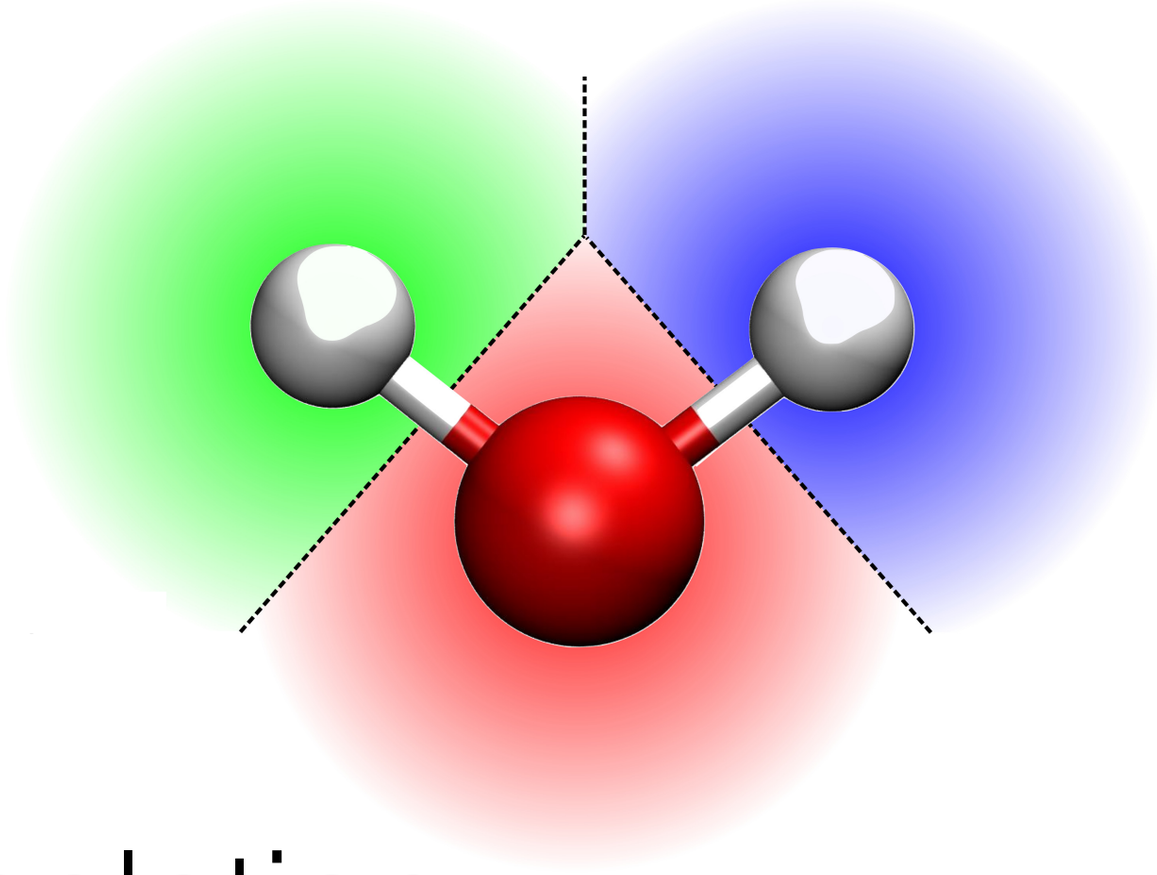
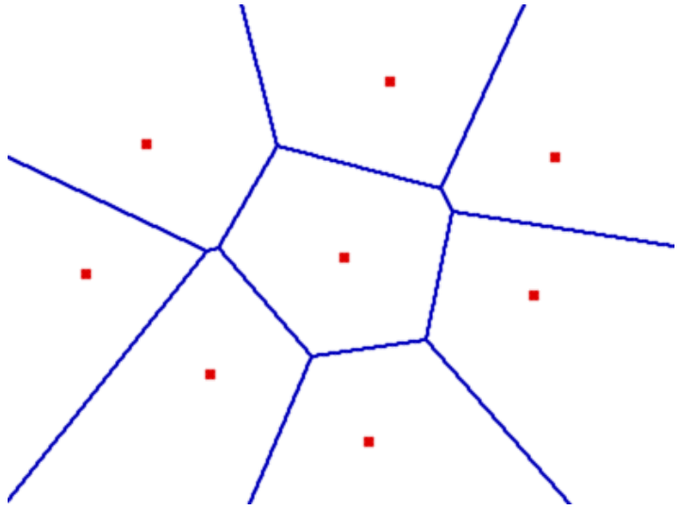


$n(\mathbf{r})$: electron density

~~DFT~~ Voronoi tesselation

$$R_k = \{x \in X \mid d(x, P_k) \leq d(x, P_j) \text{ for all } j \neq k\}$$



Bereau and von Lilienfeld, J. Chem. Phys. **141** 034101(2014).

Voronoi polarizabilities

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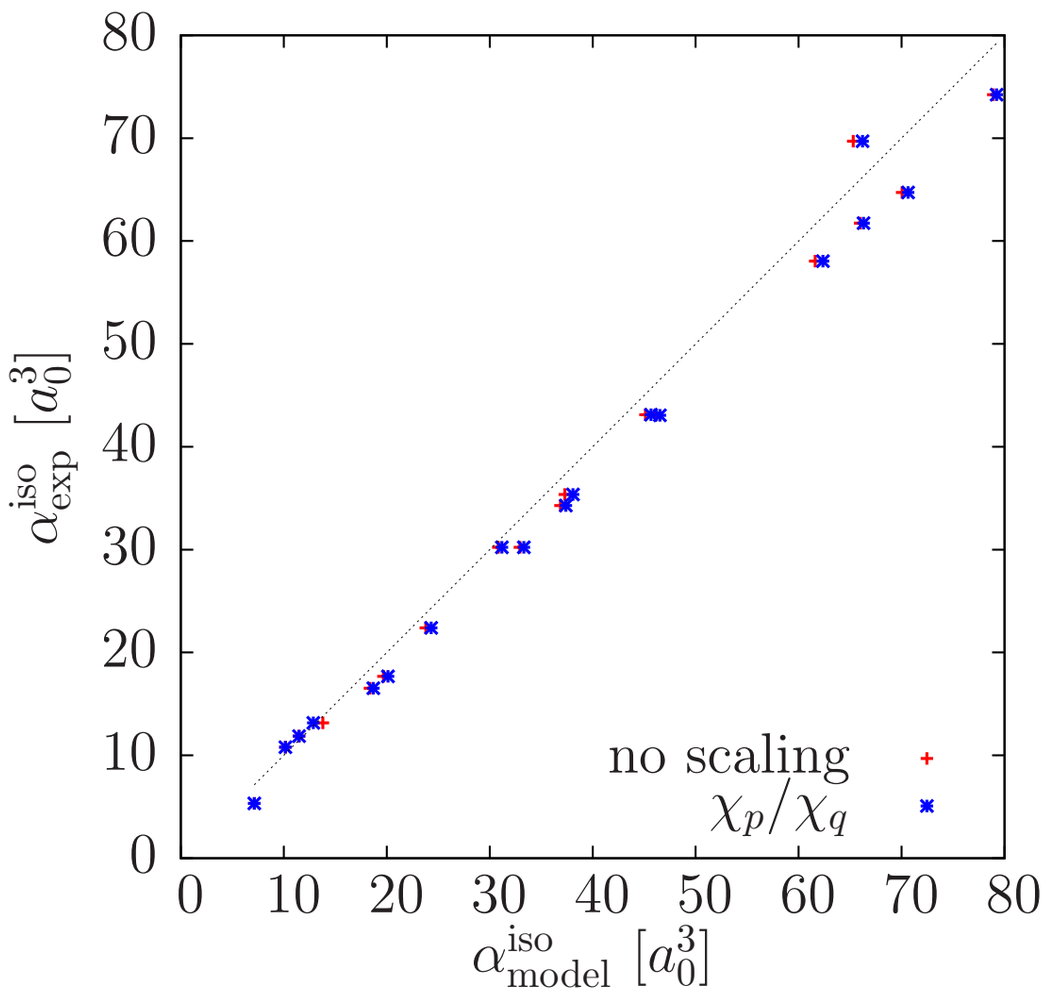
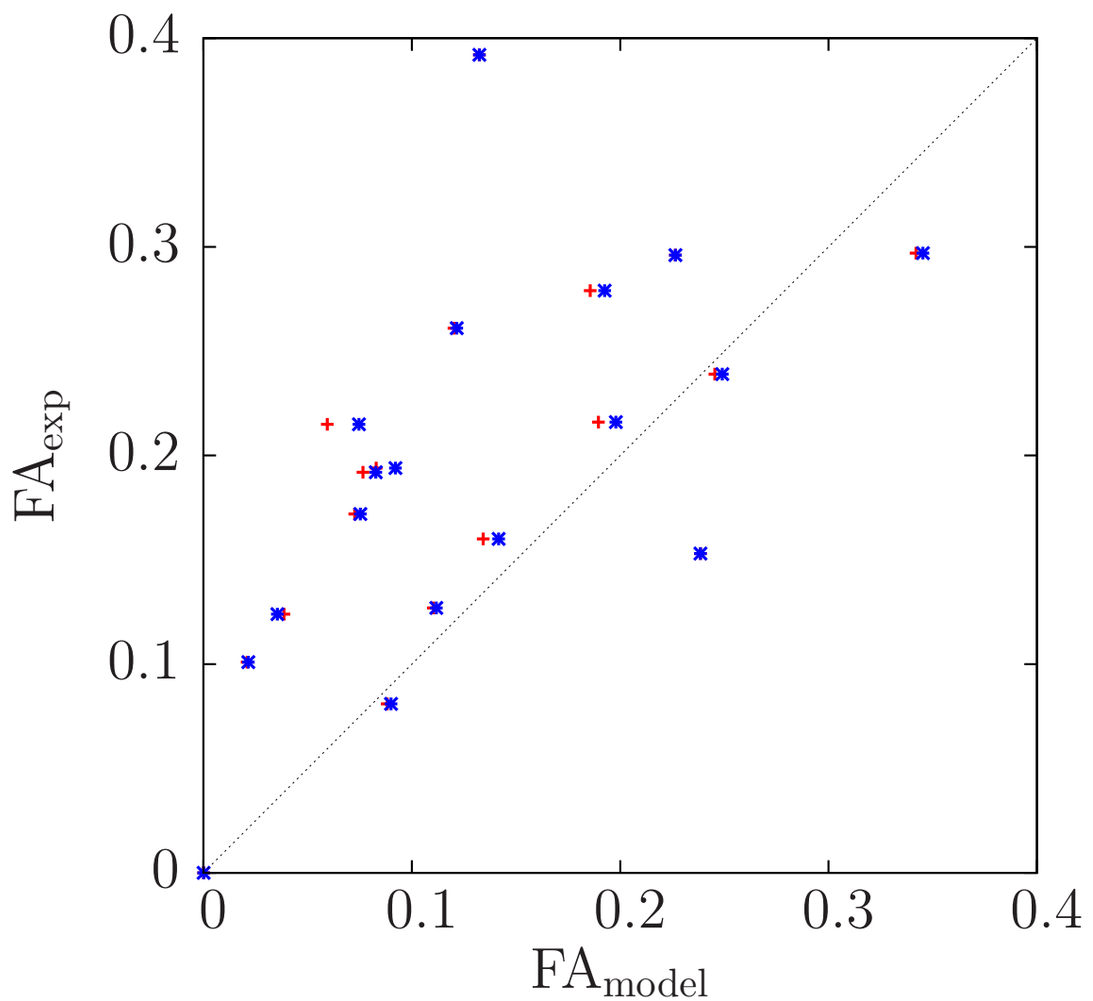
Isotropic component



Anisotropic component



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Energy benchmarks

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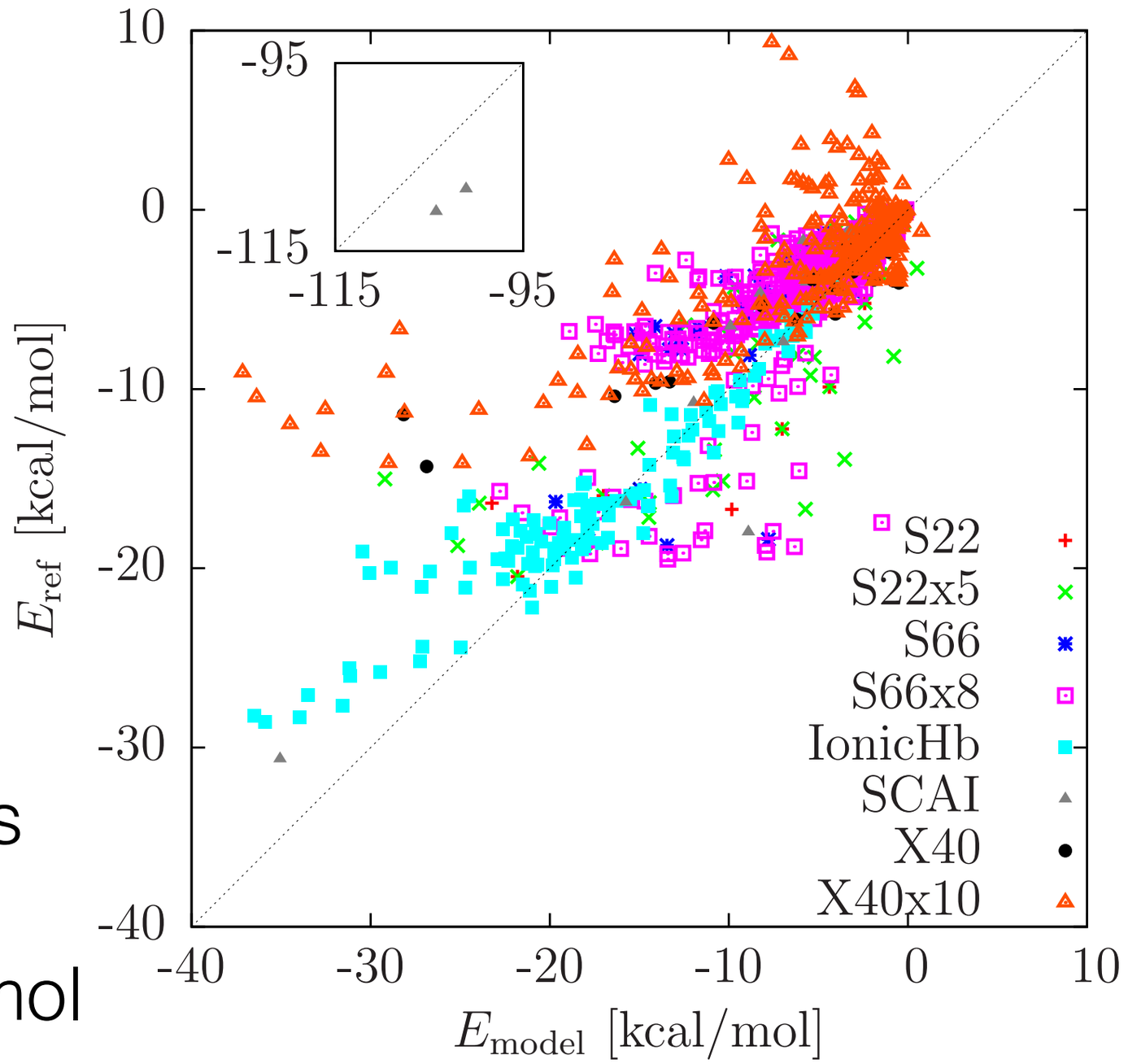
Energy:

- Dispersion
- Electrostatics

1’300 molecular dimers

Average error: 2.3 kcal/mol



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Energy benchmarks

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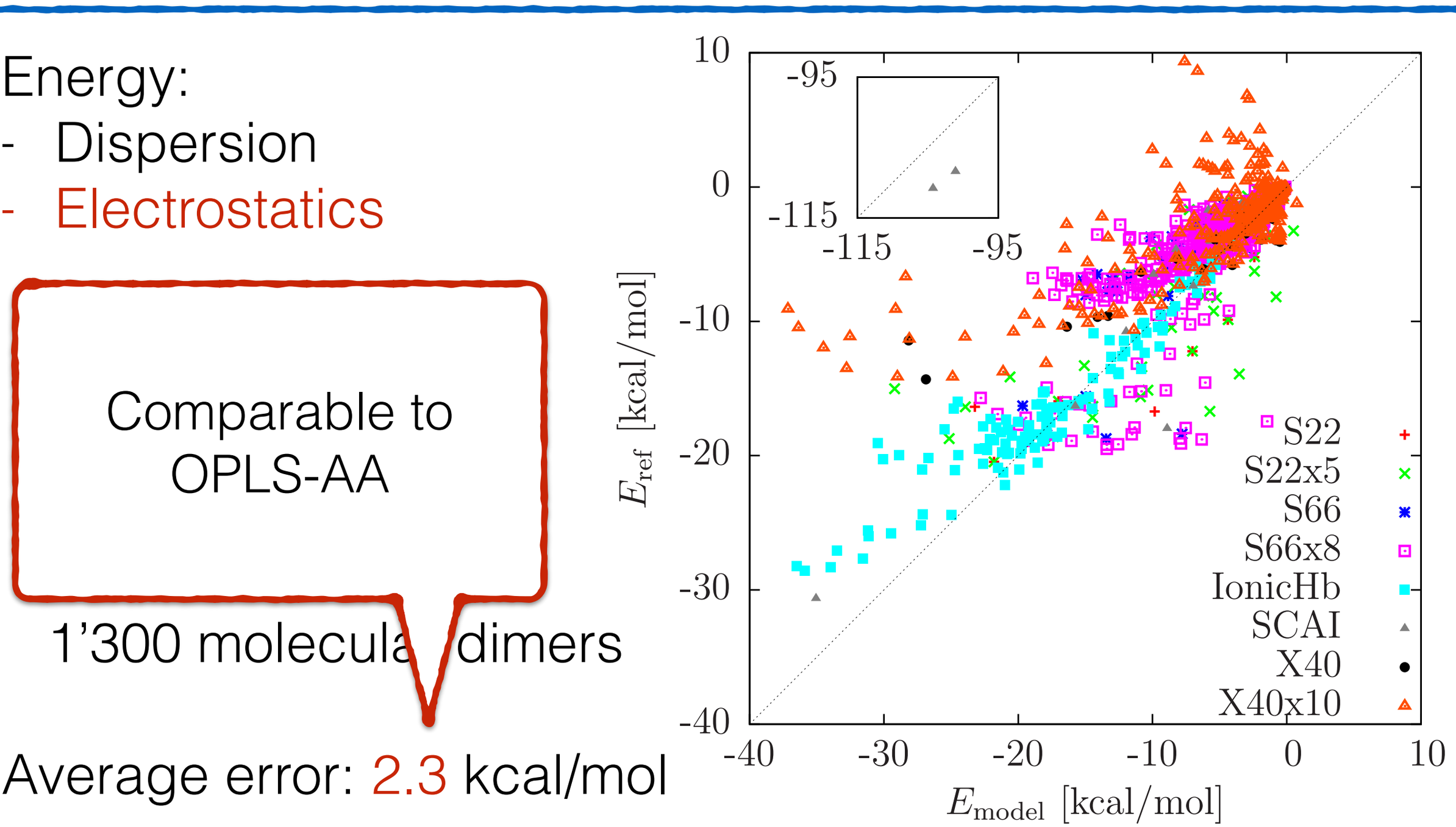

Energy:

- Dispersion
- Electrostatics

Comparable to OPLS-AA

1’300 molecular dimers

Average error: 2.3 kcal/mol

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Dispersion energy

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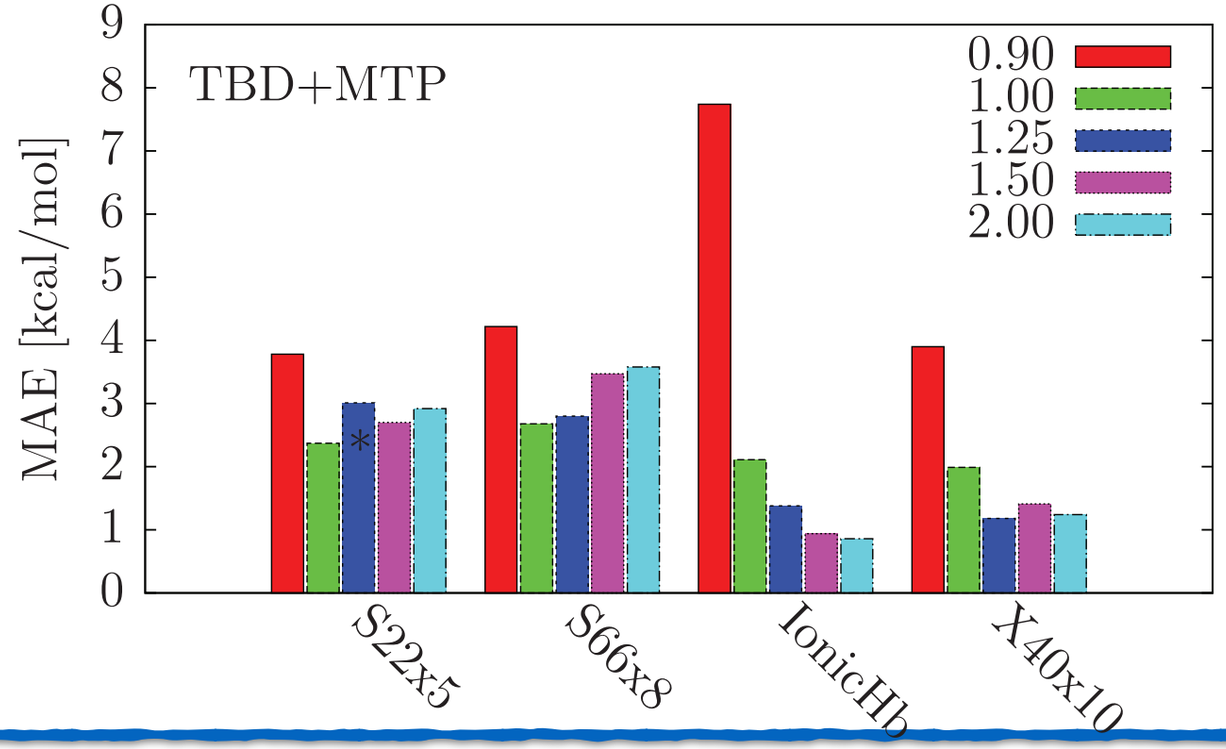
Two-body

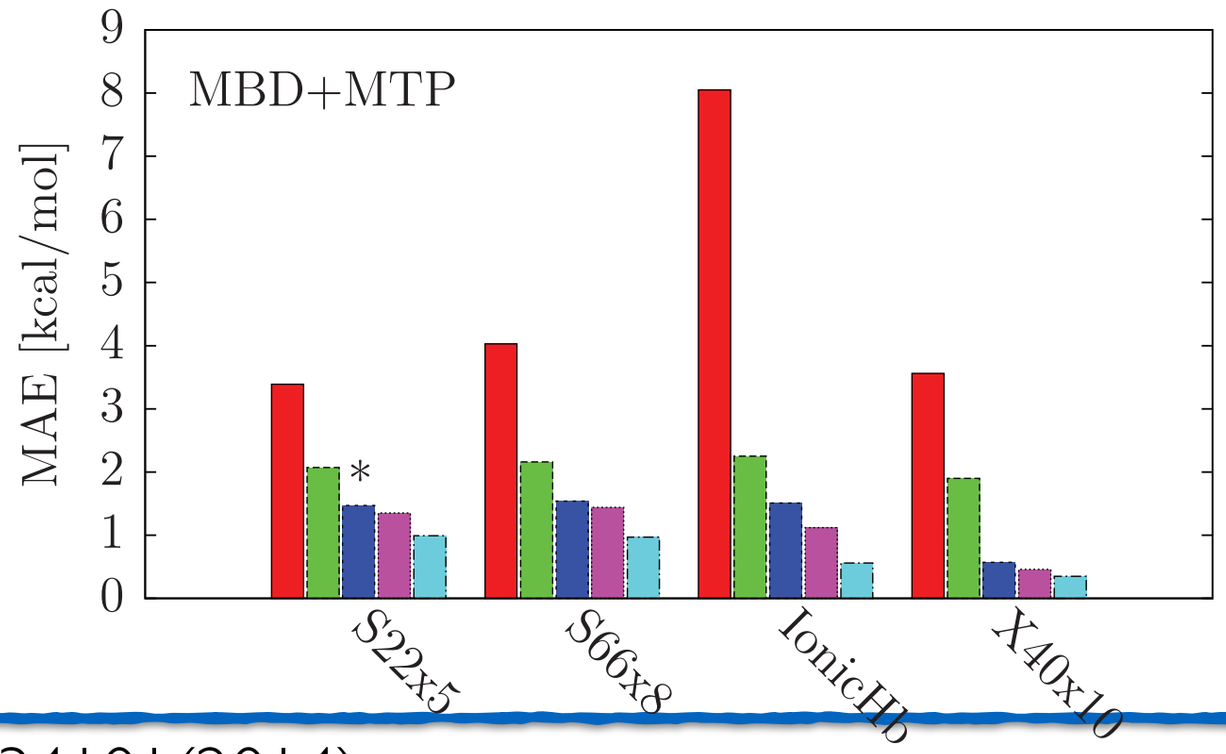
$$E_{\mathrm{TBD}} = -\frac{1}{2}\sum_{p,q} f_{\mathrm{damp}}(r_{pq}, R_p^{\mathrm{vdW}}, R_q^{\mathrm{vdW}})\frac{C_{6pq}}{r_{pq}^6}$$



Many-body

$$\mathcal{H} = -\frac{1}{2}\sum_{p=1}^{N}\nabla_{\chi_p}^2 + \frac{1}{2}\sum_{p=1}^{N}\omega_p^2\chi_p^2 + \sum_{p>q}\omega_p\omega_q\sqrt{\alpha_p\alpha_q}\chi_p\mathcal{T}'_{pq}\chi_q$$

$$E_{MBD} = \frac{1}{2}\sum_{p=1}^{3N}\sqrt{\lambda_p} - \frac{3}{2}\sum_{p=1}^{N}\omega_p^{\mathrm{SCS}}$$



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Dispersion energy

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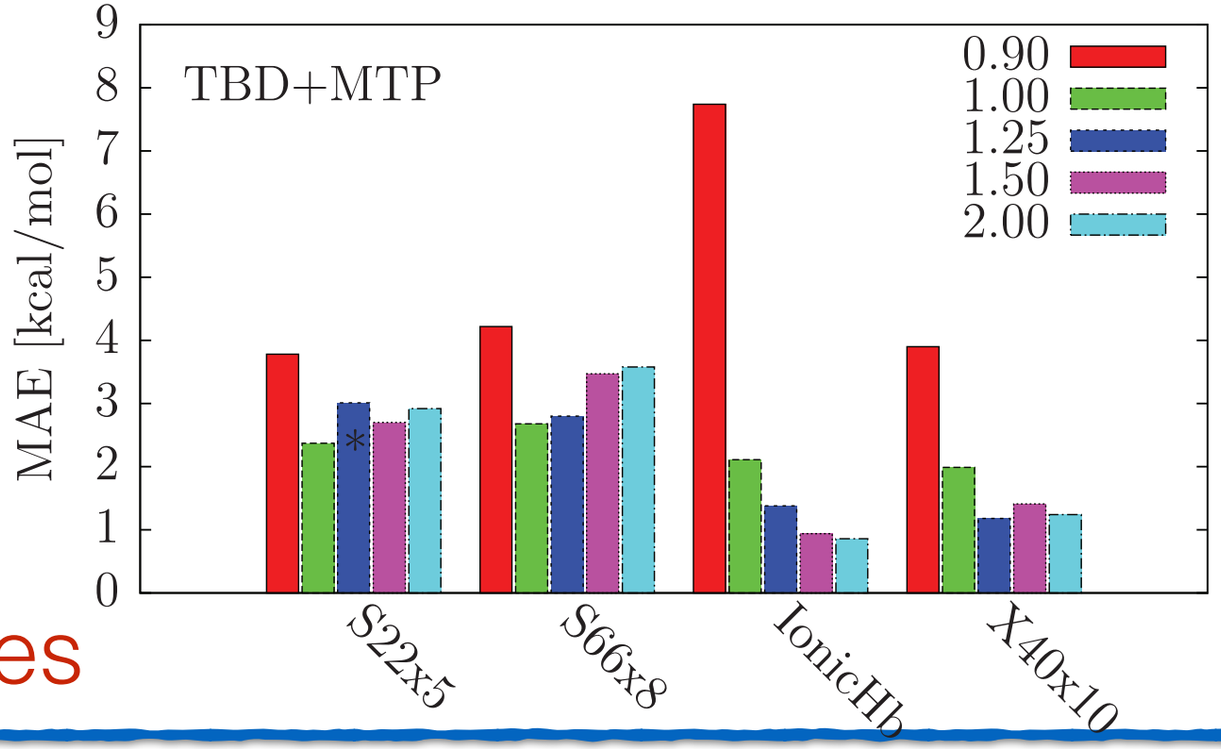
Voronoi polarizabilities



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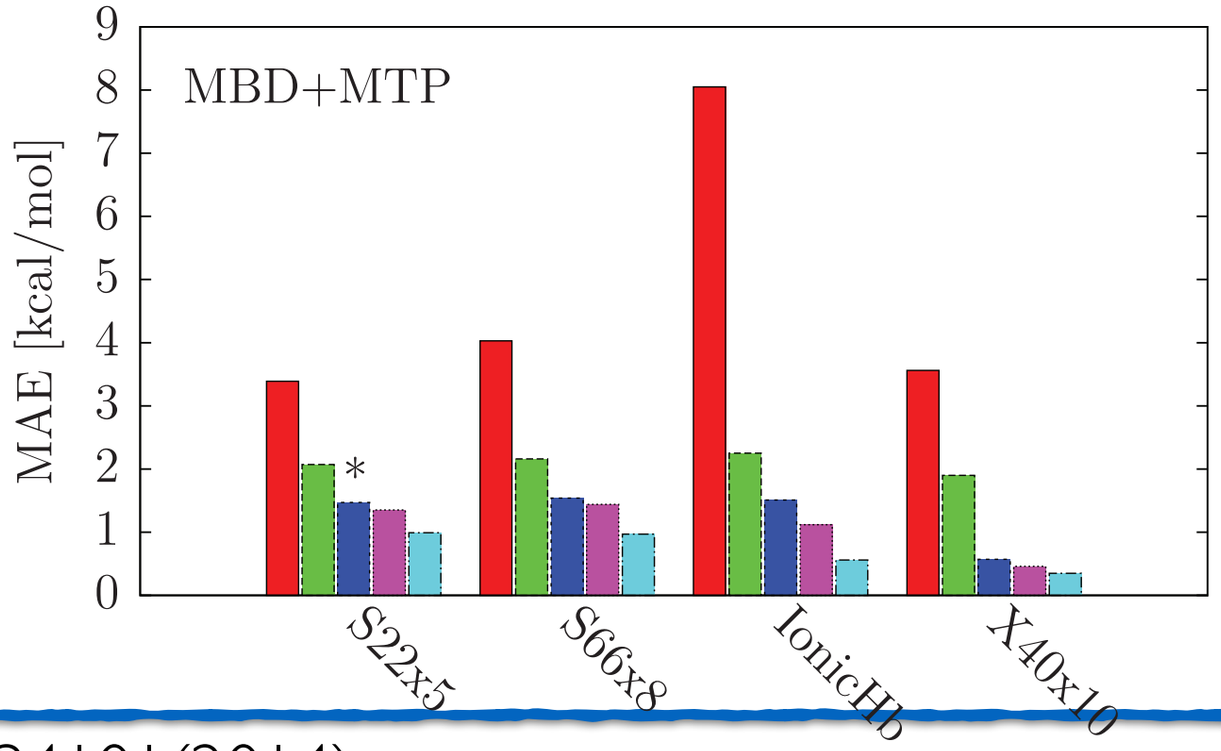

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Dispersion energy

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Two-body

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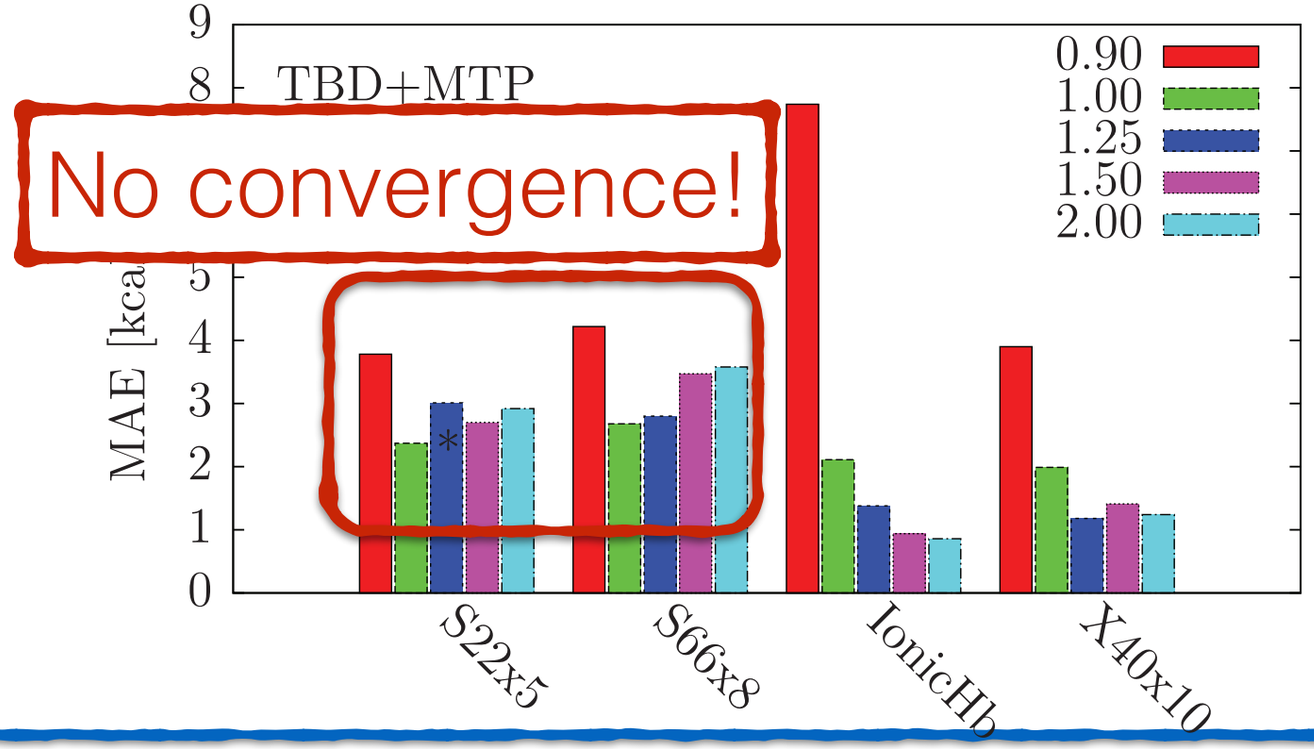
Dissociative tails



Many-body

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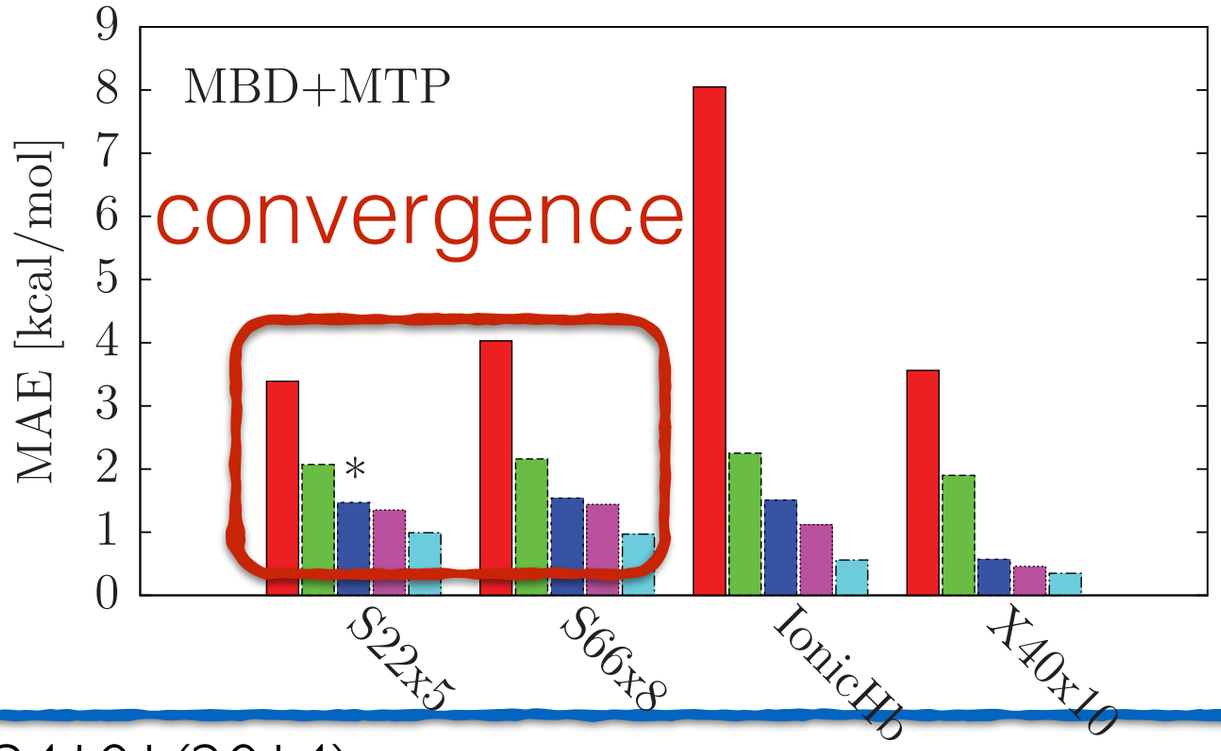

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Energy benchmarks

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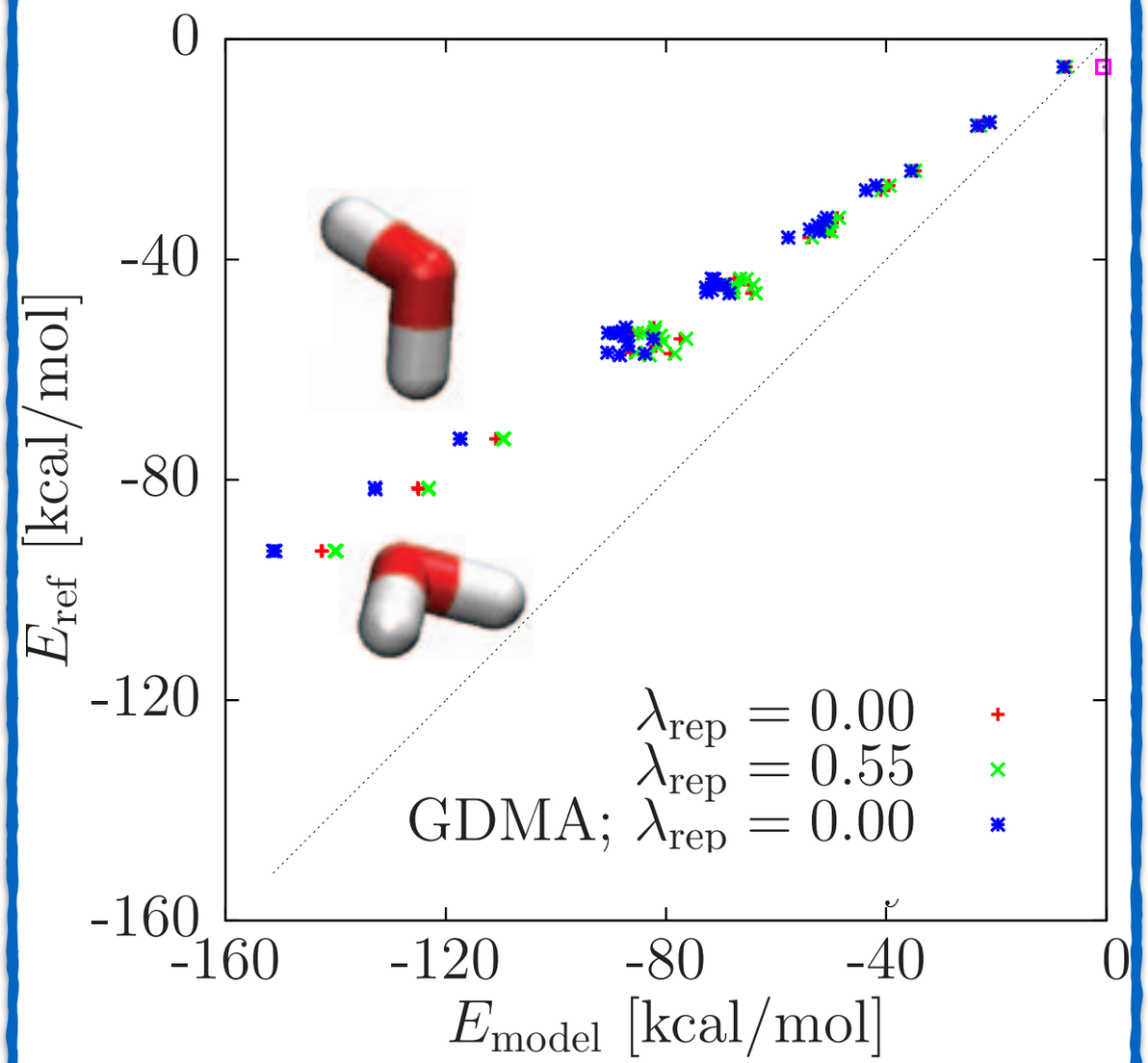
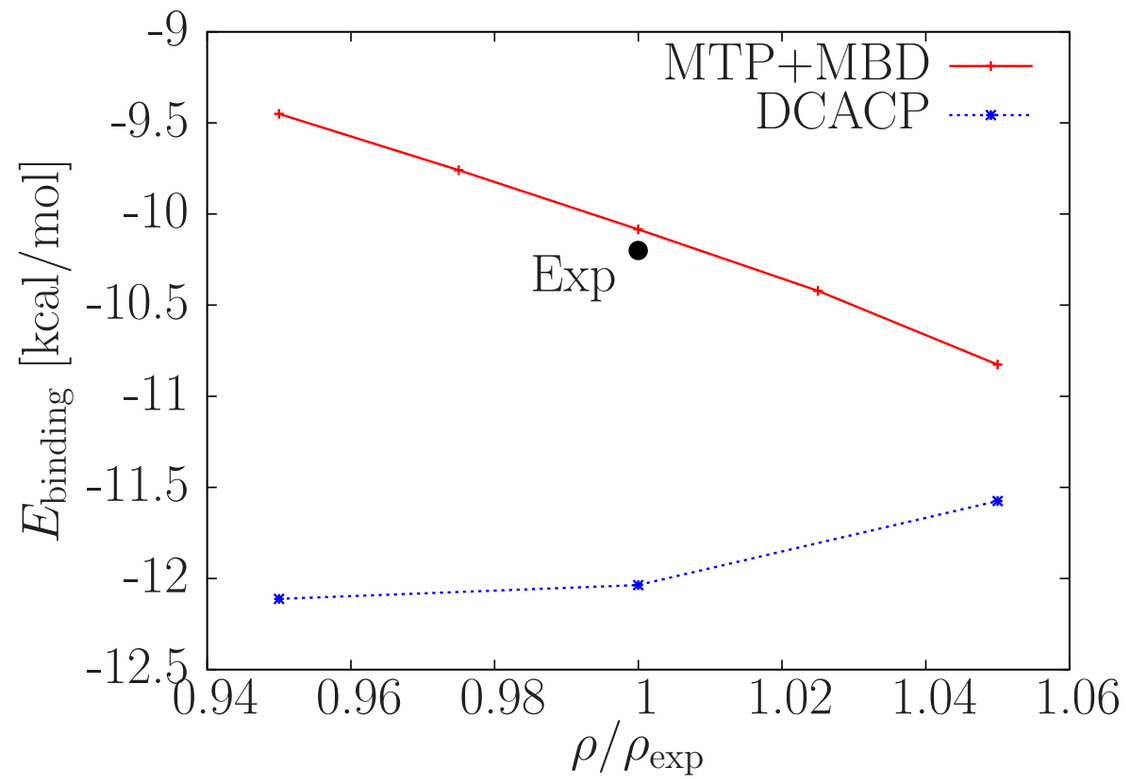
Water clusters



Benzene crystal



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Conclusions

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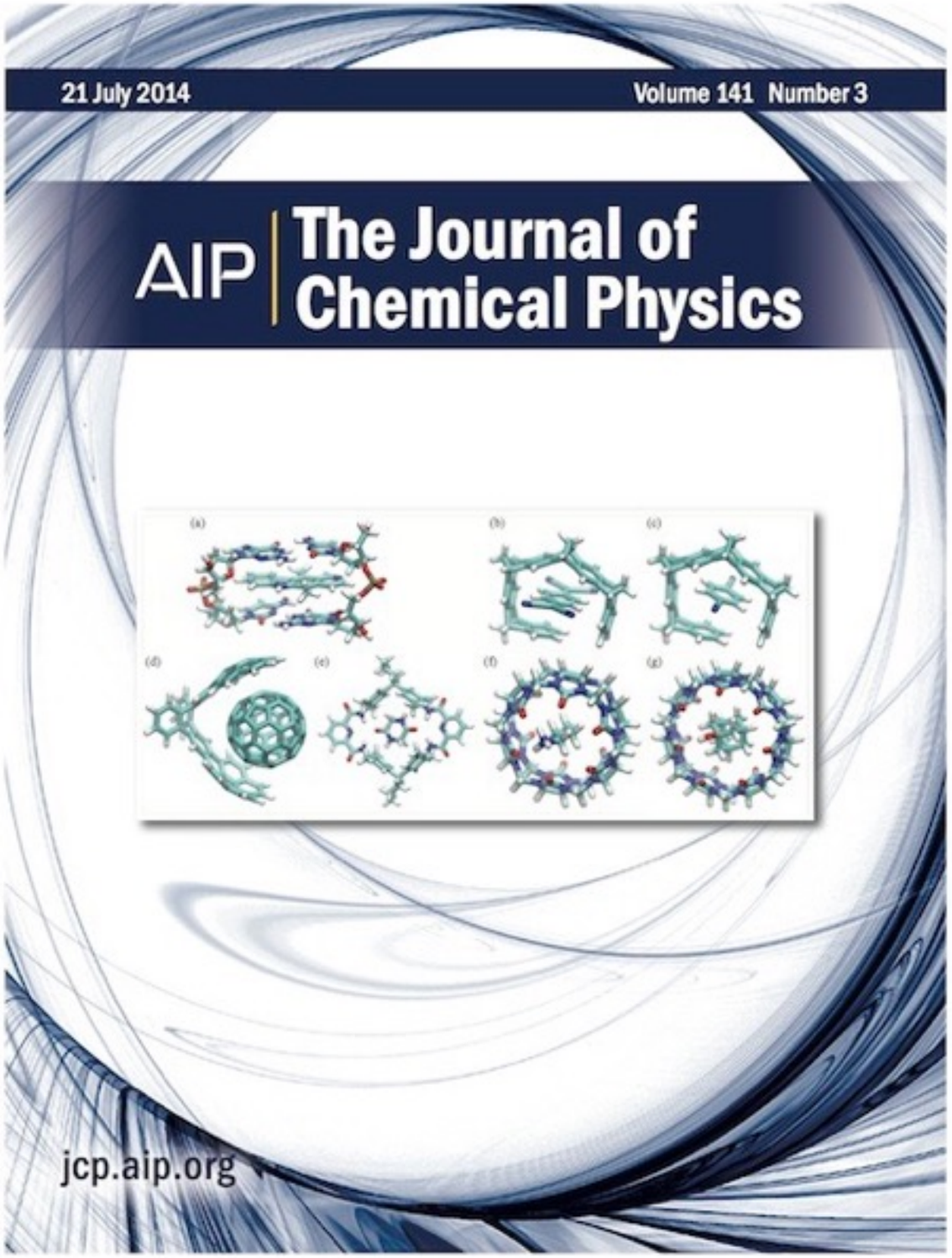
- Many-body dispersion without electrons
- Pairwise dispersion: poor dissociative asymptotics
- Benchmark energy: comparable to standard force fields, but no parametrization



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