Many-Body Molecular Dynamics for Chemically Accurate Simulations from the Gas to the Condensed Phase

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IPAM - Machine Learning for Many-Particle Systems

Acknowledgments

Current

Greg Medders
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Past

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Jason Grosch
David Sanchez
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Jeff Sung
Matt Agee
Porter Howland

Collaborators

Daniel Arismendi-Arrieta (CSIC)
Andrea Zonca (SDSC)
Andy Götz (SDSC)
Bob Sinkovits (SDSC)

UCSD

NSF ECS DMR CAREER

Hellman Fellows

DOE BES

CAICE

NSF CCI: Center for Aerosol Impacts on Climate and the Environment

NERSC

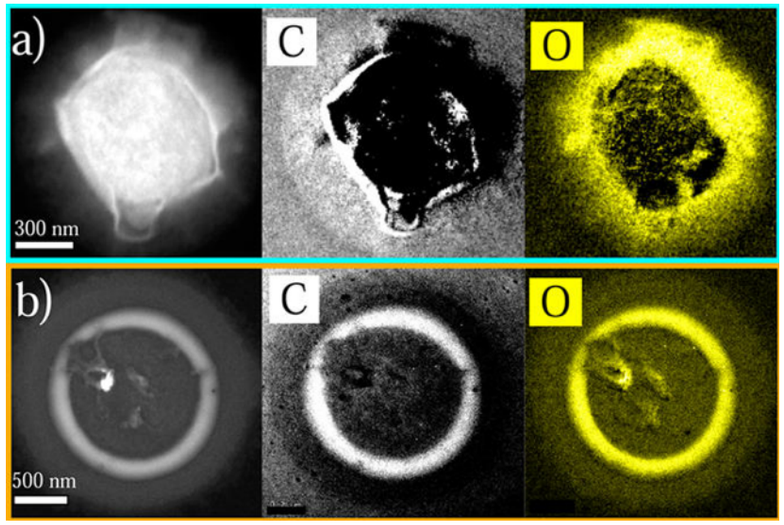
Triton Resource

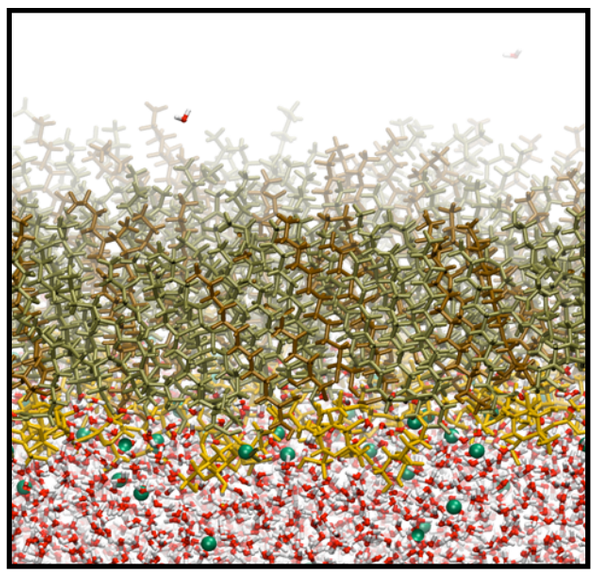
XSEDE
Extreme Science and Engineering Discovery Environment

NVIDIA

Hello, My Name Is…

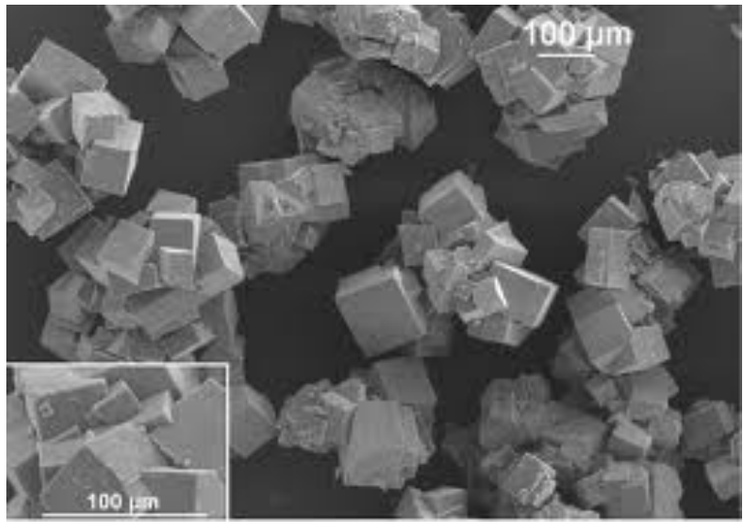
Aqueous Chemistry

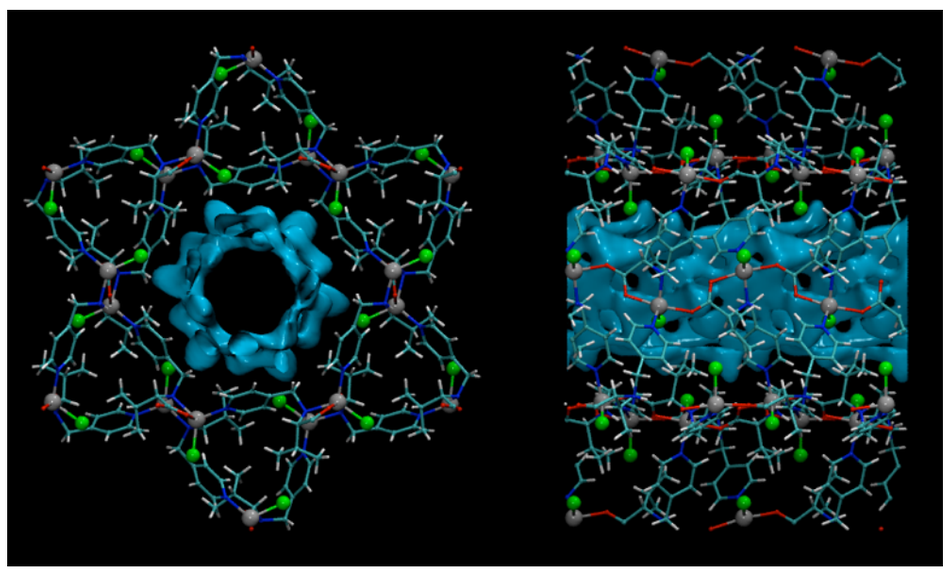




NSF & CCI: CAICE

Porous Materials

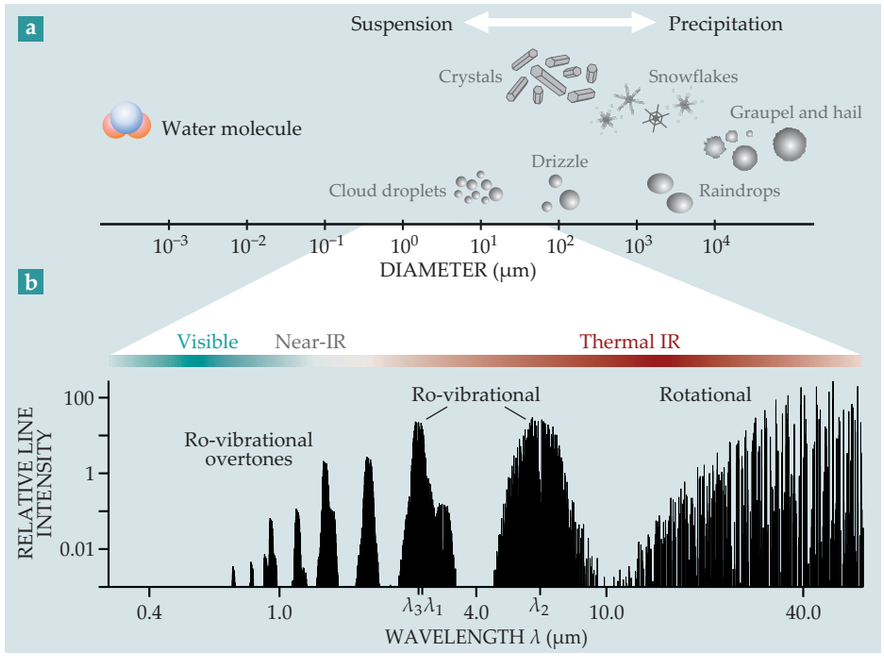


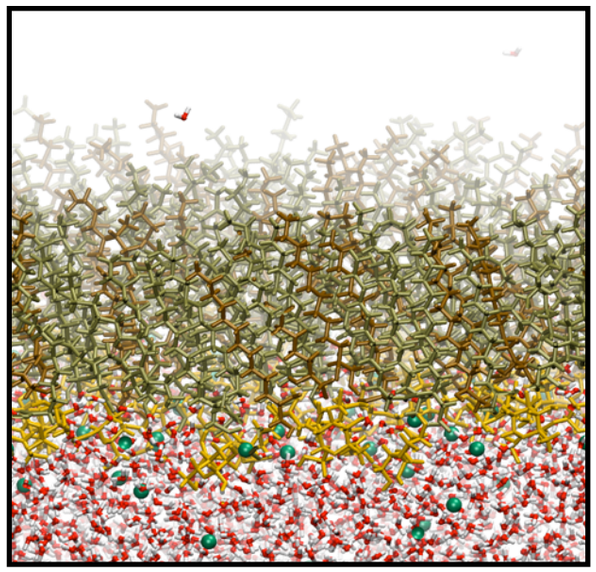


NSF & DOE

From Clusters to Bulk

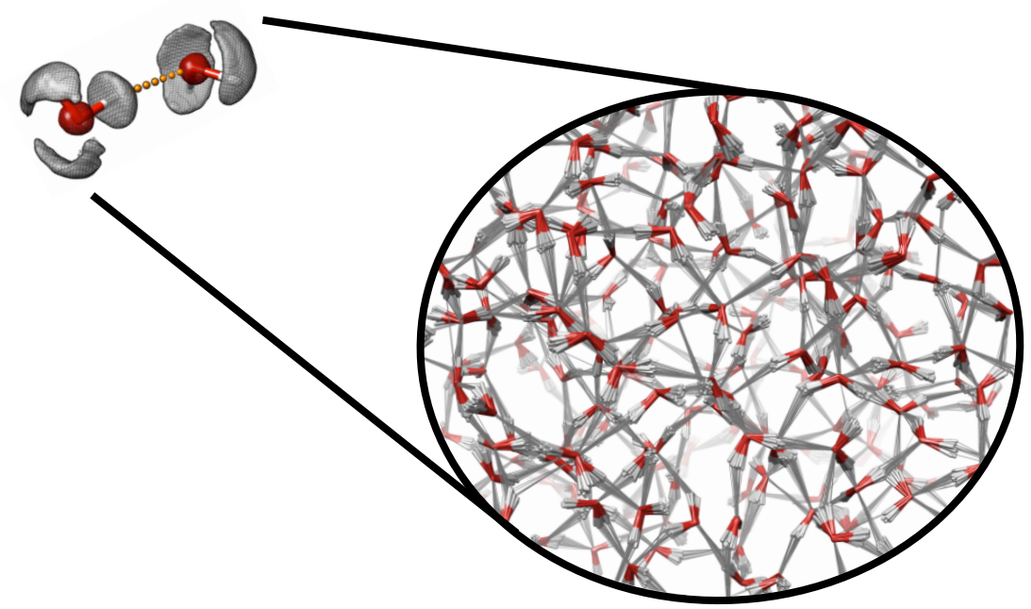
Aqueous Chemistry

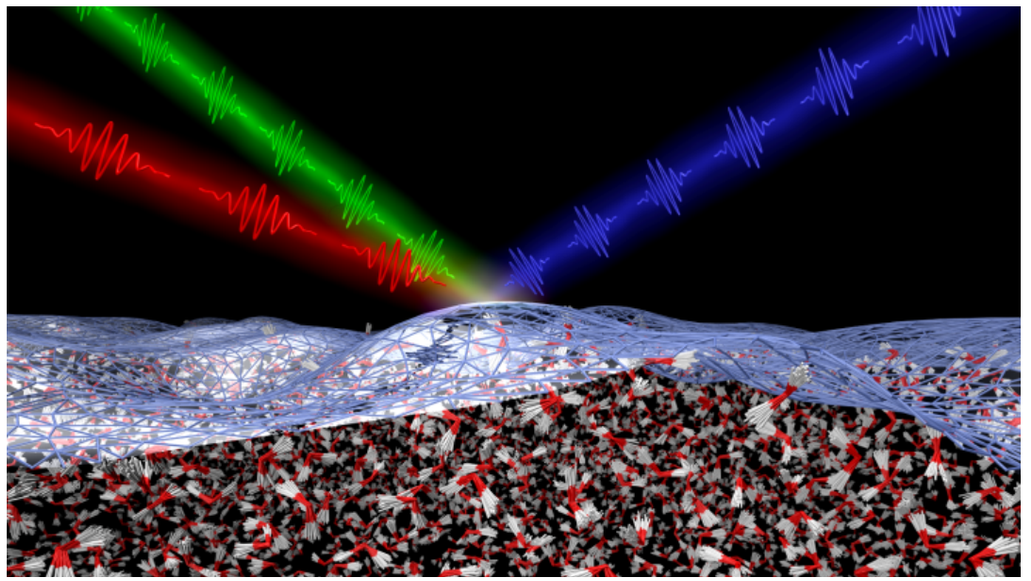




NSF & CCI: CAICE

Many-Body Molecular Dynamics





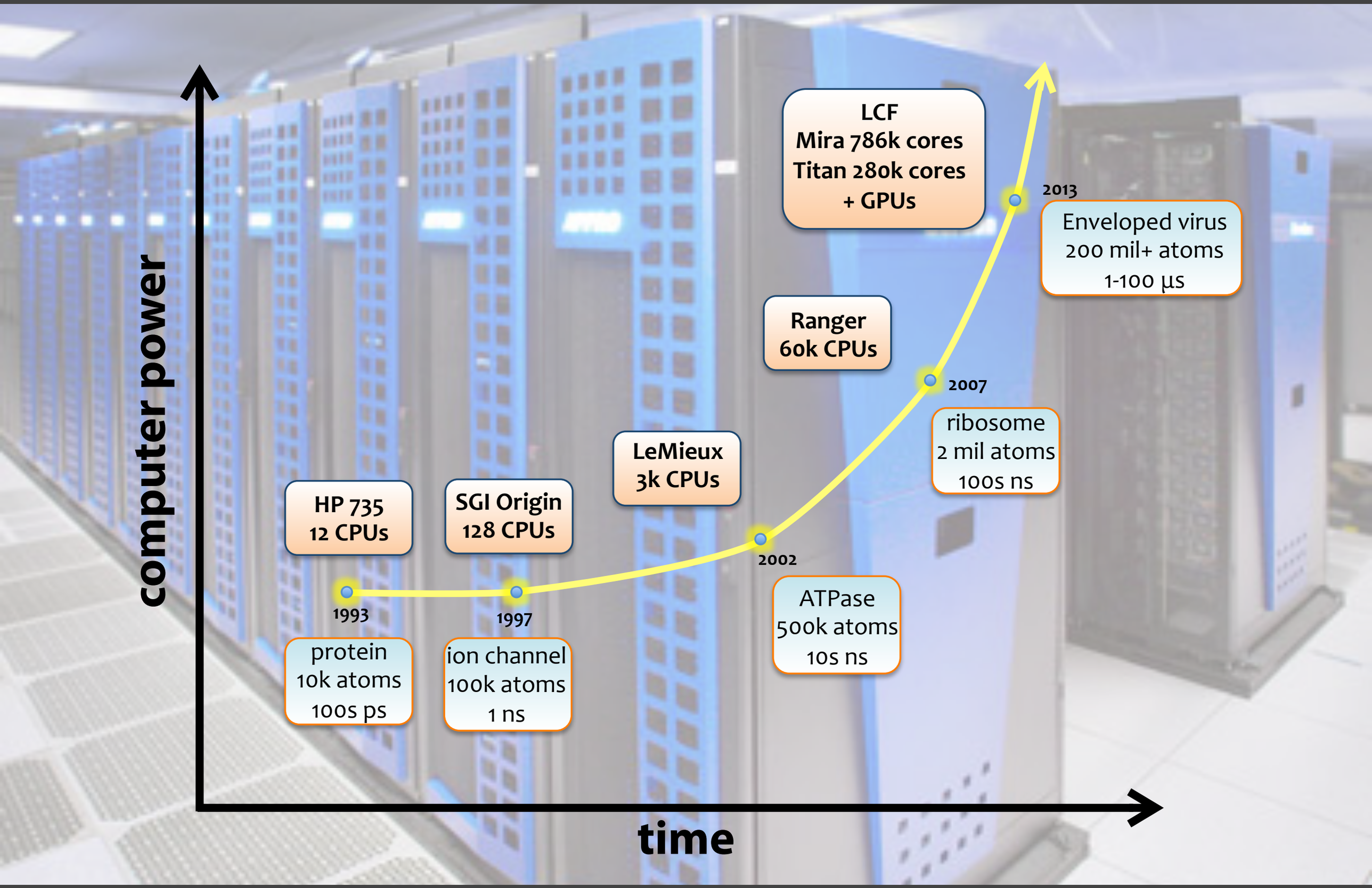
Molecular Simulations: Where We Are, Where We Are Going...

The Computer Age

"I fear the day that technology will surpass our human interaction. The world will have a generation of idiots."

Albert Einstein

The Computer Age

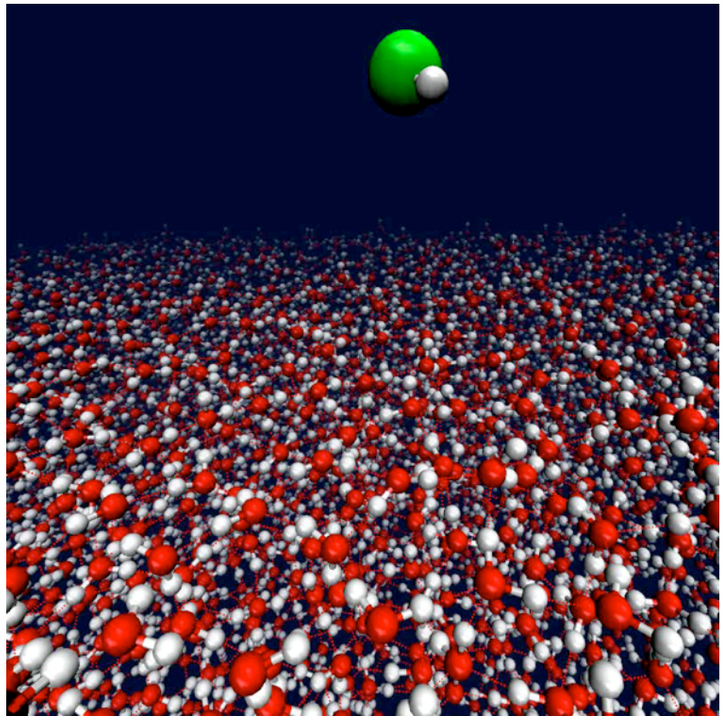


Courtesy of Rommie Amaro (UCSD)

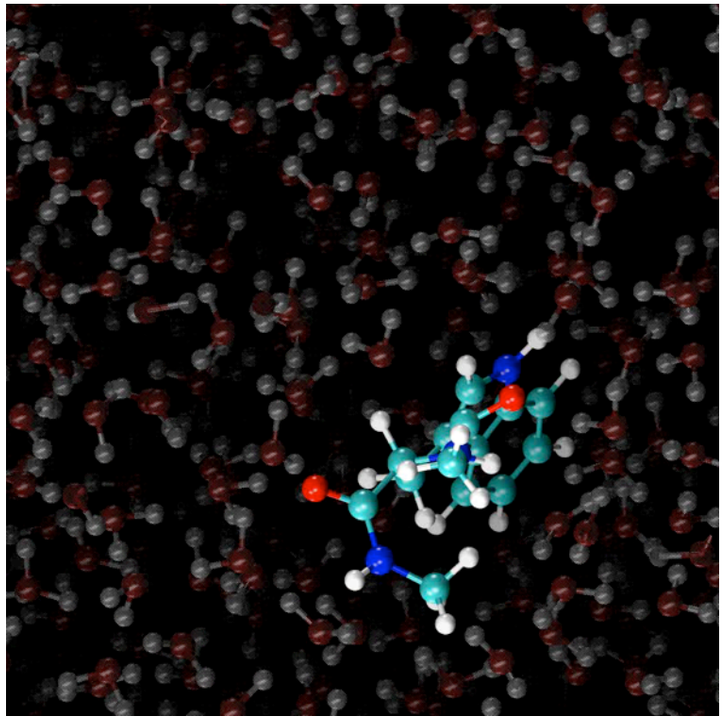
Molecular Simulations: What We Need...

Potential energy functions and **simulation approaches** that:

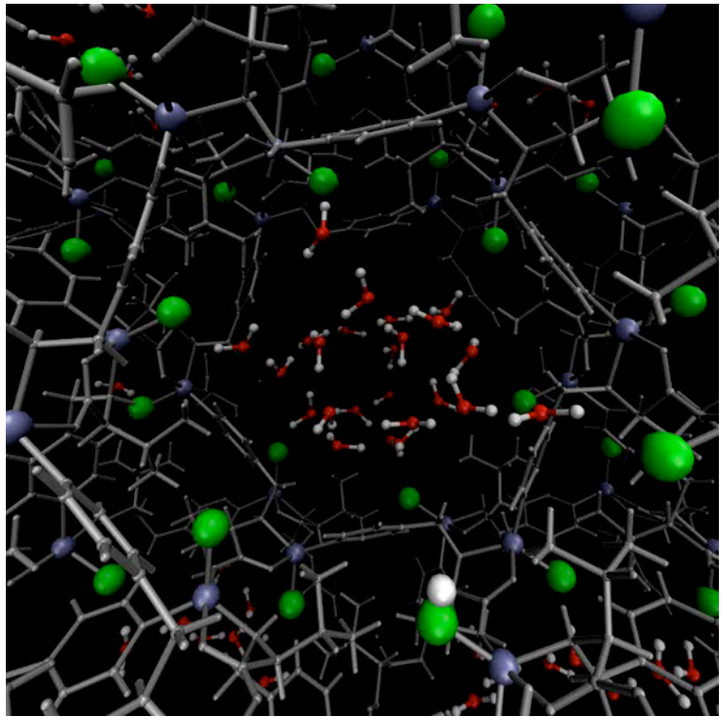
- are easily **computable** and **implementable**
- **accurately** represent **both** molecular interactions and dynamics
- are **transferable** across different phases
- are **predictive**
- enable **direct** comparisons with **experiments**



chemistry



biophysics



materials

Water: The Perfect Example

A

- AMOEBA
- ASP-S
- ASP-W

B

- Baranyai
- BBL
- Bell-Lavis
- Ben-Naim models
- BF
- BJH
- BKd1
- BKd2
- BKd3
- BNS
- Bol
- BSV

C

- CC-pol
- CF
- CI
- COS
- COS/B2
- COS/G2
- COS/G3
- CMP
- CKL

D

- Dahl and Anderse n
- Dang97
- DCF
- DEC
- DPP
- DPP2

E

- E3B
- ENCS
- EPEN/2

F

- F3C

G

- Gaussian model
- GCPM

H

- HBB
- HBB2-pol

K

- KJ
- KKY

M

- MCDHO
- MCHO
- MCY
- MCYL
- Mercedes-Benz model
- mW

N

- NCC
- NCCvib
- NCF
- NEMO
- NSPCE
- NvdE

P

- PE
- PMW
- POL3
- POL4D
- POL5
- POLIR
- PPC
- PTIP4P
- PSRWK
- PW

Q

- QCT
- q-SPC/Fw
- q-TIP4P/F

R

- R
- RPOL
- RSL2
- RWFF
- RWK

S

- SAPT-5s
- SAPT-pp
- SCPDP
- SDFT-5s

Simple Point Charge models

- SPC
- SPC/A
- SPC/E
- SPC/F
- SPC/F2
- SPC/FP
- SPC/FQ
- SPC/Fw
- SPC/HW
- SPC/L
- SPCP
- SPC-pol
- SSD
- ST2
- ST2RF
- SWFLEX
- SWM4-NDP

T

- TCPE

Transferable Intermolecular Potential models

- TIP3P
- TIP4F
- TIP4P
- TIP4P/2005
- TIP4P/2005f
- TIP4P-Ew
- TIP4P/FQ
- TIP4P-HB
- TIP4P-I
- TIP4P/Ice
- TIP4P-pol
- TIP4PQ/2005
- TIP4PQ_D2O
- TIP4PQ_T2O
- TIP4P-QDP
- TIP4P-QDP-LJ
- TIP4Q
- TIP5P
- TIP5P-E
- TIPS
- TIPS2
- TTM2-F
- TTM2-R
- TTM2.1
- TTM2.1-F
- TTM3-F

V

- VRT(MCY-5f)
- VRT(ASP-W)III

W

WK

Hundreds of models... **None** correctly predicts the **properties** of water **across different phases!**

http://www.sklogwiki.org/SklogWiki/index.php/Water_models

The "Traditional" Toolkit

Molecular mechanics

$$V(\vec{R}^N) = \sum_{bonds} \frac{k_b}{2}(r_b - r_{b,o})^2 + \sum_{angles} \frac{k_a}{2}(\theta_a - \theta_{a,o})^2 + \sum_{torsion} \left[\sum_n \frac{V_n}{2}(1 + \cos(n\omega - \gamma)) \right]$$

$$+ \sum_{i<j} \left\{ 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\epsilon_0 R_{ij}} \right\}$$

Hill, J. Chem. Phys. 14, 465 (1946) - Westheimer & Mayer, J. Chem. Phys. 14, 733 (1946)

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Quantum mechanics

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

$$E[\rho] = T[\rho] + V_{ee}[\rho] + V_{xc}[\rho]$$

1930: Hartree-Fock equations

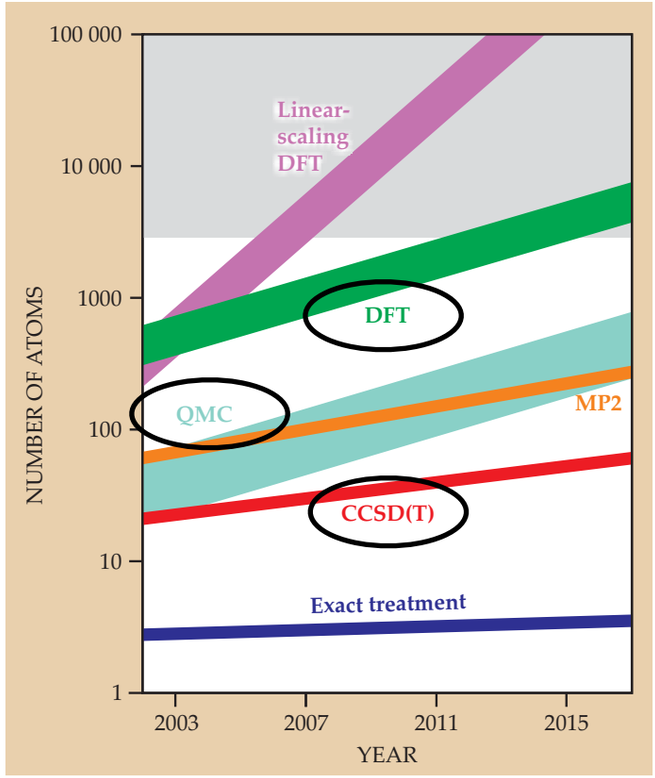
1951: Hartree-Fock-Roothan equations

1965: Kohn & Sham equations

1966: Coupled-Cluster equations

1970: Gaussian 70

1985: CPMD



Head-Gordon & Artacho, Phys. Today 61, 58 (2008)

Putting Things in Perspective...

1966

Mulliken

1963

First man on the Moon

1969

Woodstock

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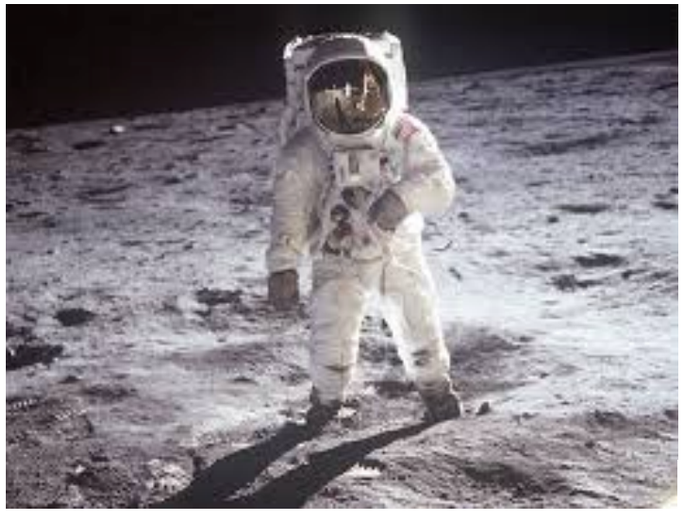

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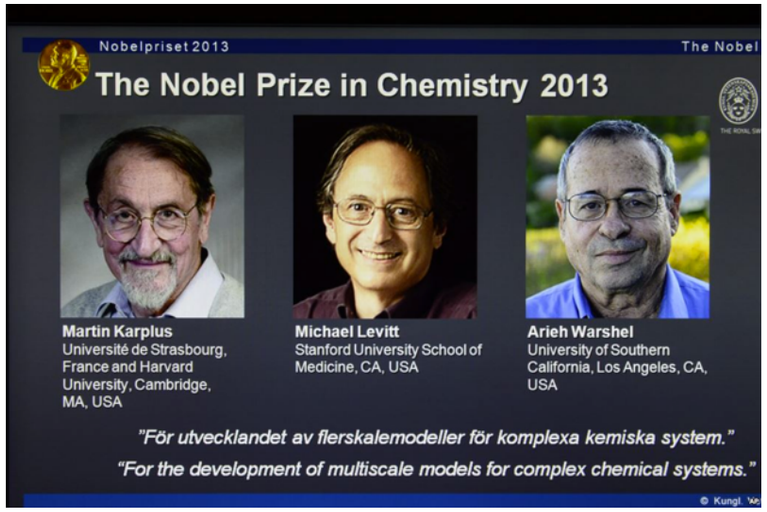

Karplus, Levitt, Warshel

2014

Driverless Cars

2014

Pharrell

Beyond the "Traditional" Toolkit?

Molecular mechanics

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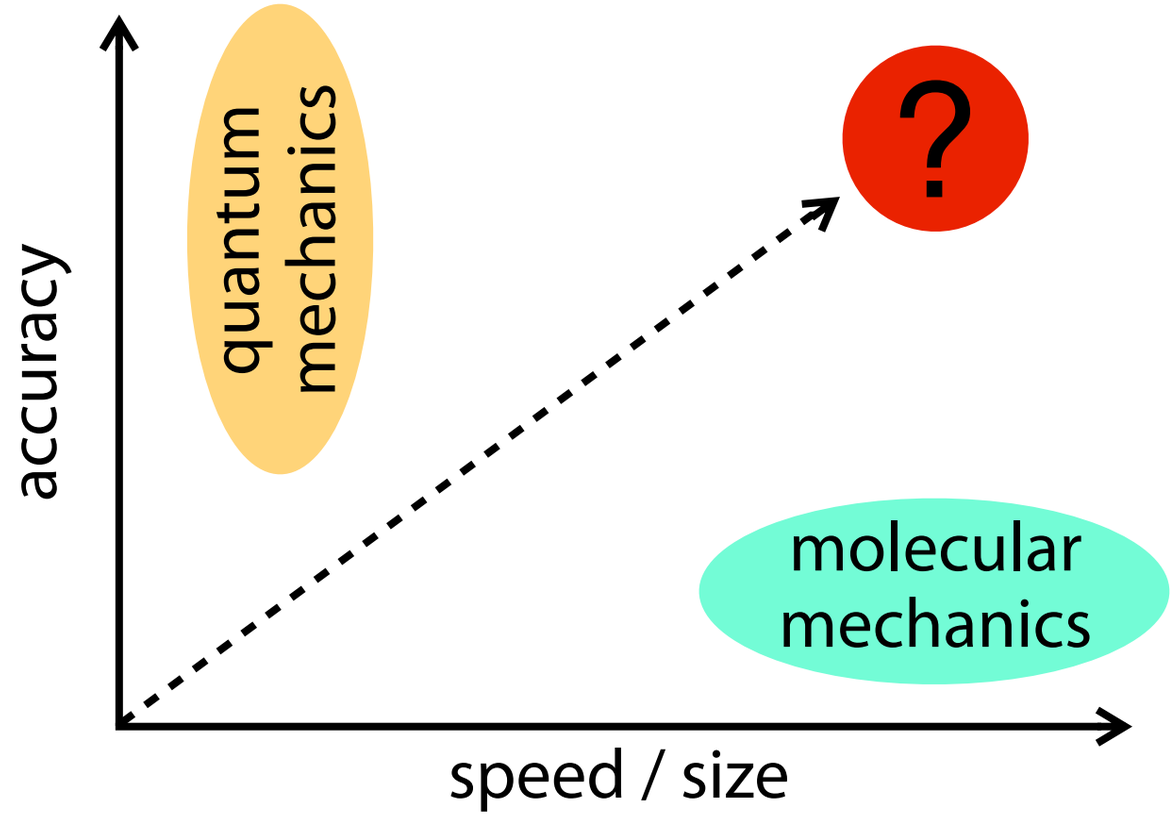

Beyond the "Traditional" Toolkit?

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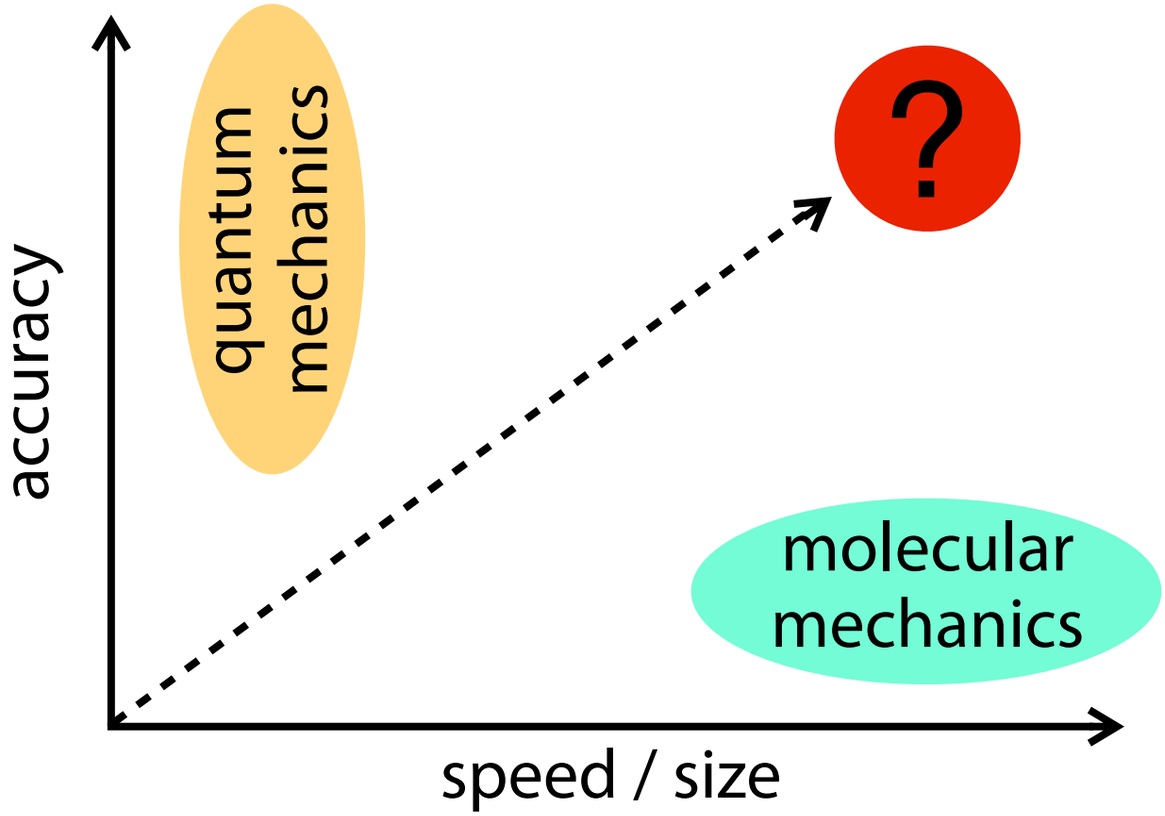
- are easily **computable** and **implementable**
- **accurately** represent **both** molecular interactions and dynamics
- are **transferable** across different phases
- are **predictive**
- enable **direct** comparisons with molecular-level **experiments**

1) **Can** such a simulation approach **exist**?

2) **If** it exists, **what** does it require?

3) **Can** it be applied to **complex systems**?



Not the First Nor the Only Ones...

1892 - Roentgen: mixture model (liquid-like & ice-like)

1933 - Bernal & Fowler: tetrahedral arrangement

1946 - Samoilov: interstitial model

1951 - Pauling: hydrate with clathrate-like structure

1951 - Pople: tetrahedral water with 4 distorted H-bonds

60s - 70s: computer simulations with force fields

1985 - Car & Parrinello: CPMD

...

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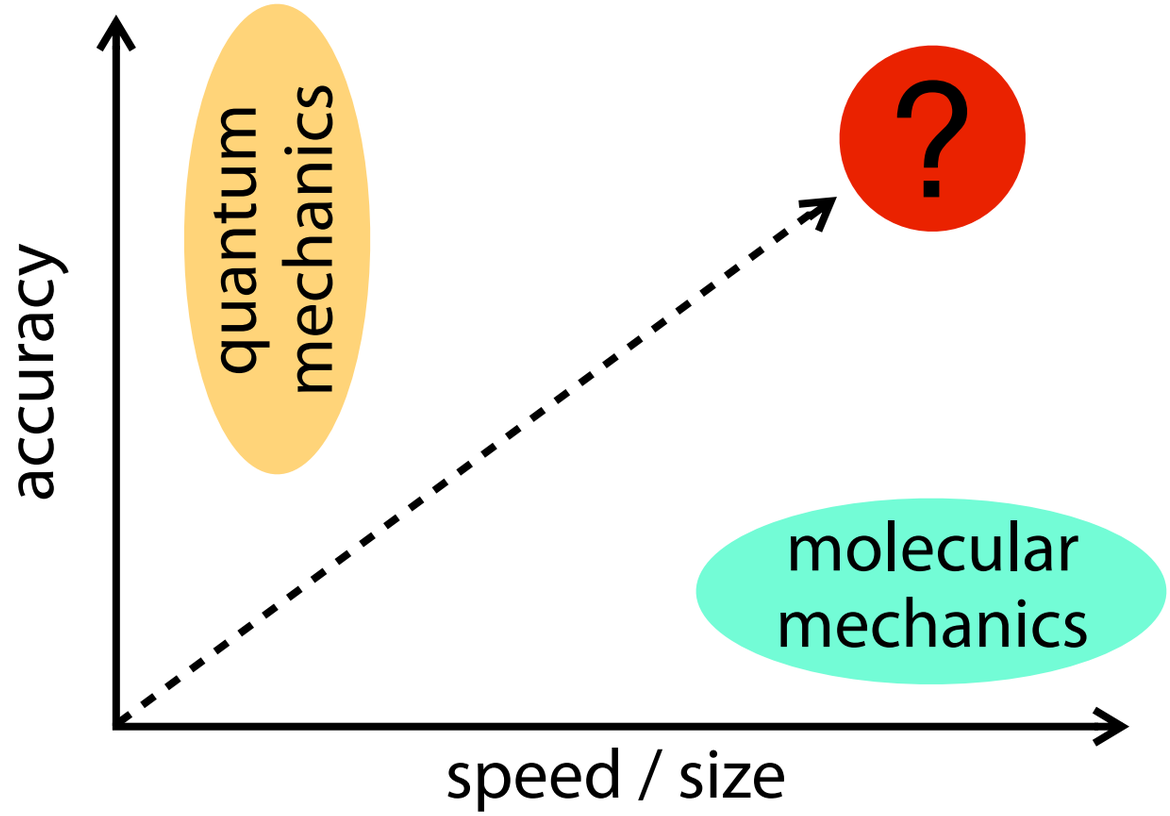


Many-Body Expansion of Molecular Interactions

$$E_N = \sum_i^N V^{1B}(i) \qquad \text{1-body}$$

$$+ \sum_{i<j}^N V^{2B}(i,j) \qquad \text{2-body}$$

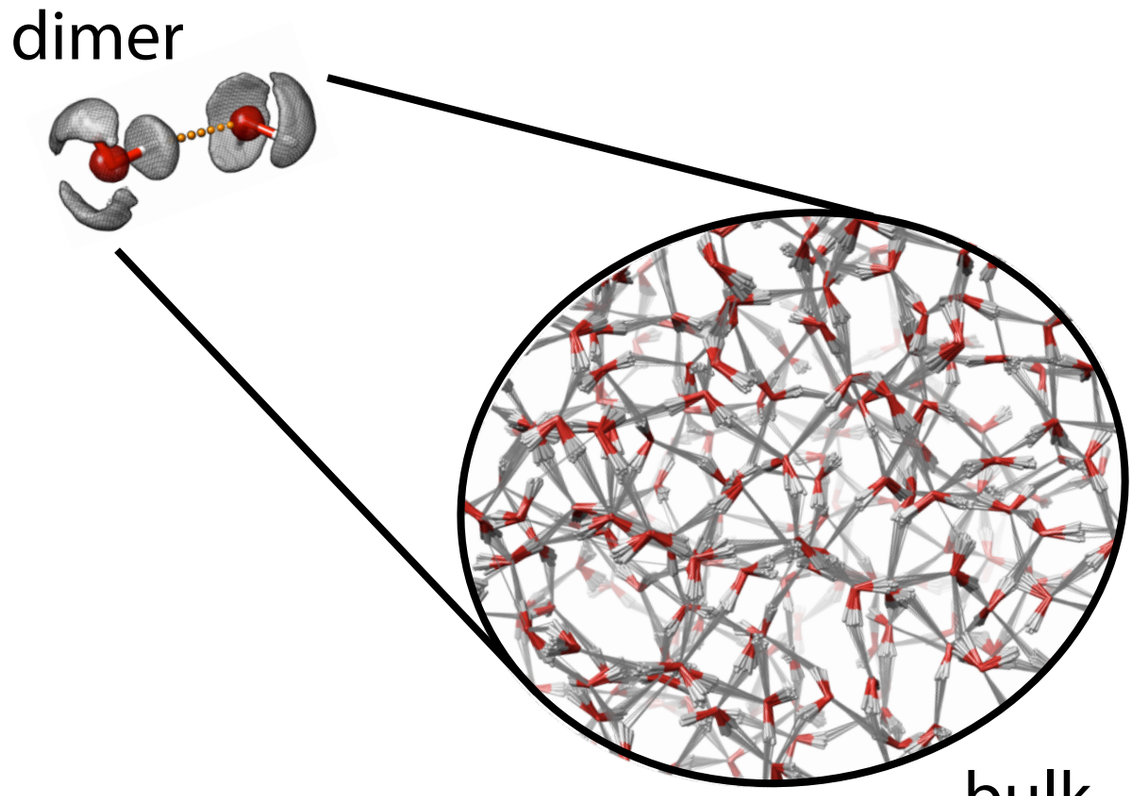
$$+ \sum_{i<j<k}^N V^{3B}(i,j,k) \qquad \text{3-body}$$

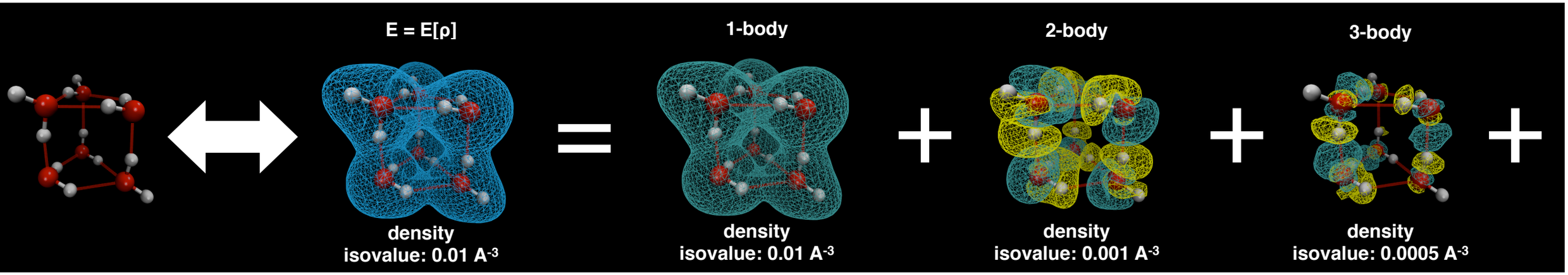
$$+ \ldots$$

$$+ V^{NB}(1,\ldots,N) \qquad \text{N-body}$$

MB expansion for water converges quickly

Xantheas, Jordan, Szalewicz ...





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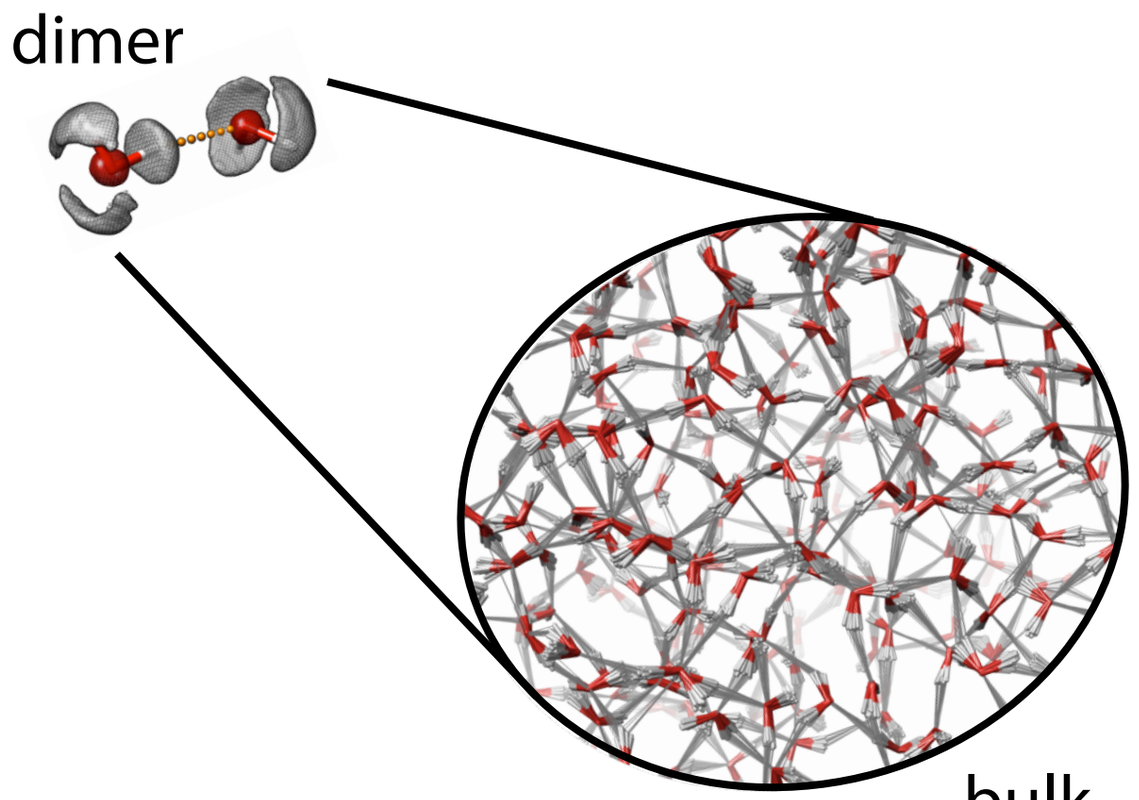
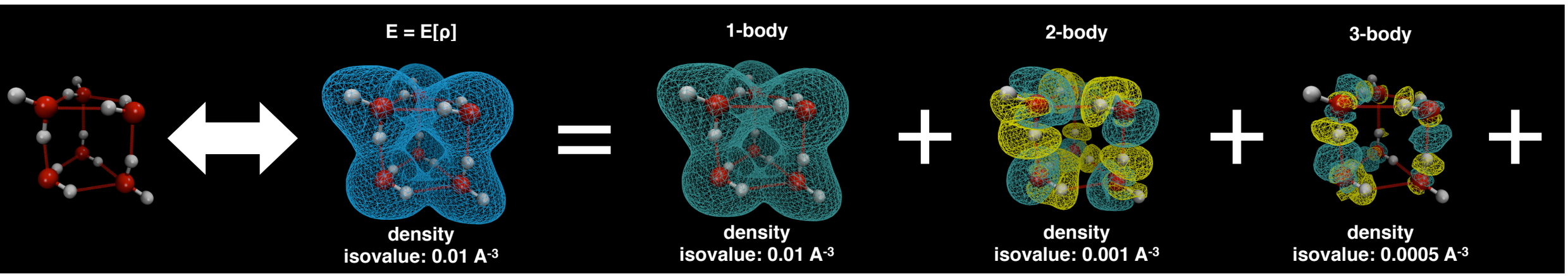
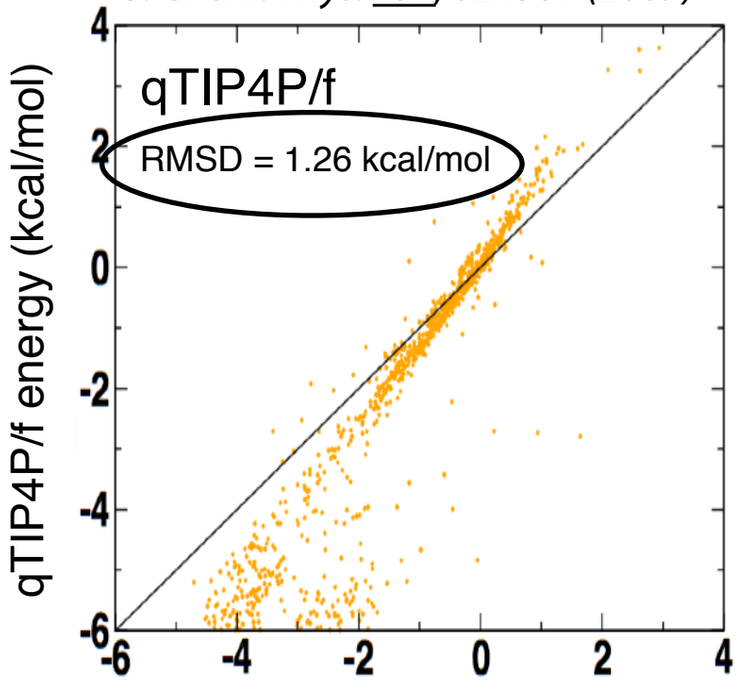




2-Body Interaction Energies: Models vs. CCSD(T)

Habershon, Markland & Manolopoulos
J. Chem. Phys. 131, 024501 (2009)



Tainter & Skinner
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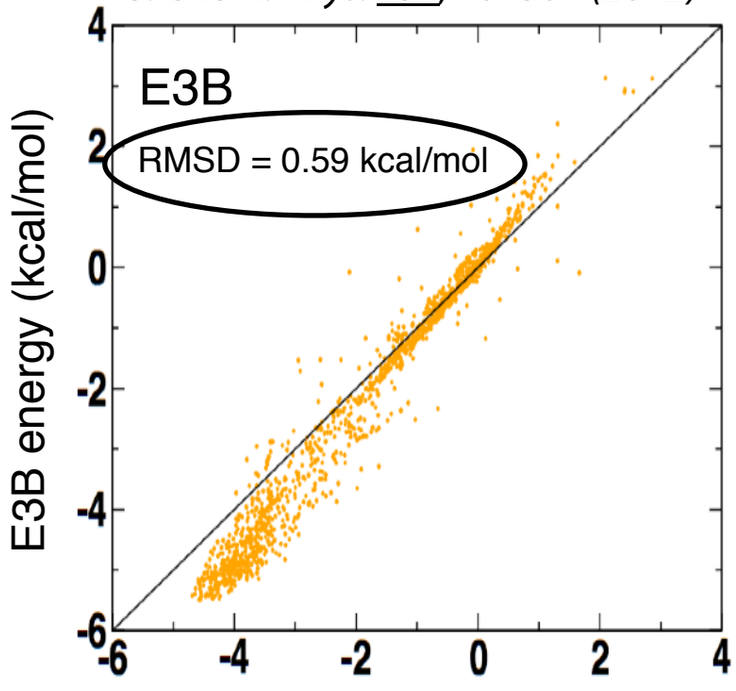

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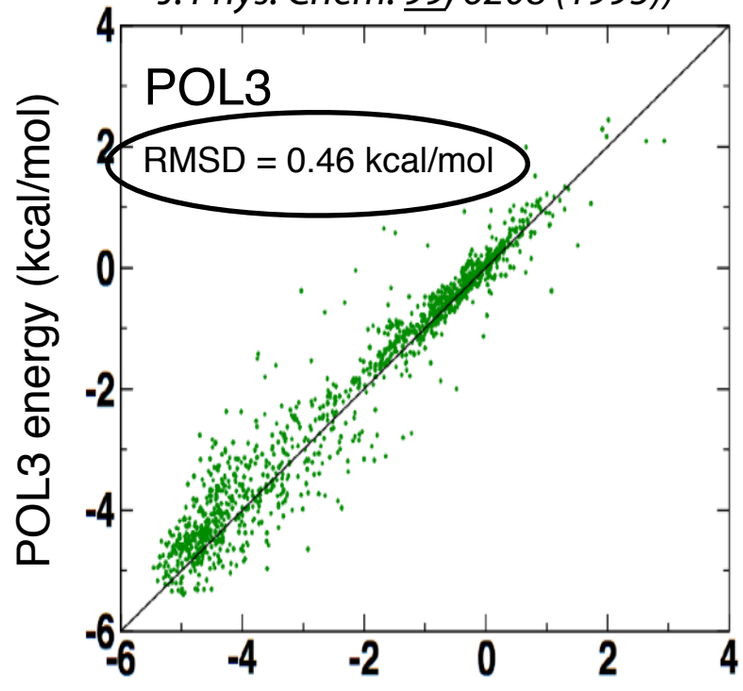

Vydrov & Van Voorhis
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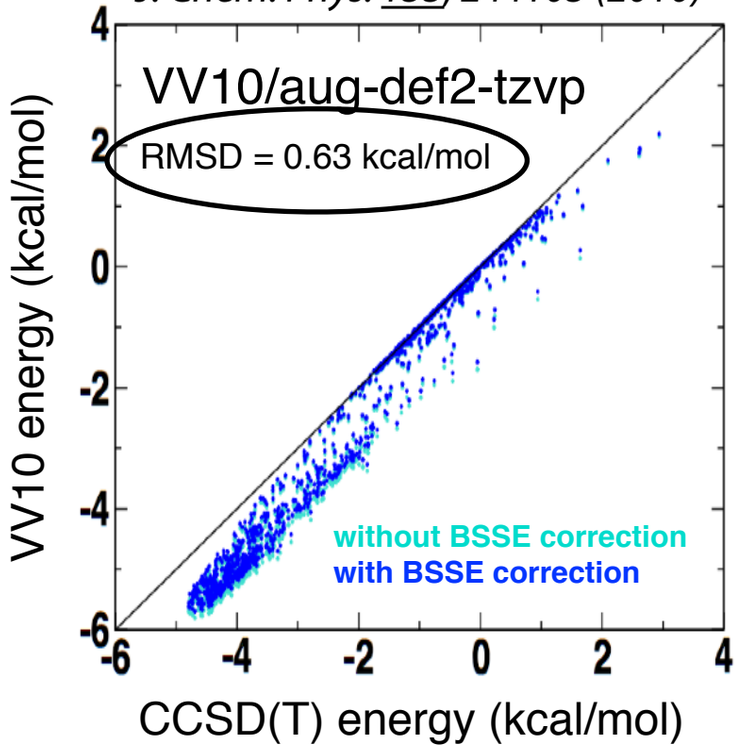

Grimme
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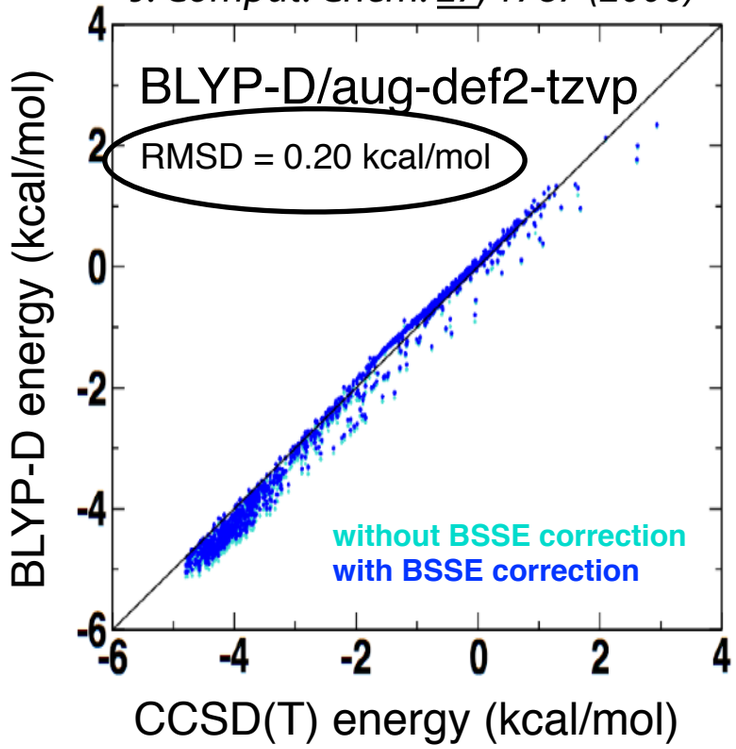

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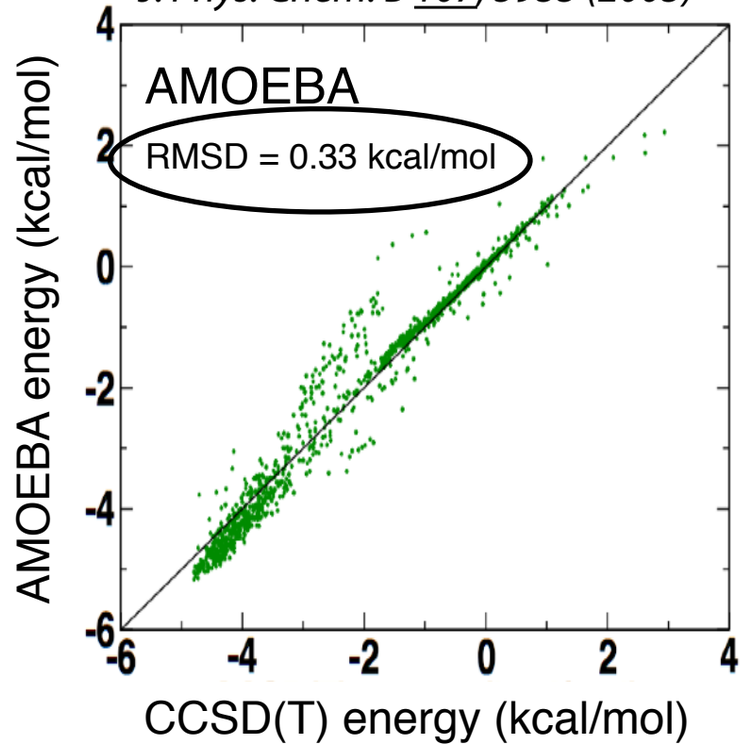

Medders, Babin & FP, J. Chem. Theory Comput. 9, 1103 (2013)

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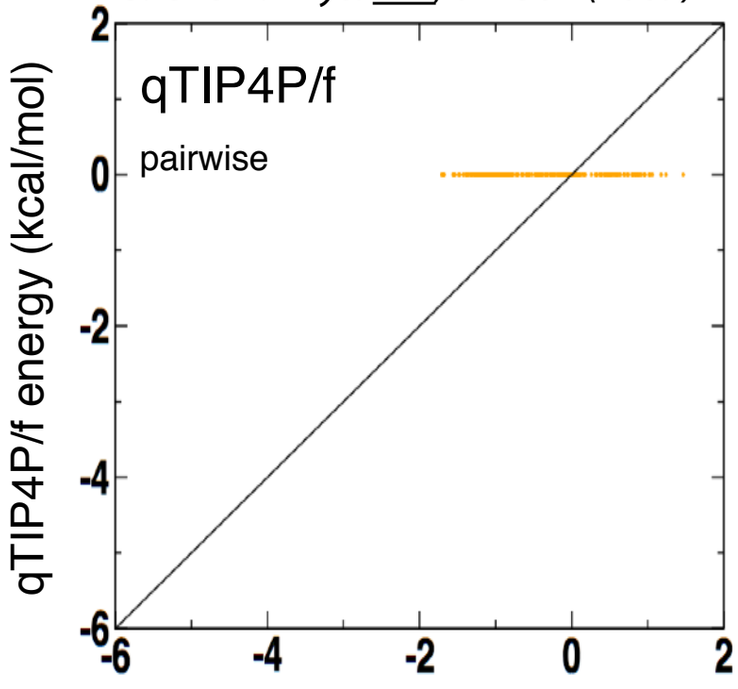

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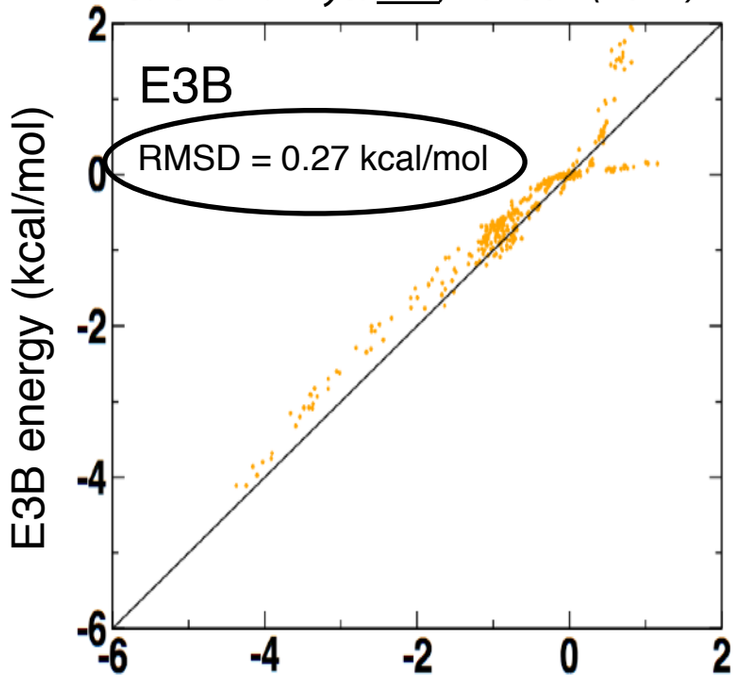

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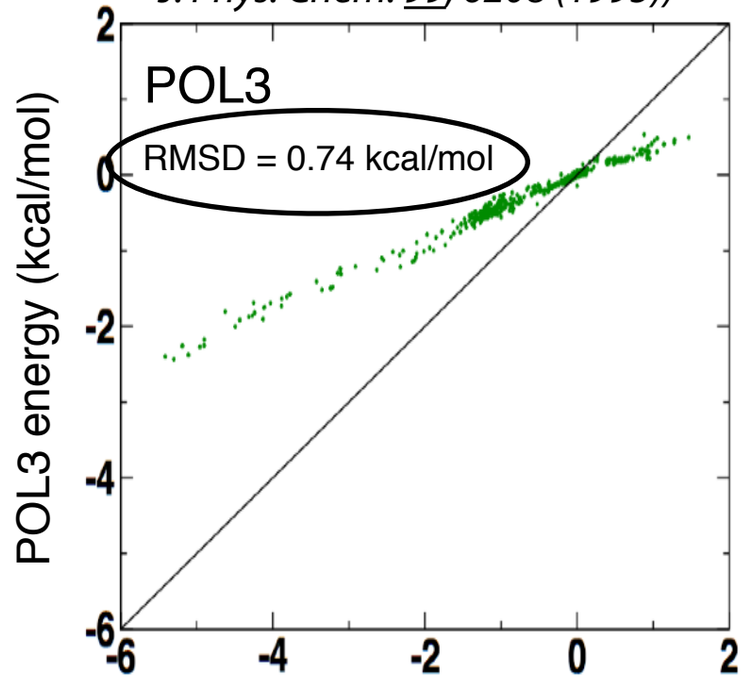
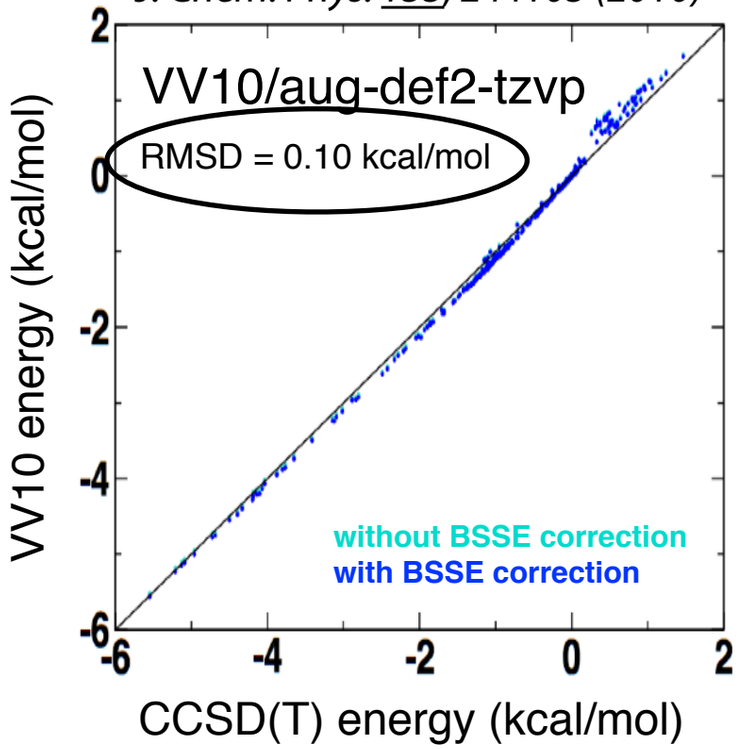


Vydrov & Van Voorhis
J. Chem. Phys. 133, 244103 (2010)



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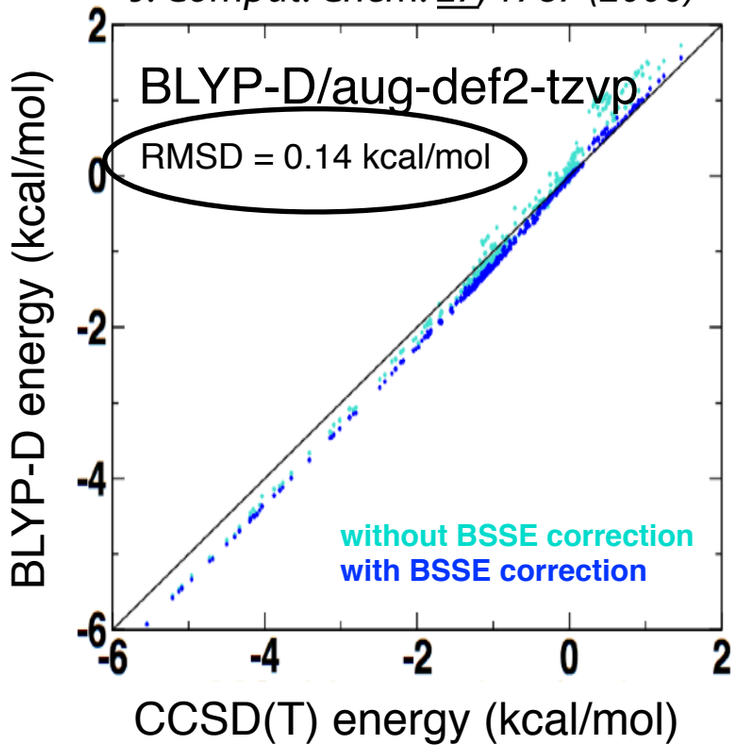

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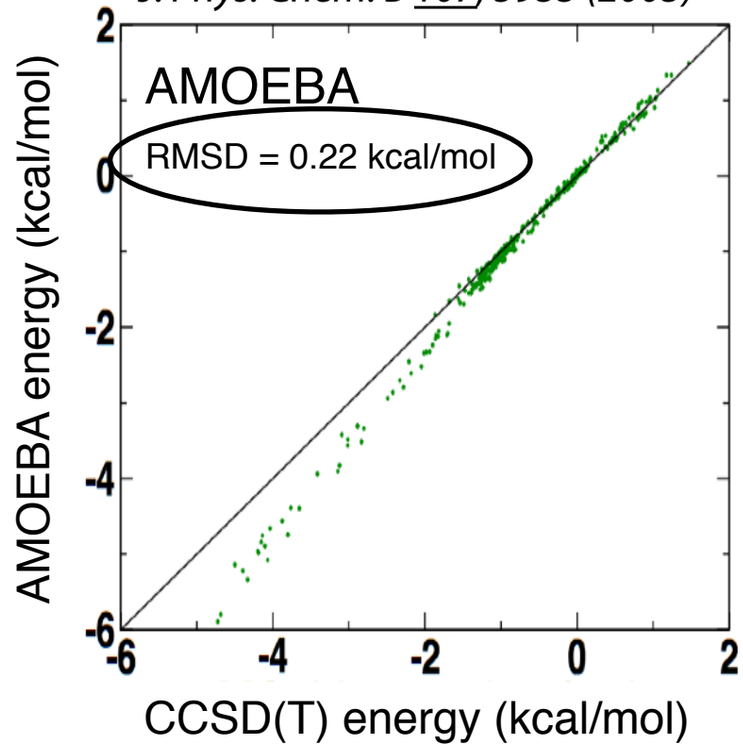

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Ab Initio Potentials from the Many-Body Expansion

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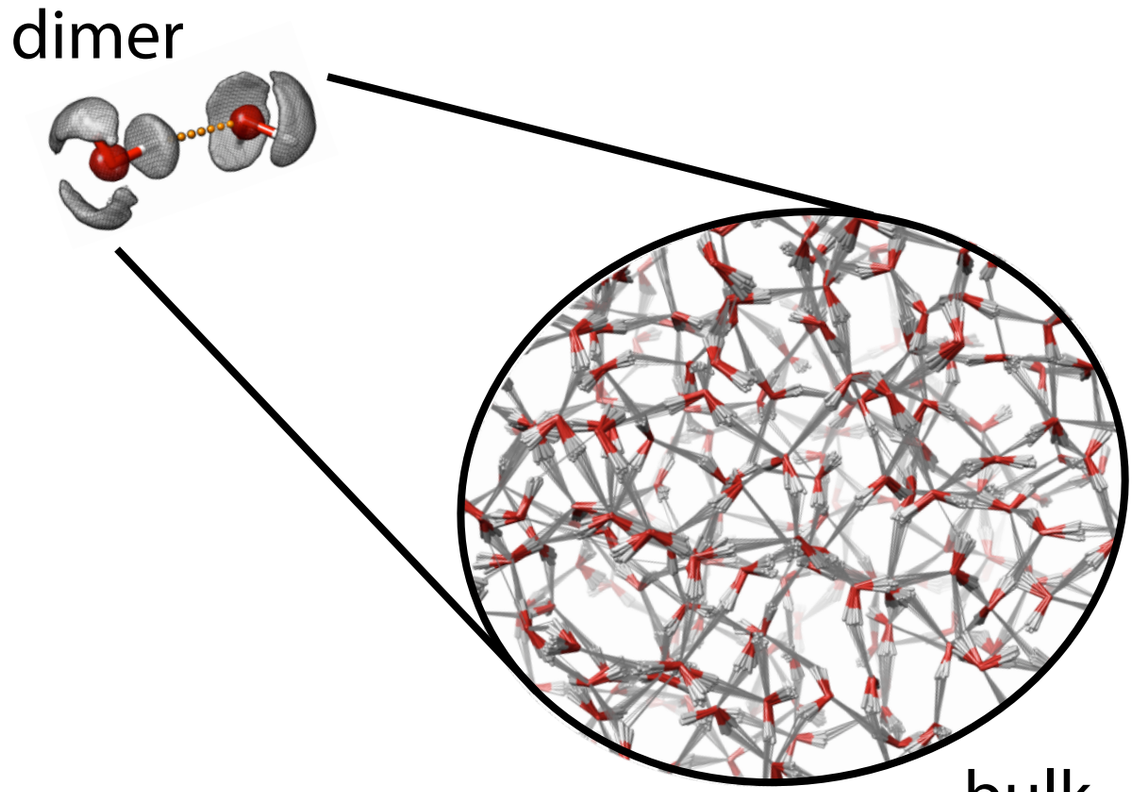
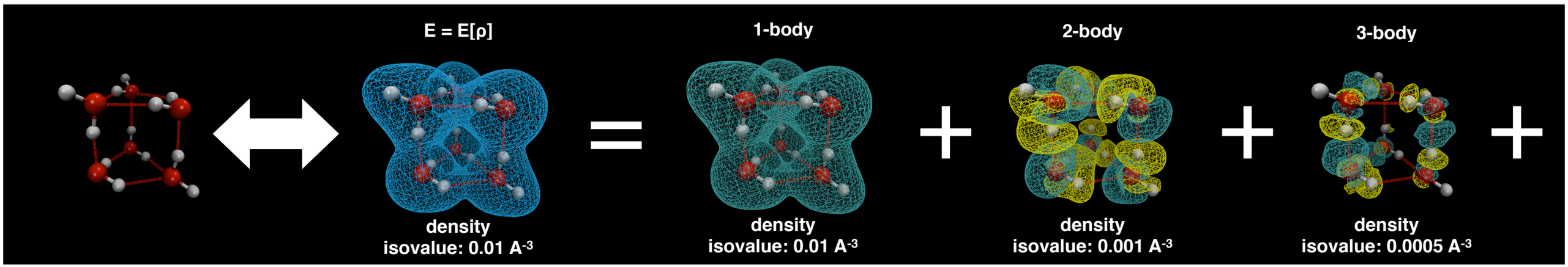
MB expansion for water converges quickly

Xantheas, Jordan, Szalewicz ...





MB-nrg:
CCSD(T)-Level
Multidimensional
Potential Energy Surfaces

MB-pol: A Transferable Many-Body Water Potential

$$E_N = \sum_i^N V^{1B}(i) \qquad \text{1-body}$$

$$+ \sum_{i<j}^N V^{2B}(i,j) \qquad \text{2-body}$$

$$+ \sum_{i<j<k}^N V^{3B}(i,j,k) \qquad \text{3-body}$$

$$+ \ldots$$

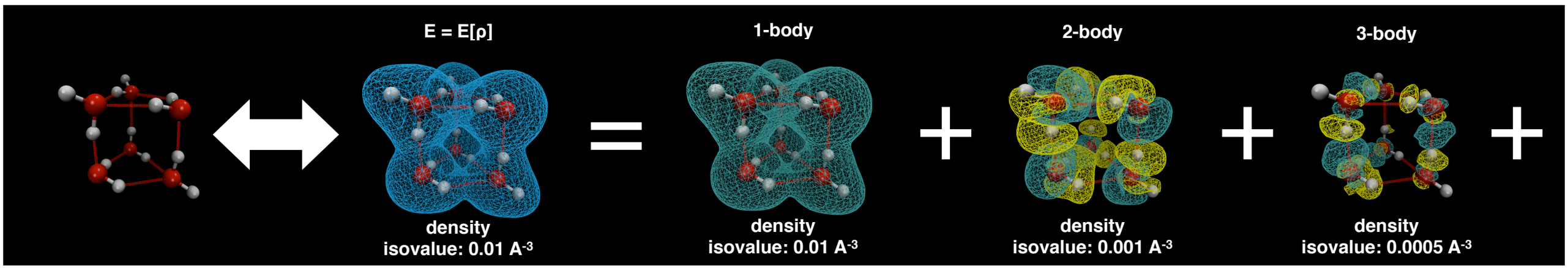
$$+ V^{NB}(1,\ldots,N) \qquad \text{N-body}$$

explicit 1B, 2B, and 3B terms
from CCSD(T)/CBS

+

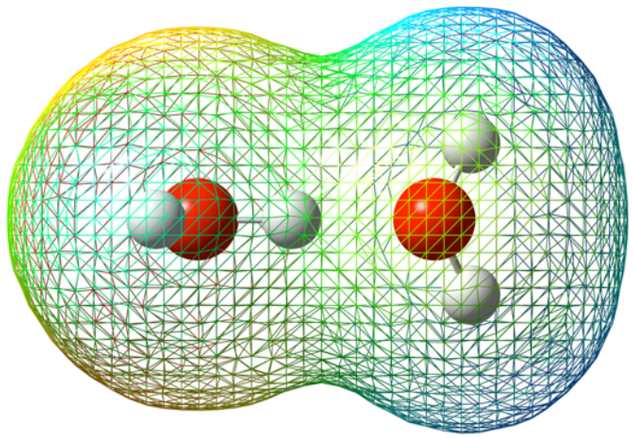
higher-body terms
from many-body polarization

- *J. Phys. Chem. Lett. 3, 3765 (2012)*
- *J. Chem. Theory Comput. 9, 1103 (2013)*
- *J. Chem. Theory Comput. 9, 4844 (2013)*
- *J. Chem. Theory Comput. 9, 5395 (2013)*
- *J. Chem. Theory Comput. 10, 1599 (2014)*
- *J. Chem. Theory Comput. 10, 2906 (2014)*
- *J. Chem. Theory Comput. DOI: 10.1021/ct501131j*



Molecular Interactions & Electronic Structure

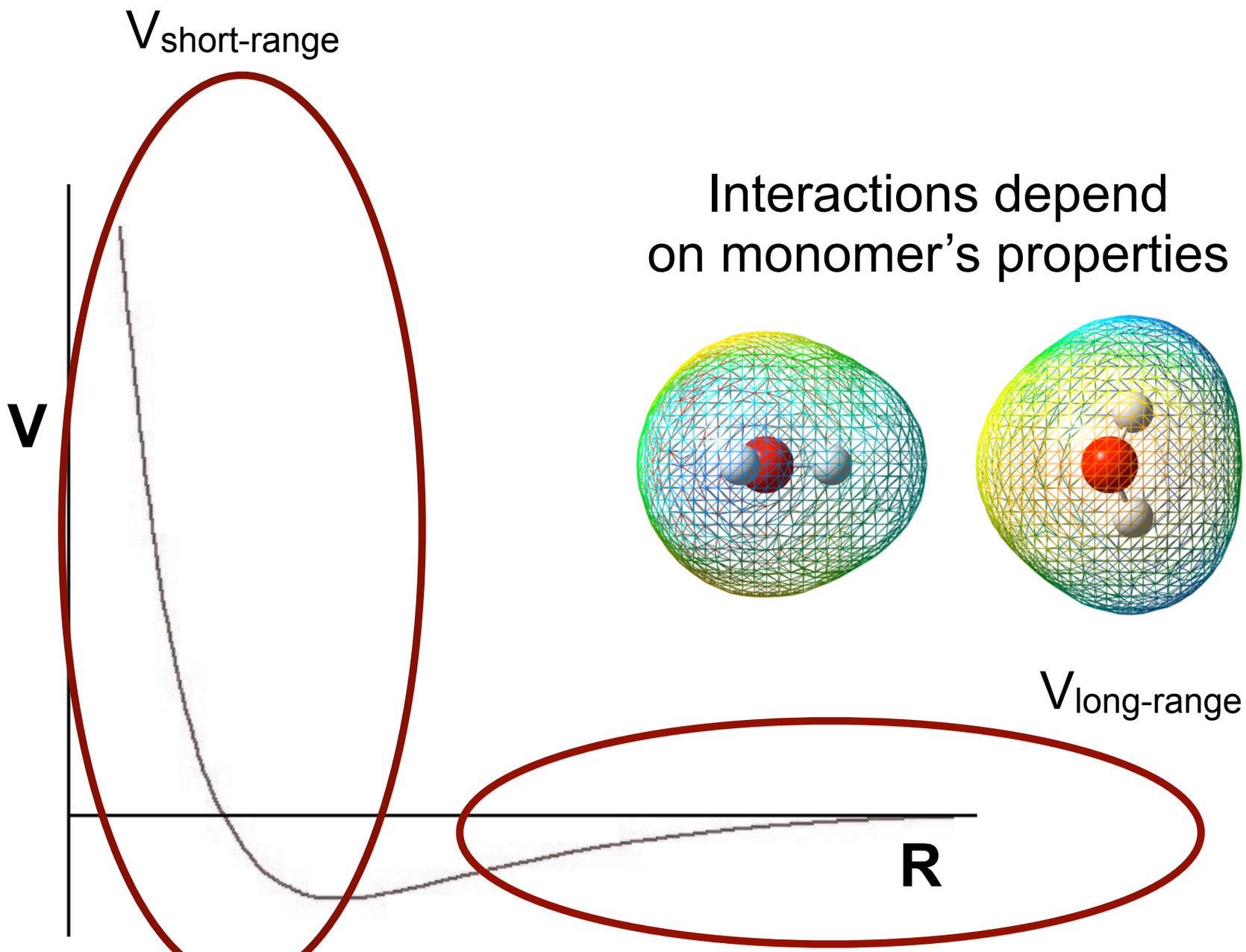
Interactions depend
on the density overlap



Multidimensional fits to highly-correlated ab initio data

Suhm
Chem. Phys. Lett. 223, 474 (1994)

Braams & Bowman
Int. Rev. Phys. Chem. 28, 577 (2009)

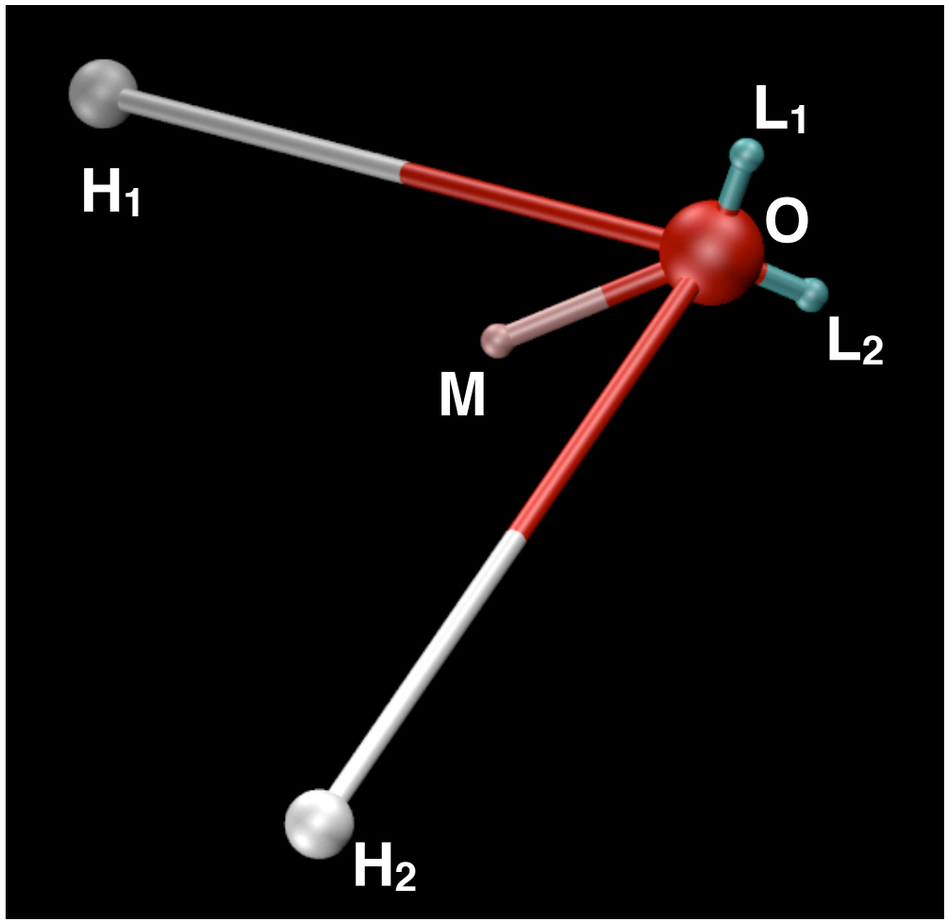


Interactions depend
on monomer's properties

Classical electrostatics

Stone, "Intermolecular Interactions"

MB-pol: A Transferable Many-Body Water Potential



$$V^{1B} = V^{1B}_{PS}$$ *Partridge & Schwenke, J. Chem. Phys. 106, 4618 (1997)*

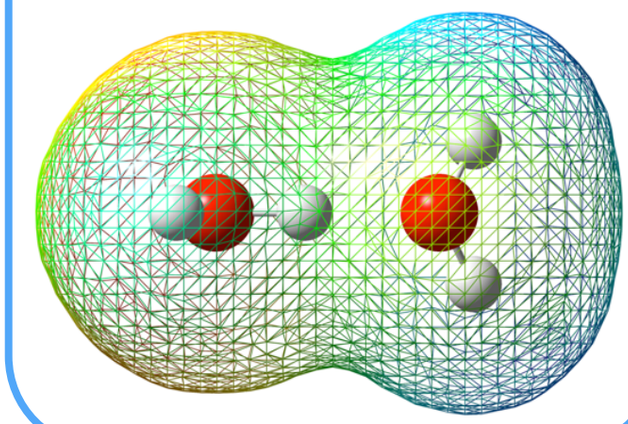
$$V^{2B} = s_2 V^{2B}_{poly} + V^{2B}_{elect} + V^{2B}_{ind} - \sum_{i<j} f_{ij} \frac{C_{ij,6}}{R^6_{ij}}$$

$$V^{3B} = s_3 V^{3B}_{poly} + V^{3B}_{ind}$$

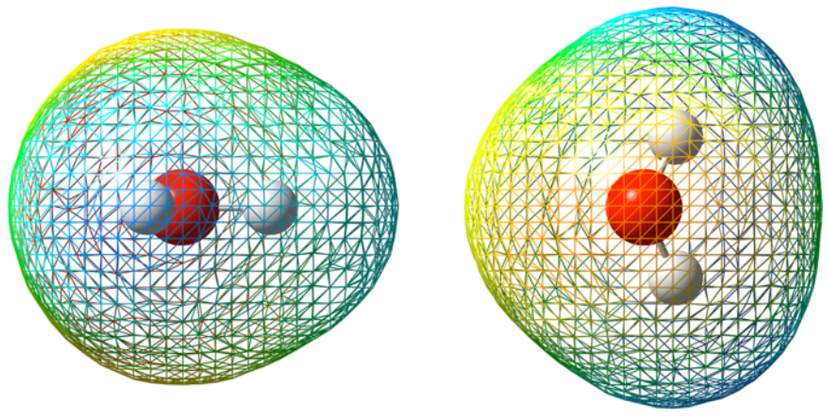
$$V^{>3B} = V^{NB}_{ind}(1,\ldots,N)$$

classical electrostatics

short range

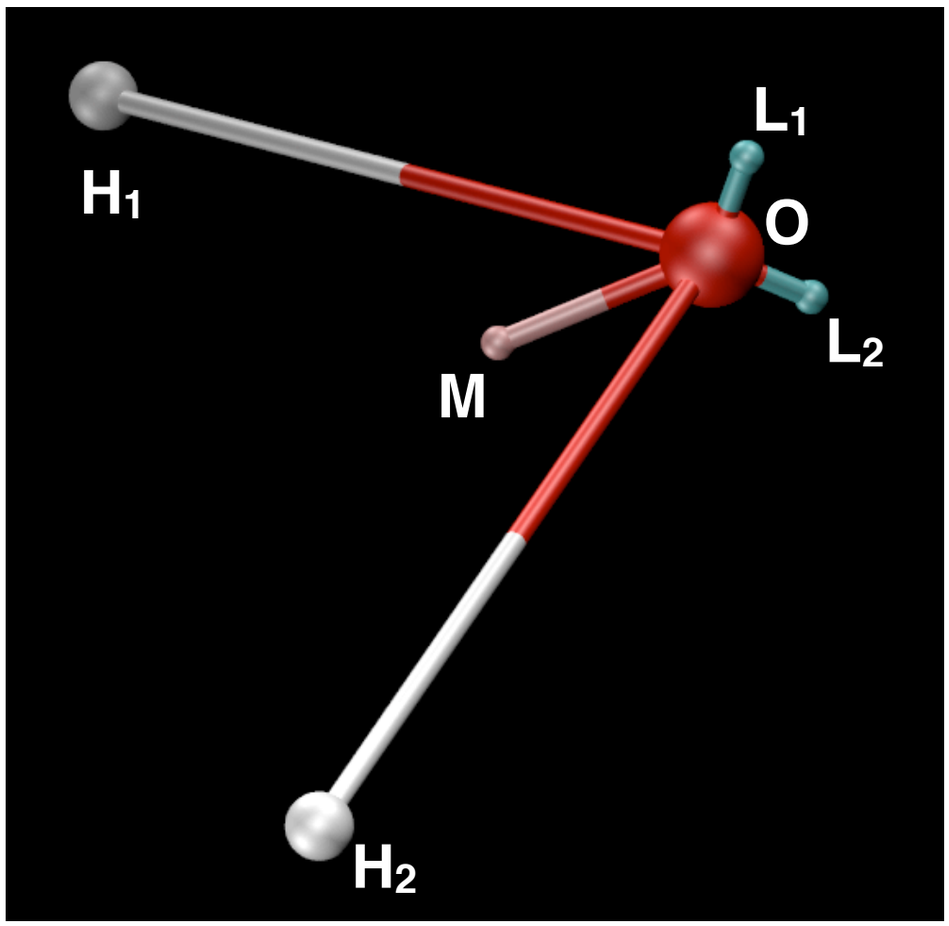


long range



Babin, Leforestier & FP, J. Chem. Theory Comput. 9, 5395 (2013); Babin, Medders & FP, J. Chem. Theory Comput. 10, 1599 (2014)

MB-pol: A Transferable Many-Body Water Potential



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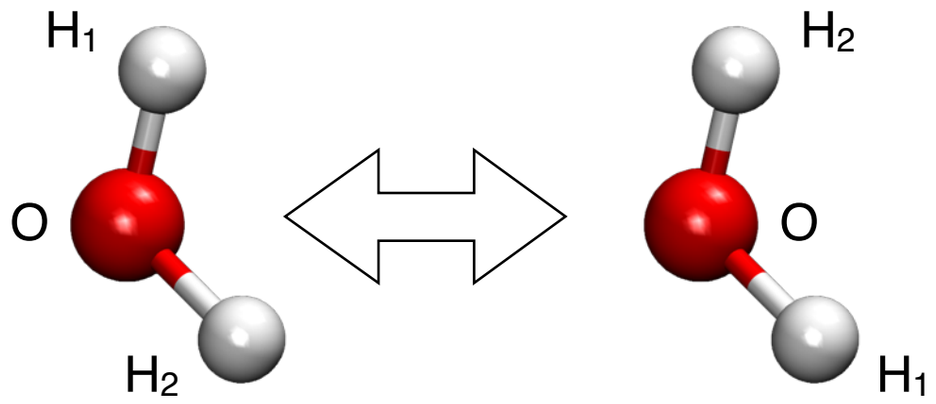
Permutationally invariant polynomials

Braams & Bowman, Int. Rev. Phys. Chem. 28, 577 (2009)



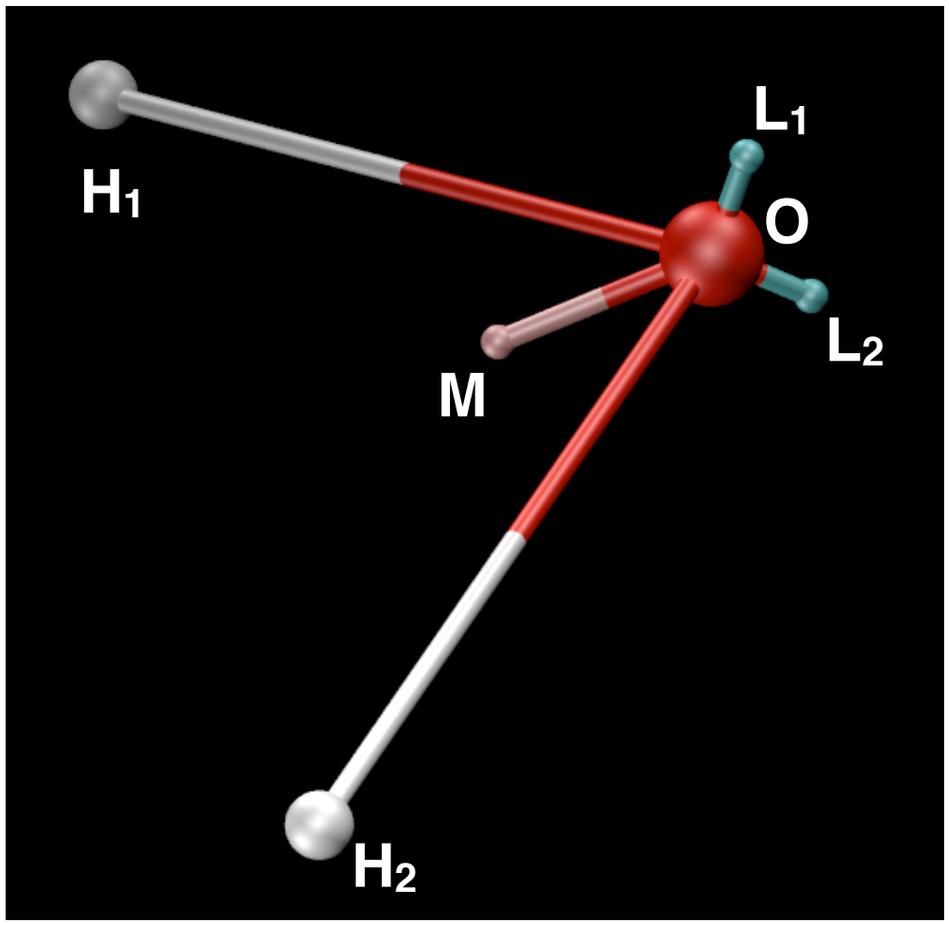
$$V = \sum_{m=a+b+c=0}^{M} D_{abc} \left\{ y^a_{12} \left[y^b_{13} y^c_{23} + y^c_{13} y^b_{23} \right] \right\}$$

Morse variables

$$y_{ij} = e^{-k r_{ij}} \qquad y_{ij} = \frac{e^{-k r_{ij}}}{r_{ij}}$$

Babin, Leforestier & FP, J. Chem. Theory Comput. 9, 5395 (2013); Babin, Medders & FP, J. Chem. Theory Comput. 10, 1599 (2014)

MB-pol: A Transferable Many-Body Water Potential



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$$V^{3B} = s_3 V^{3B}_{poly} + V^{3B}_{ind}$$

$$V^{>3B} = V^{NB}_{ind}(1, \ldots, N)$$

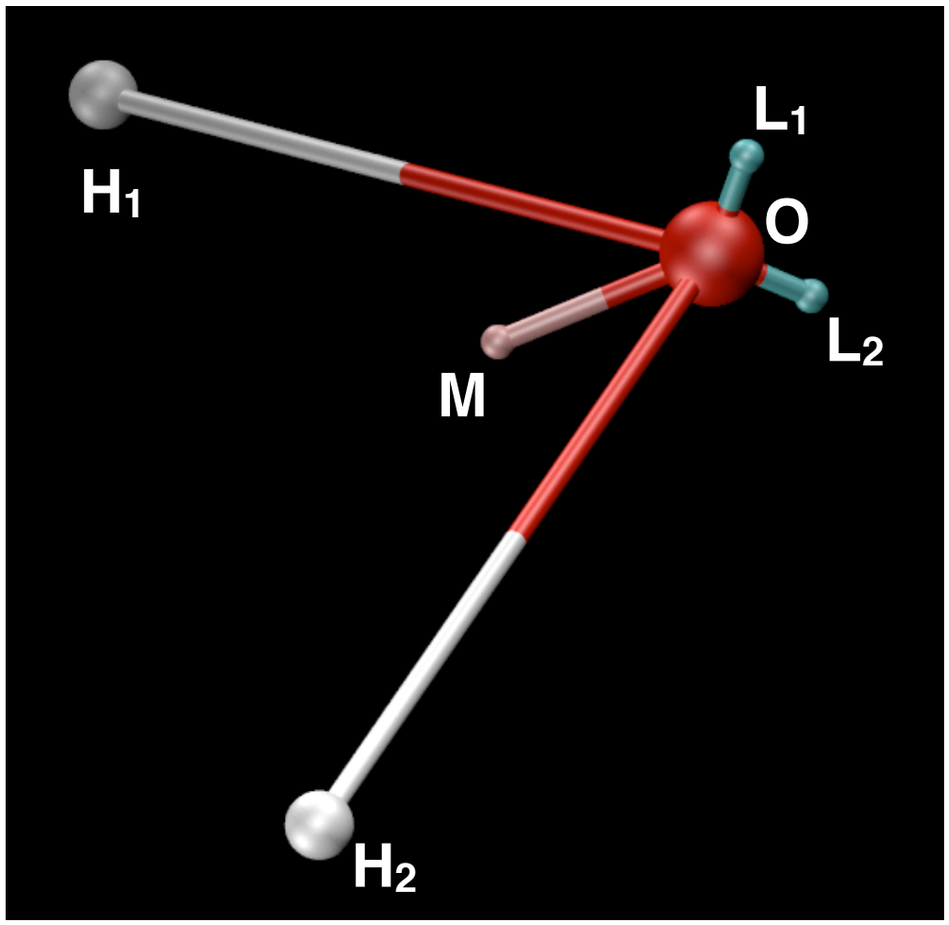
V2B

1153 linear parameters + 16 nonlinear parameters

$$V^{2B}_{poly} = \sum_{l=1}^{1153} c_l \eta_l \qquad s_2(x) = \begin{cases} 1 & \text{if } x < 0 \\ 1 + x^2(2x - 3) & \text{if } 0 \leq x < 1 \\ 0 & \text{if } 1 \leq x \end{cases} \qquad x = \frac{R_{OO} - R_{in}}{R_{out} - R_{in}}$$

Babin, Leforestier & FP, J. Chem. Theory Comput. 9, 5395 (2013); Babin, Medders & FP, J. Chem. Theory Comput. 10, 1599 (2014)

MB-pol: A Transferable Many-Body Water Potential



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$$V^{>3B} = V^{NB}_{ind}(1, \ldots, N)$$

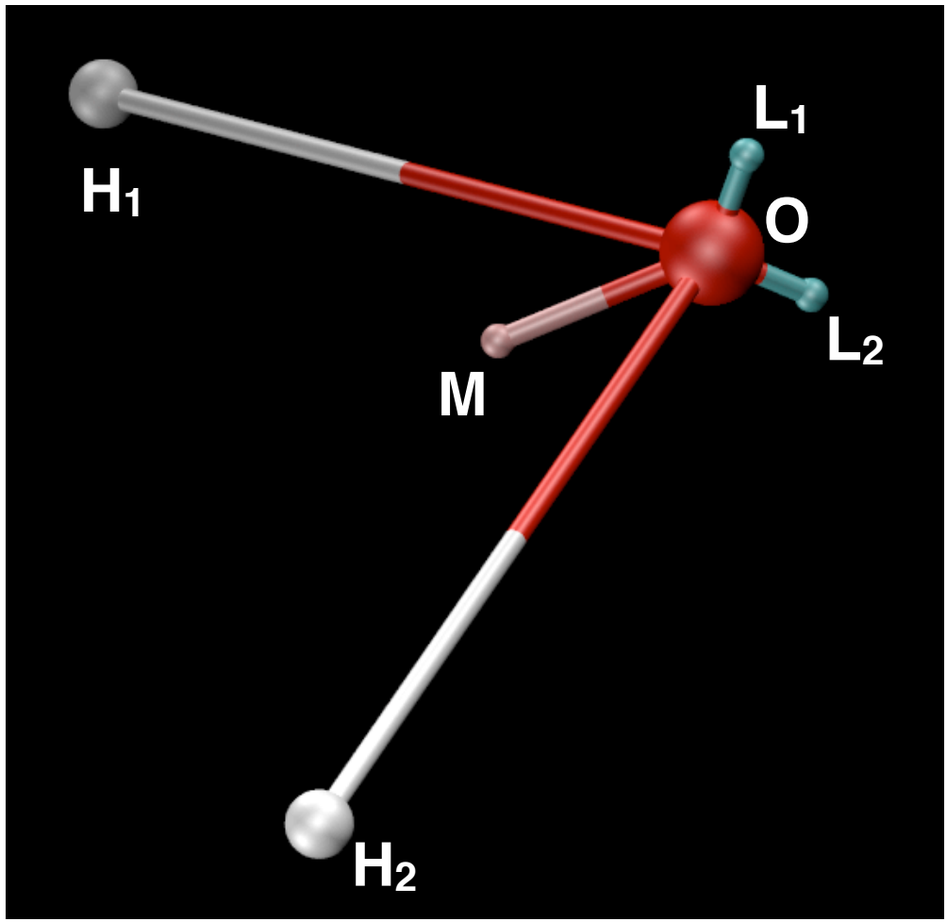
V2B

1153 linear parameters + 16 nonlinear parameters

$$\chi^2 = \sum_{n \in \mathcal{S}} w_n [V_2^{\text{model}}(n) - V_2^{\text{ref}}(n)]^2 + \Gamma^2 \sum_{l=1}^{1153} c_l^2 \qquad w(E) = \left(\frac{\Delta E}{E - E_{\text{min}} + \Delta E} \right)^2 \qquad \Gamma = 5 \times 10^{-4}$$

Babin, Leforestier & FP, J. Chem. Theory Comput. 9, 5395 (2013); Babin, Medders & FP, J. Chem. Theory Comput. 10, 1599 (2014)

MB-pol: A Transferable Many-Body Water Potential



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$$V^{>3B} = V^{NB}_{ind}(1, \ldots, N)$$

V3B

1163 linear parameters + 10 nonlinear parameters

$$V^{3B}_{poly} = \sum_{m=1}^{1163} c_m \xi_m$$

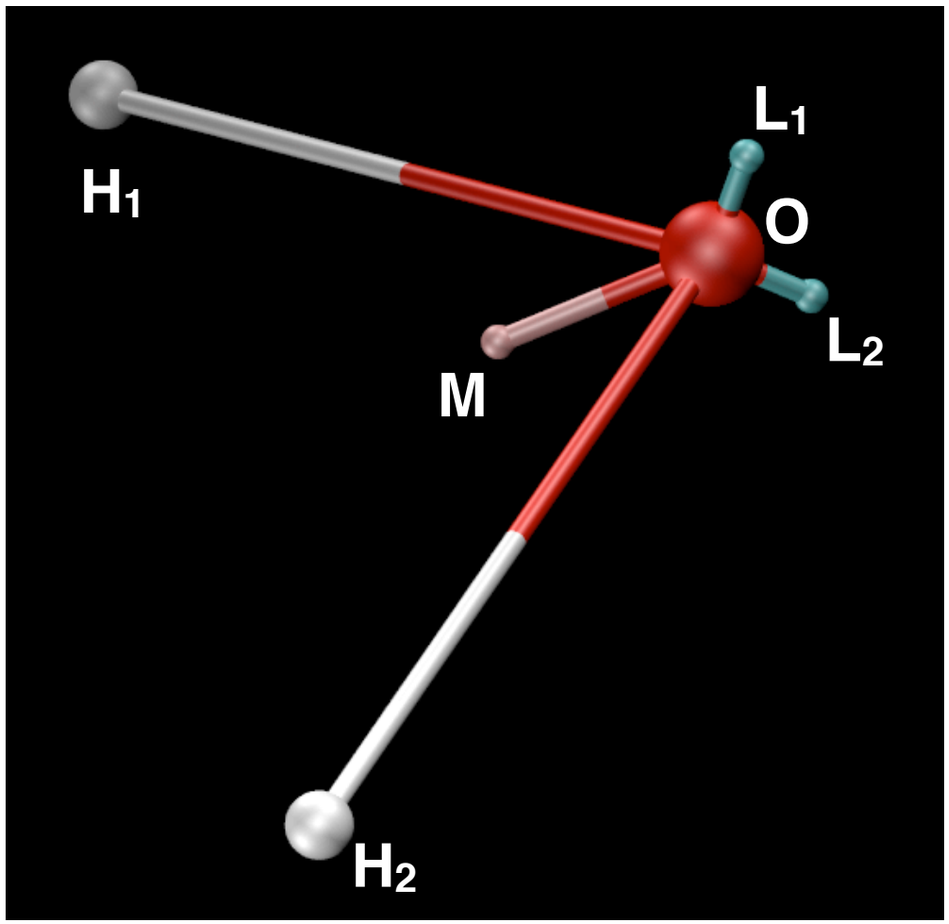
$$\begin{aligned} s_3 = {} & s(t_{ab})s(t_{ac}) \\ & + s(t_{ab})s(t_{bc}) \\ & + s(t_{ac})s(t_{bc}) \end{aligned}$$

$$t_{mn} = \frac{R_{mn}}{R^{(3B)}_{cut}}$$

$$s(t) = \begin{cases} 1 & \text{if} \quad t < 0 \\ \cos^2 \frac{\pi}{2} t & \text{if} \quad 0 \le t < 1 \\ 0 & \text{if} \quad 1 \le t \end{cases}$$

Babin, Leforestier & FP, J. Chem. Theory Comput. 9, 5395 (2013); Babin, Medders & FP, J. Chem. Theory Comput. 10, 1599 (2014)

MB-pol: A Transferable Many-Body Water Potential



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$$V^{2B} = s_2 V_{poly}^{2B} + V_{elect}^{2B} + V_{ind}^{2B} - \sum_{i<j} f_{ij} \frac{C_{ij,6}}{R_{ij}^6}$$

$$V^{3B} = s_3 V_{poly}^{3B} + V_{ind}^{3B}$$

$$V^{>3B} = V_{ind}^{NB}(1, \ldots, N)$$

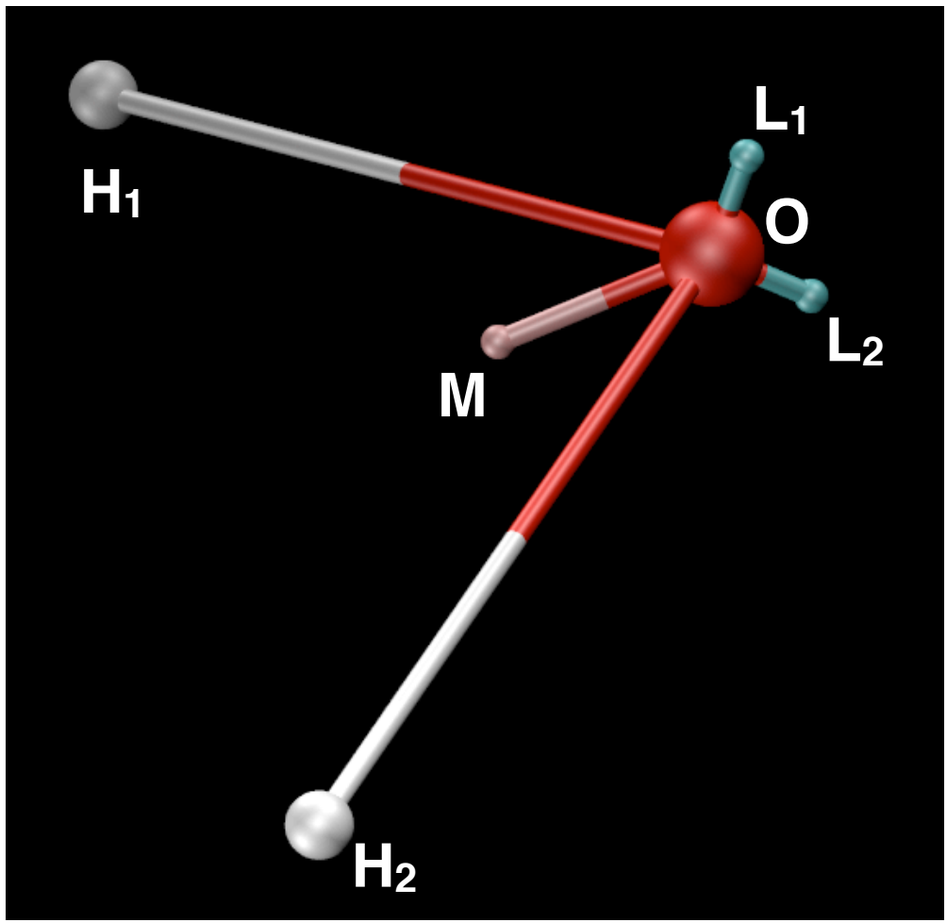
V3B

1163 linear parameters + 10 nonlinear parameters

$$\chi^2 = \sum_{n \in \mathcal{J}} w_n [V_{\text{model}}^{(3B)}(n) - V_{\text{ref}}^{(3B)}(n)]^2 + \Gamma^2 \sum_{l=1}^{1163} c_l^2 \qquad w(E) = \left(\frac{\Delta E}{E - E_{\text{min}} + \Delta E} \right)^2 \qquad \Gamma = 1 \times 10^{-4}$$

Babin, Leforestier & FP, J. Chem. Theory Comput. 9, 5395 (2013); Babin, Medders & FP, J. Chem. Theory Comput. 10, 1599 (2014)

MB-pol: A Transferable Many-Body Water Potential



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$$V^{3B} = s_3 V^{3B}_{poly} + V^{3B}_{ind}$$

$$V^{>3B} = V^{NB}_{ind}(1, \ldots, N)$$

Reference data

2B: CCSD(T)/CBS dimers

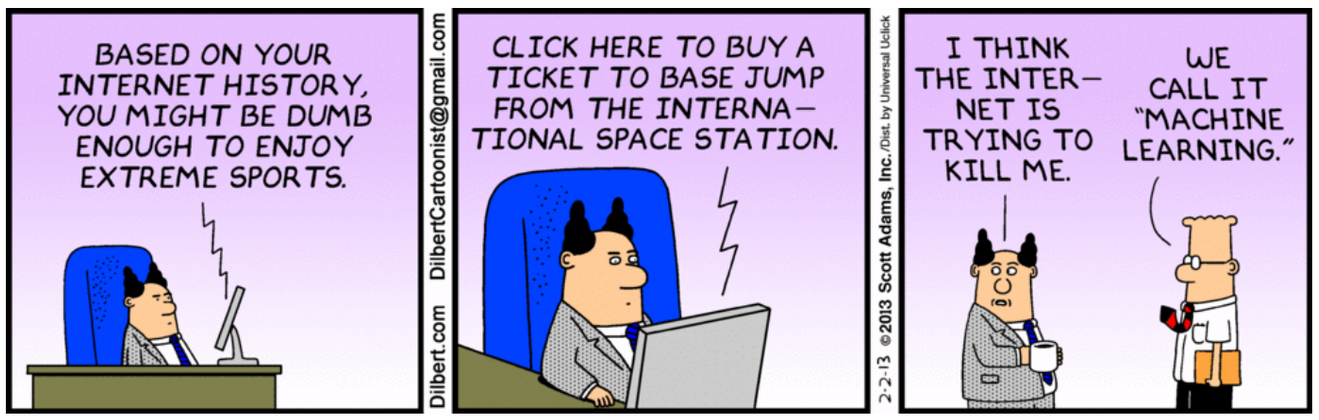
3B: CCSD(T)/CBS trimers

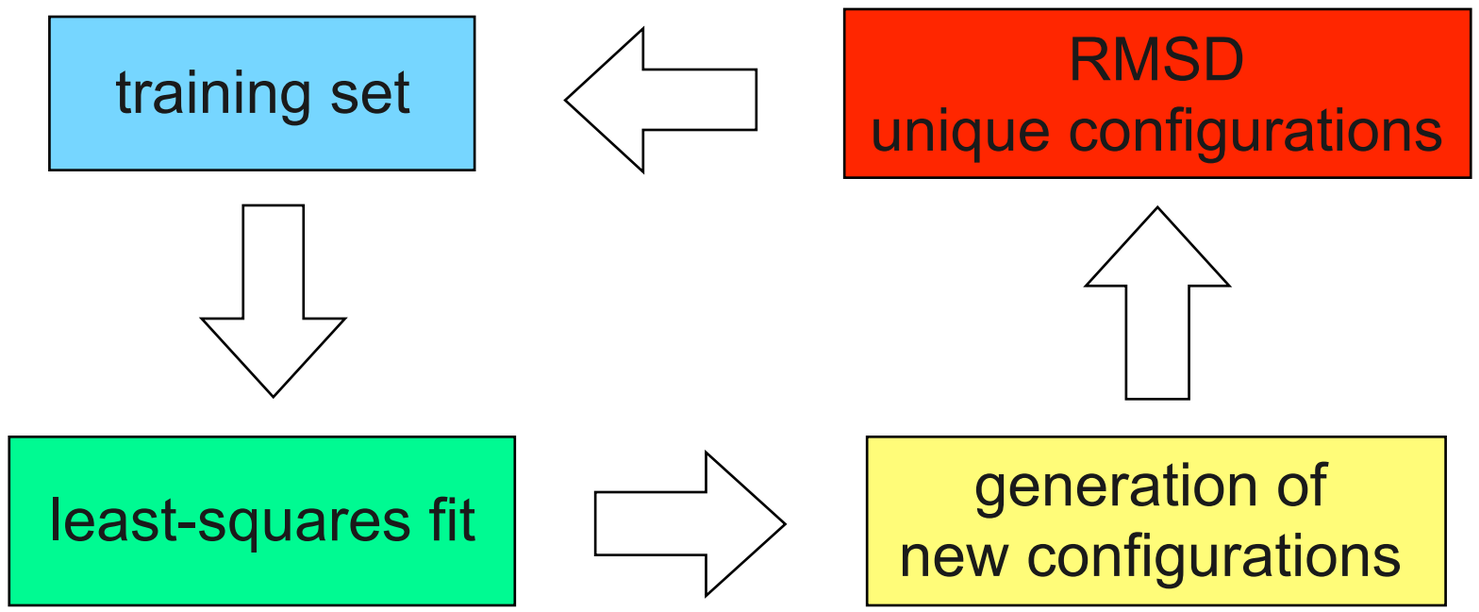
invariant polynomials,
dipole, polarizability,
and dispersion

Babin, Leforestier & FP, J. Chem. Theory Comput. 9, 5395 (2013); Babin, Medders & FP, J. Chem. Theory Comput. 10, 1599 (2014)

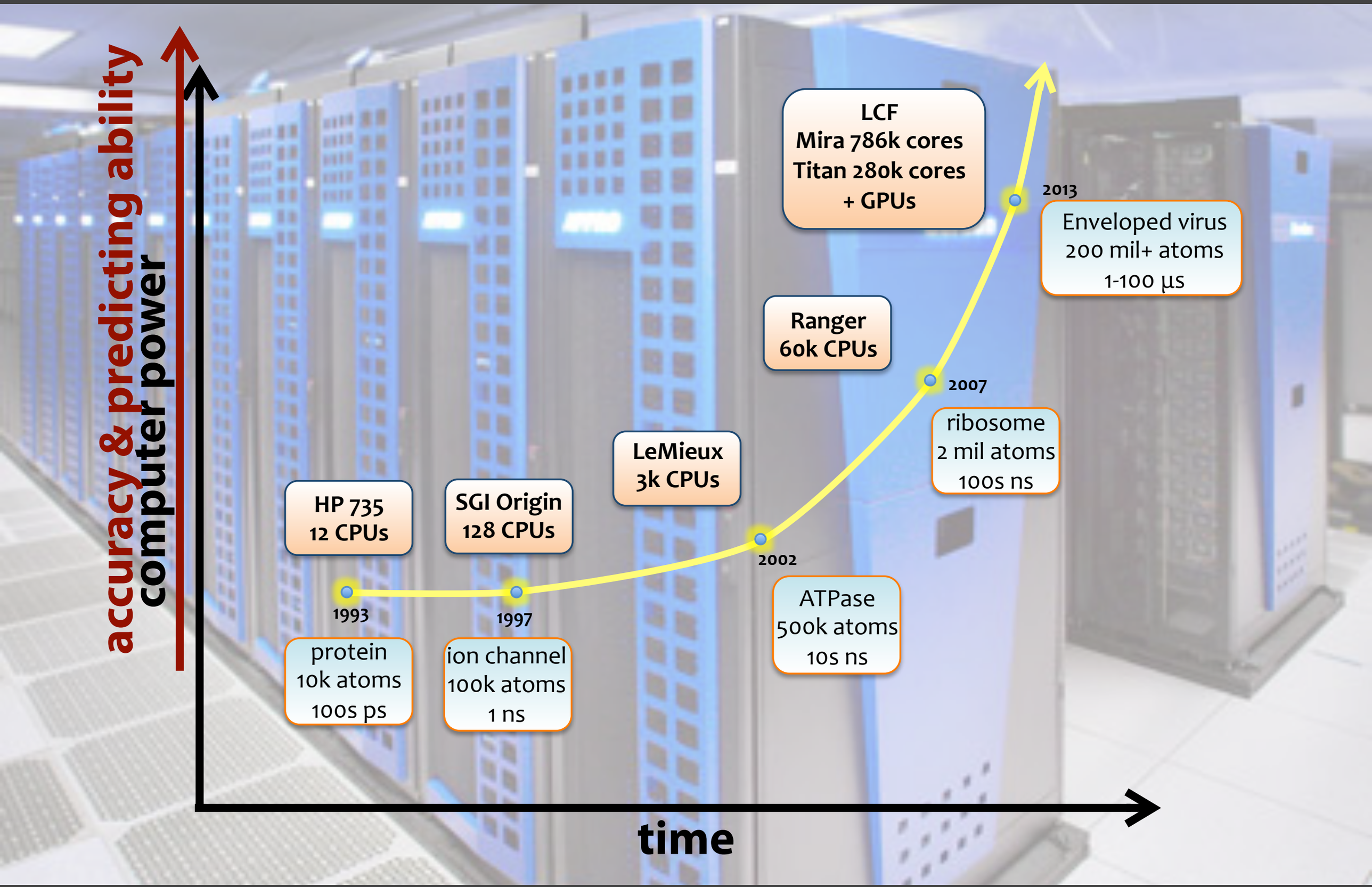
Molecular Interactions & Big Data

“Active learning”





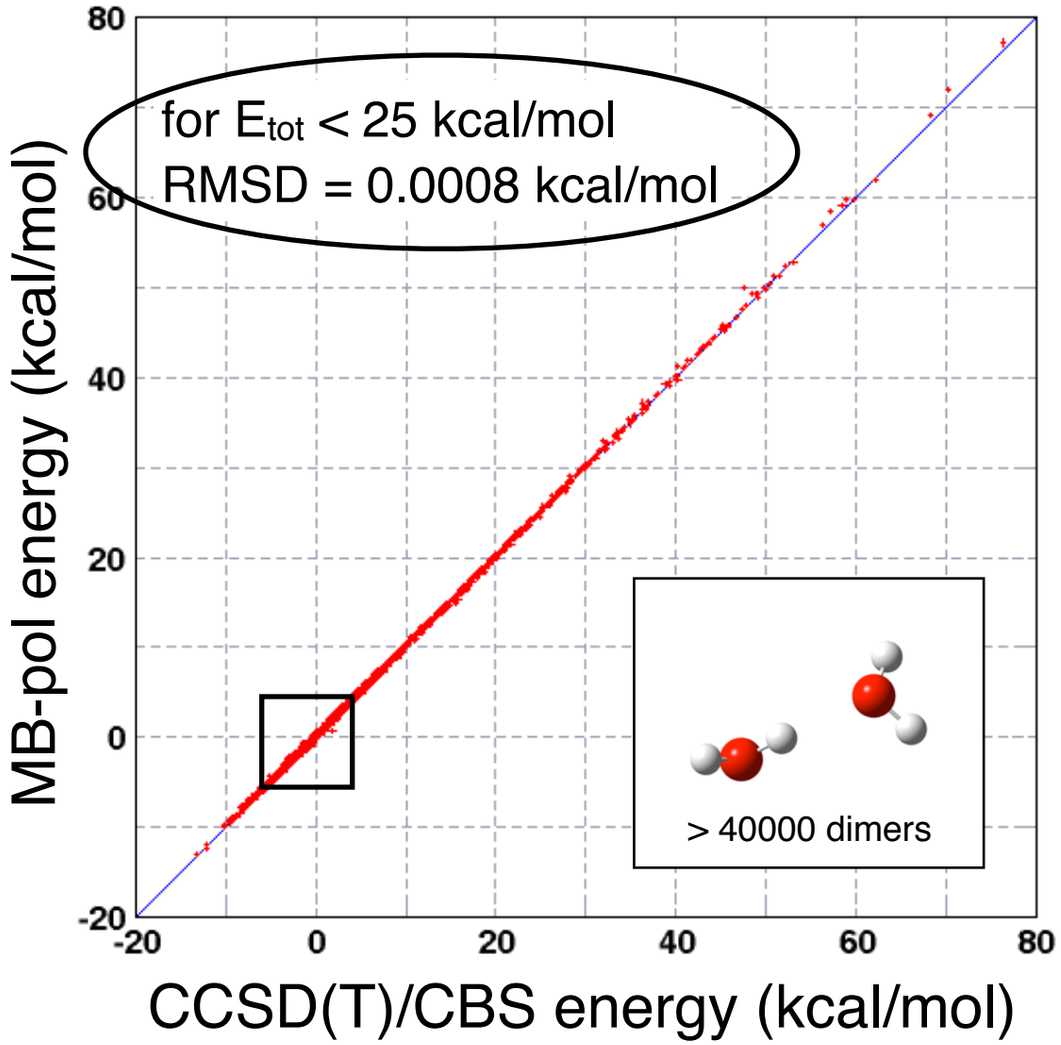
Molecular Interactions & Scientific Computing



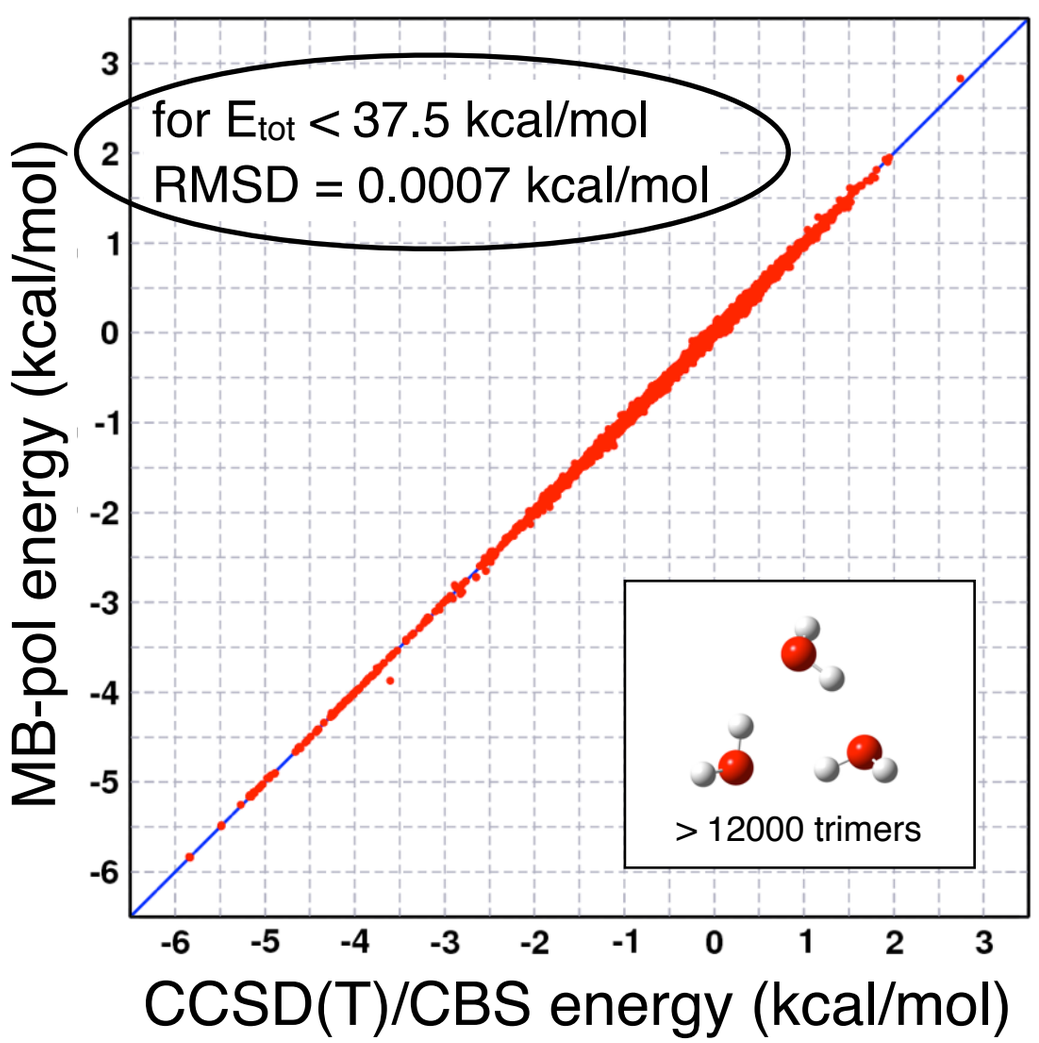
MB-pol: 2-Body & 3-Body Interaction Energies

$$E_N = \sum_i^N V^{1B}(i) + \sum_{i<j}^N V^{2B}(i,j) + \sum_{i<j<k}^N V^{3B}(i,j,k) + \cdots + V^{NB}(1,\ldots,N)$$

2B energies



3B energies

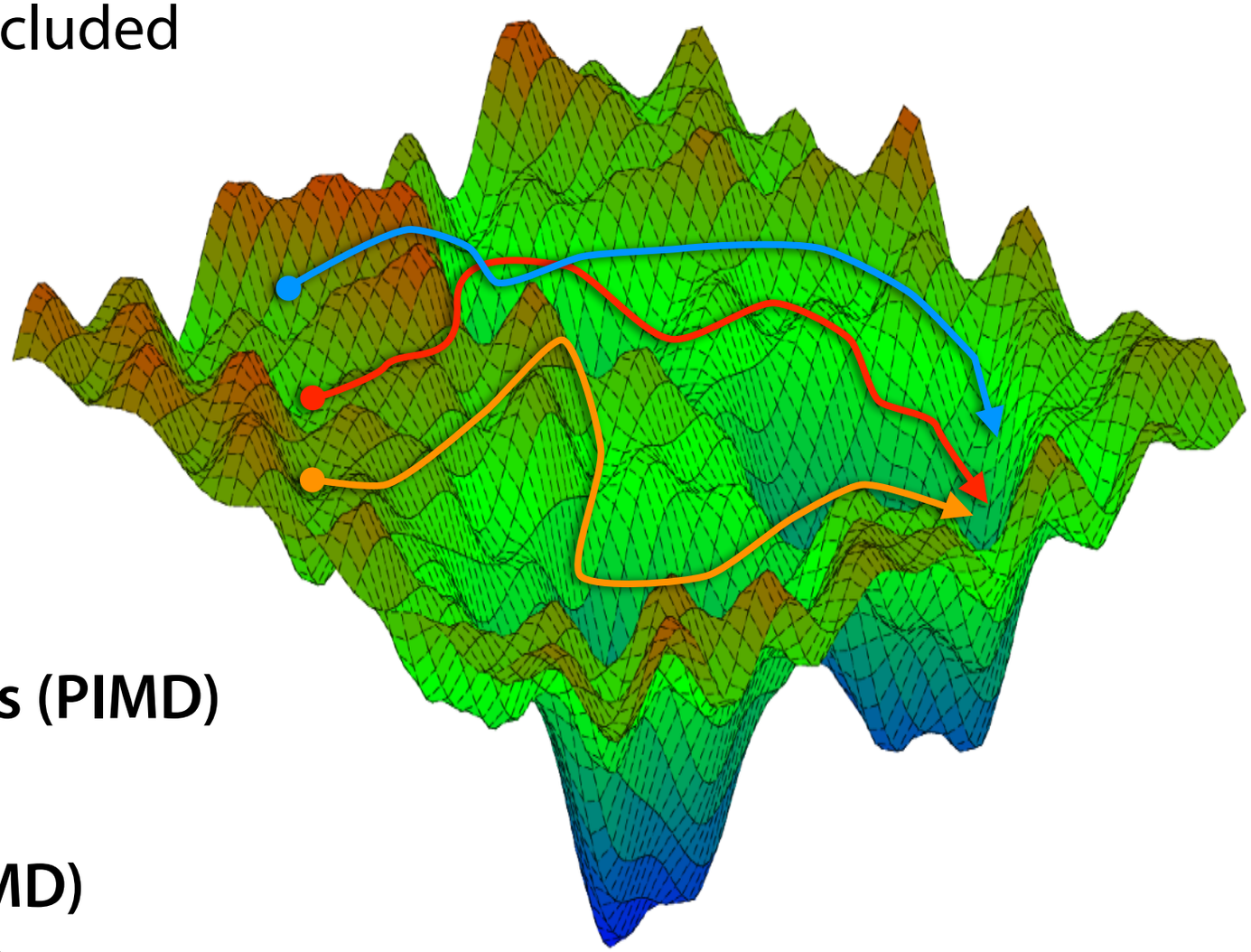


MB-pol Accuracy: Structural and Dynamical Properties of Water Across Different Phases

Molecular Simulations with MB-pol

MB-pol ⟺ Born-Oppenheimer potential energy surface

Nuclear quantum effects must be included explicitly in molecular simulations

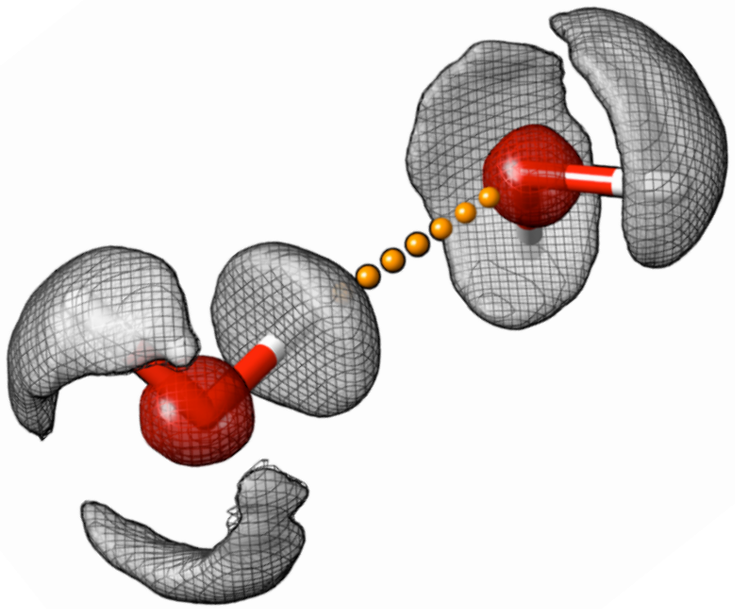


Methods based on:

- **Basis set expansions**
  (gas phase spectra)
- **Path-integral molecular dynamics (PIMD)**
  (structure & thermodynamics)
- **Centroid molecular dynamics (CMD)**
  (approximate quantum dynamics)

Nitzan, "Chemical Dynamics in Condensed Phases"; Tuckerman, "Statistical Mechanics: Theory and Molecular Simulation"

Dimer: Vibration-Rotation Tunneling Spectrum



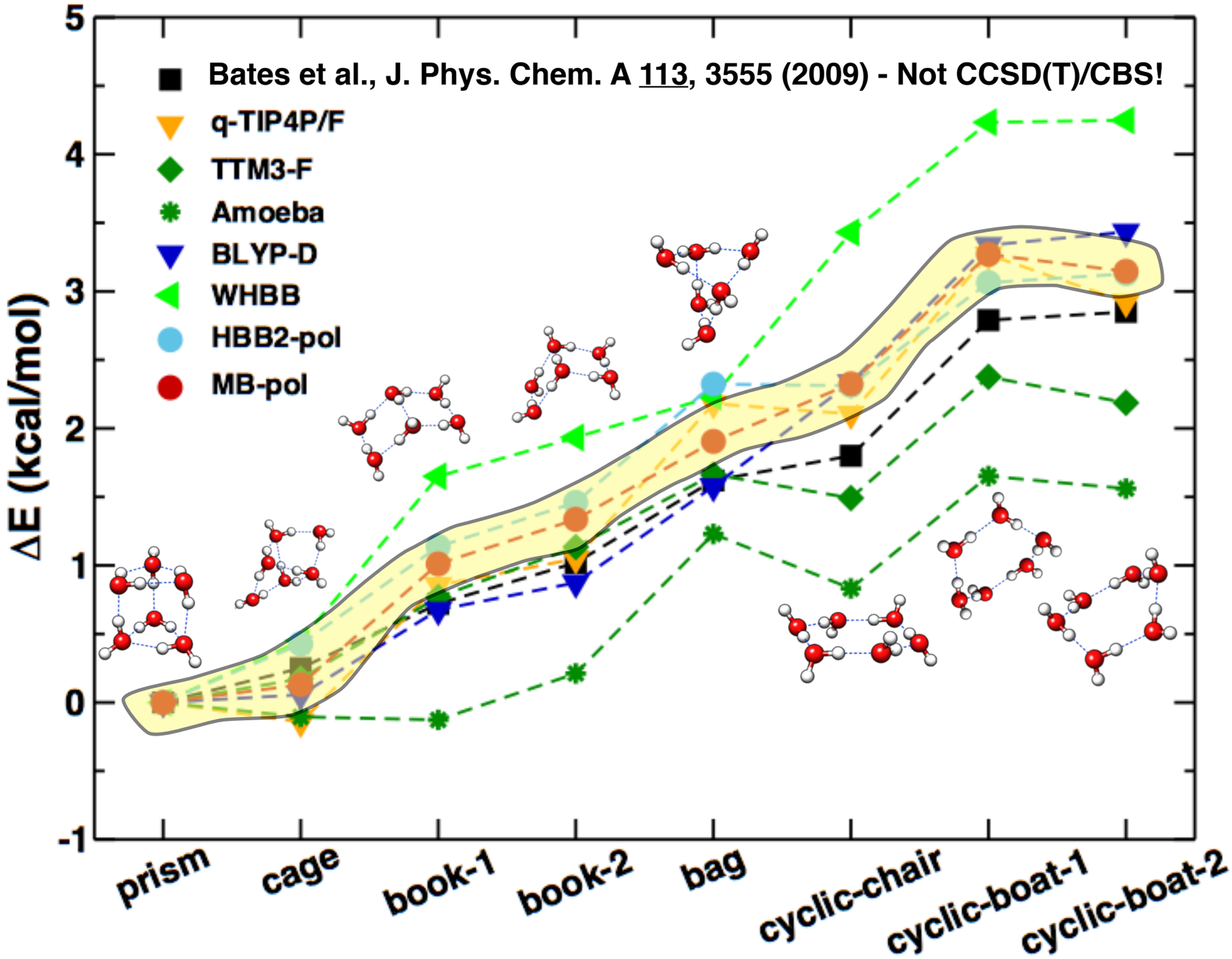
- **hydrogen tunneling**
- **energy level splitting**

Mode		Experiment (cm^{-1})	MB-pol (cm^{-1})
intermolecular stretch	2	153.62	154.77
	1		149.05
acceptor twist	1		129.49
	2	120.19	119.23
acceptor wag	2	108.89	109.14
	1	107.93	108.76
donor torsion	1		113.18
	2	64.52	61.24
ground state	2	11.18	11.88
	1	0	0

Babin, Leforestier & FP, J. Chem. Theory Comput. 9, 5395 (2013)

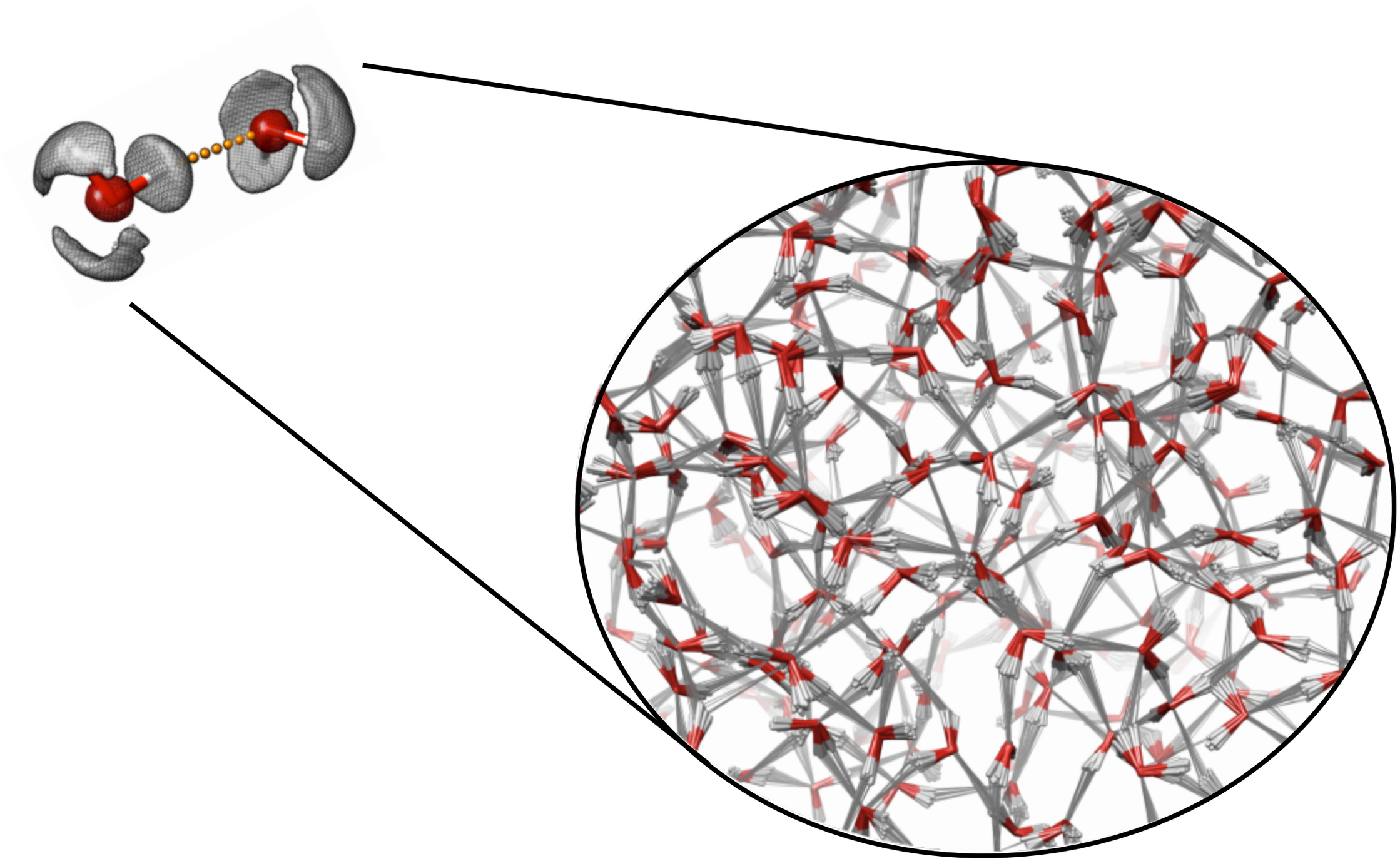
Clusters: Hexamer

Relative energies



Babin, Medders & FP, J. Phys. Chem. Lett. 3, 3765 (2012); Babin, Medders & FP, J. Chem. Theory Comput. 10, 1599 (2014)

From the Gas to the Condensed Phase



Liquid: Energies Relative to Quantum Monte Carlo

Mean abso

- Periodic boundary conditions
- Molecular configurations from MI

$$MAD = \frac{1}{N}\sum_{i}^{N}\left|\left(E_i^{model} - E\right.\right.$$

Timings - MB-pol vs. DFT

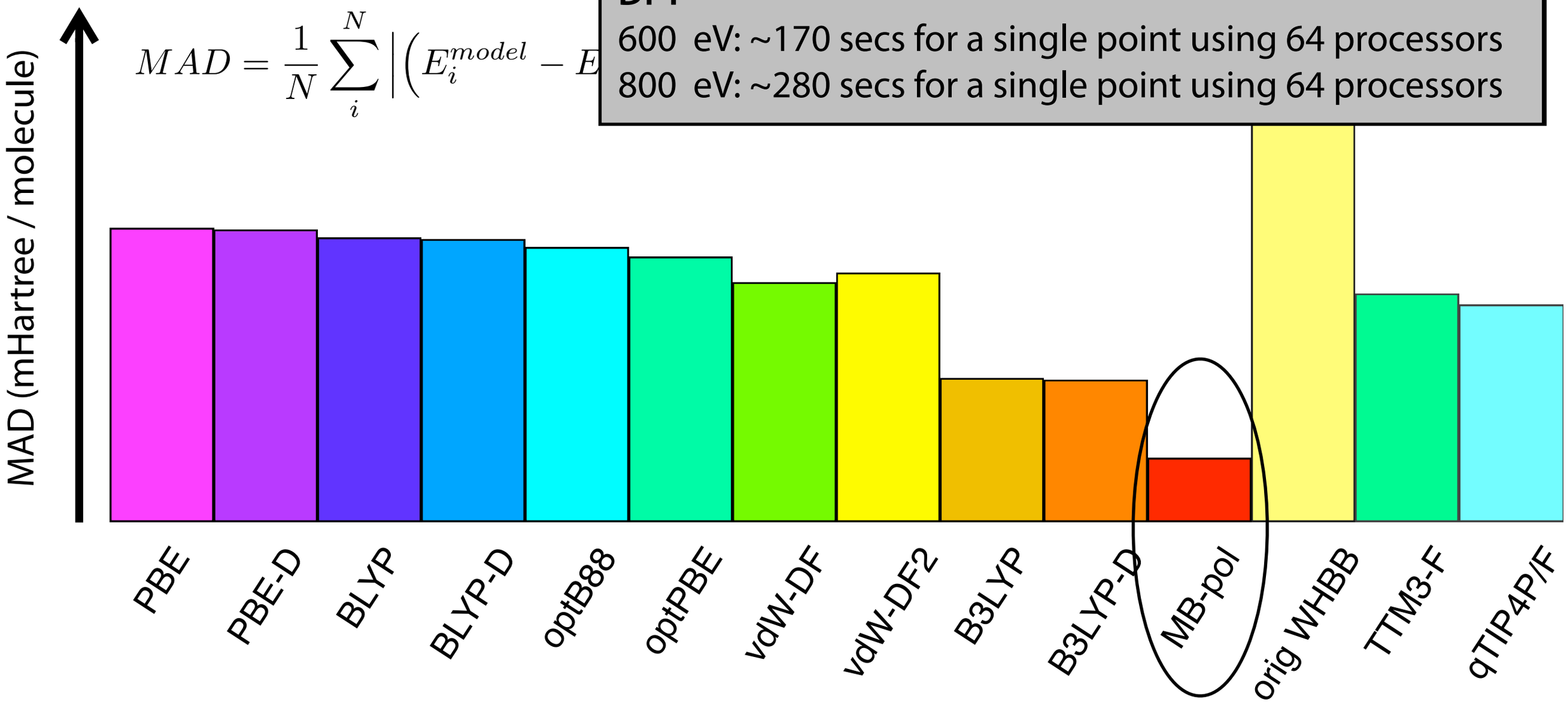
MB-Pol

~0.06 secs for a single point using 64 processors

DFT

600 eV: ~170 secs for a single point using 64 processors

800 eV: ~280 secs for a single point using 64 processors

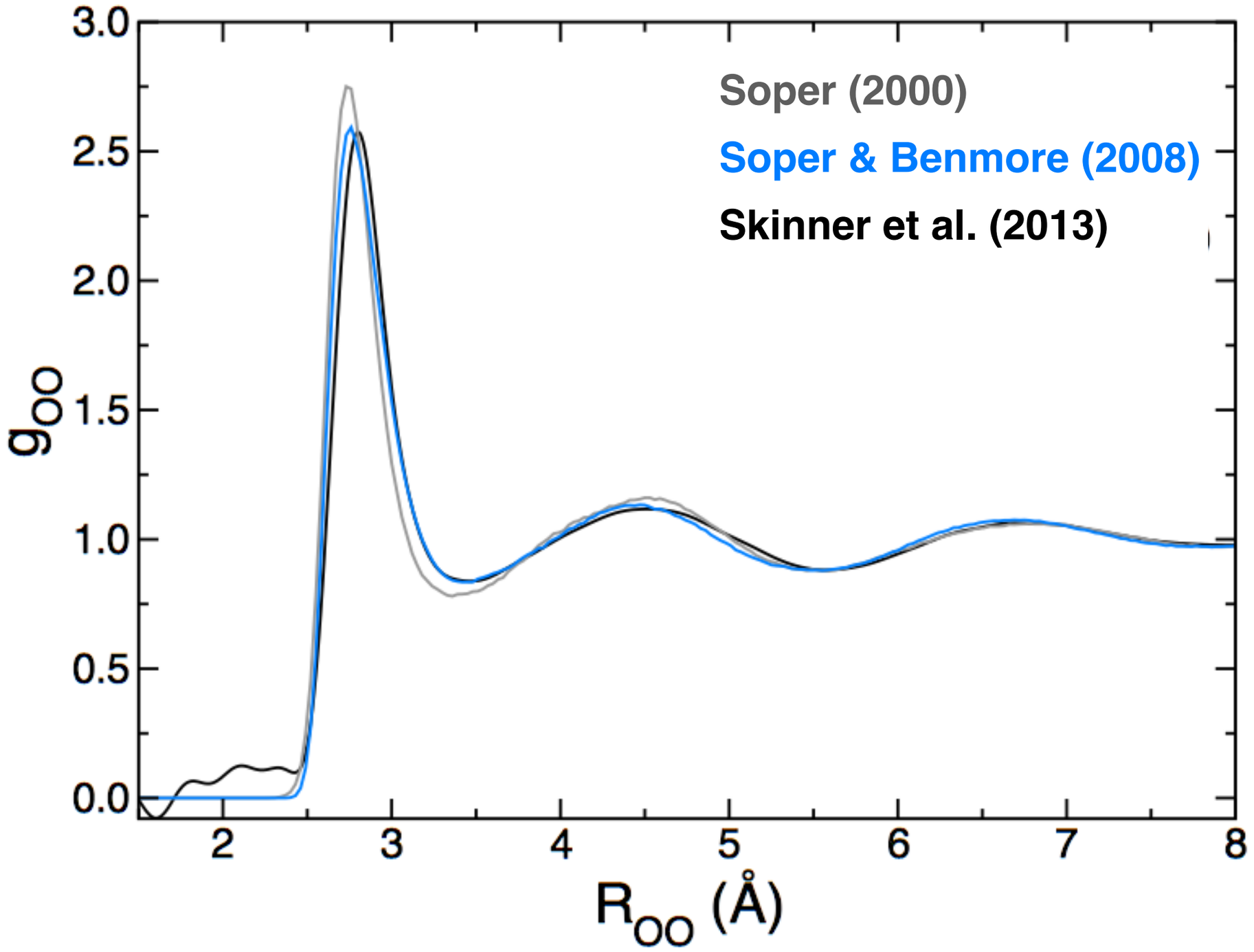


QMC: *Morales, Gergely, McMinis, McMahon, Kim & Ceperley, J. Chem. Theory Comput. 10, 2355 (2014)*

with Miguel Morales (LLNL)

Liquid: Structure

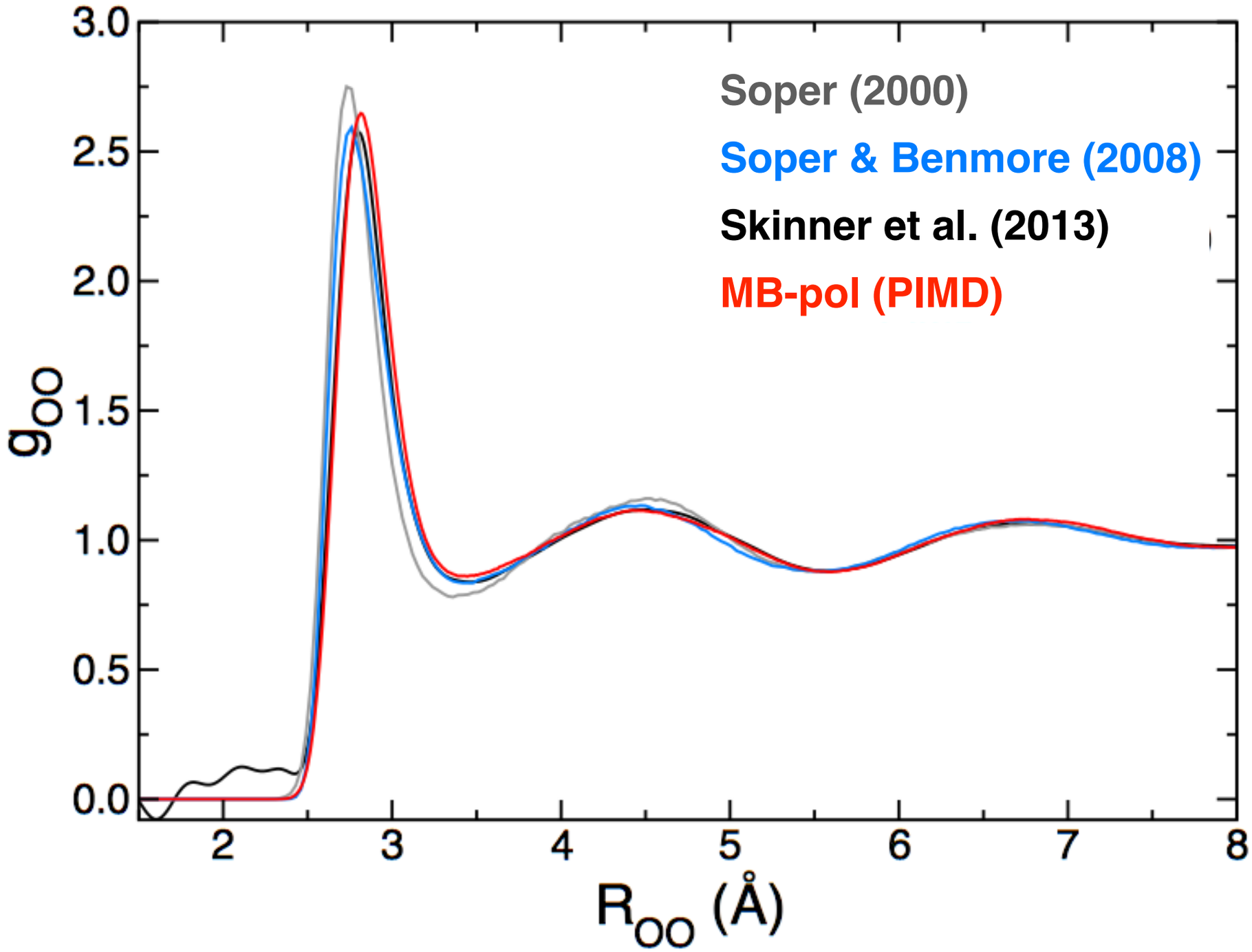
Oxygen-oxygen radial distribution function



Medders, Babin & FP, J. Chem. Theory Comput. 10, 2906 (2014)

Liquid: Structure

Oxygen-oxygen radial distribution function

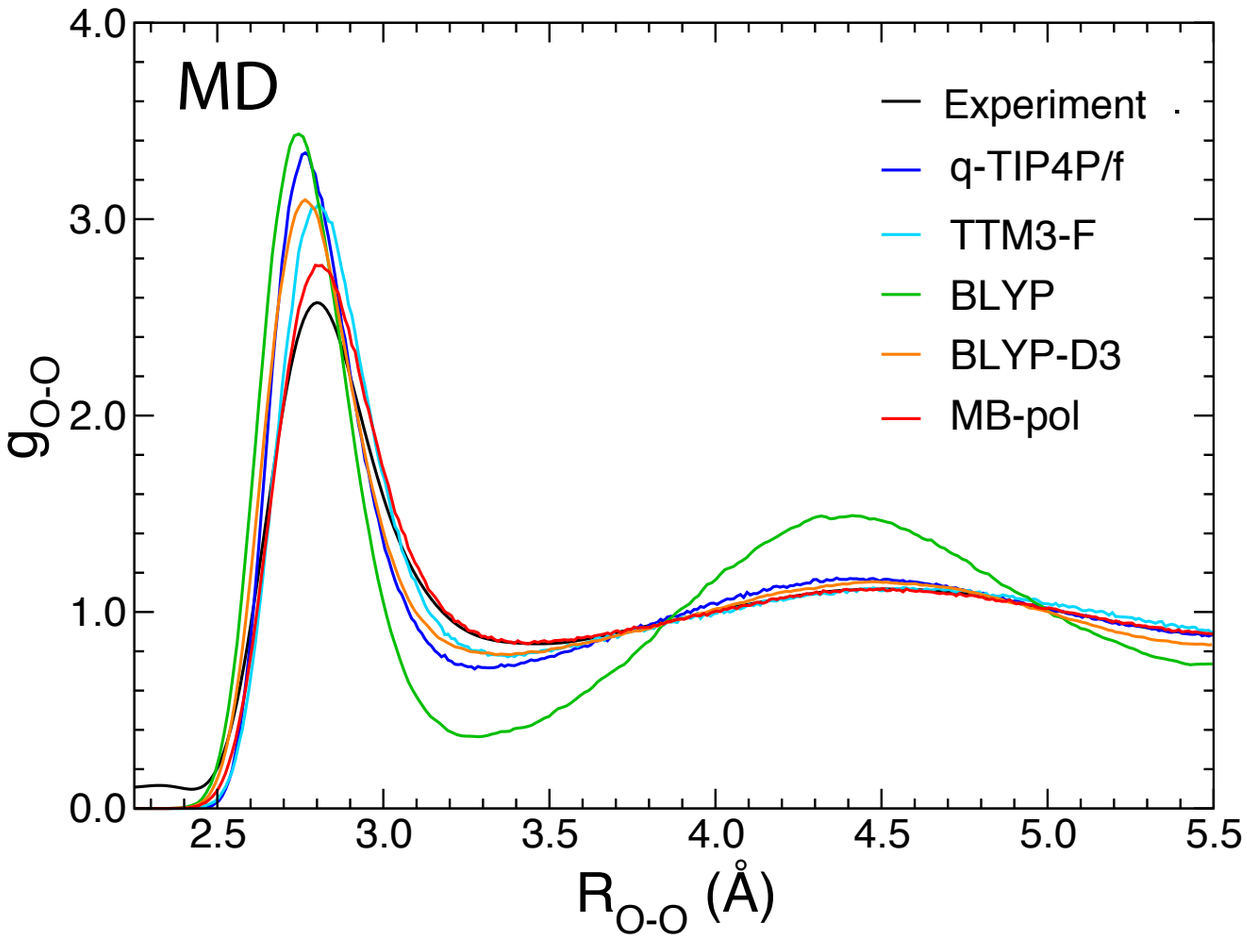


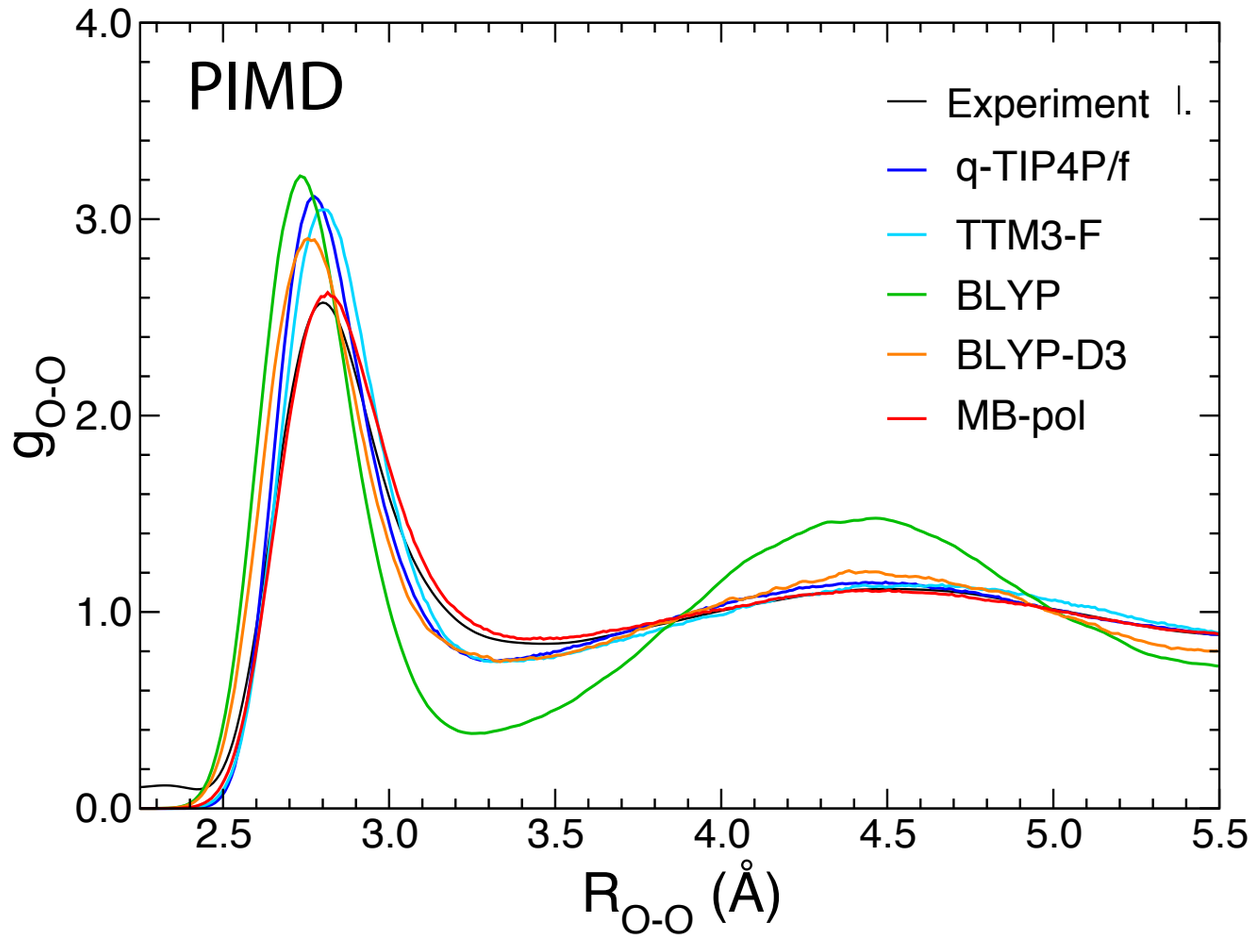
Medders, Babin & FP, J. Chem. Theory Comput. 10, 2906 (2014)

Liquid: Structure

Oxygen-oxygen radial distribution function

Nuclear quantum effects and model dependence



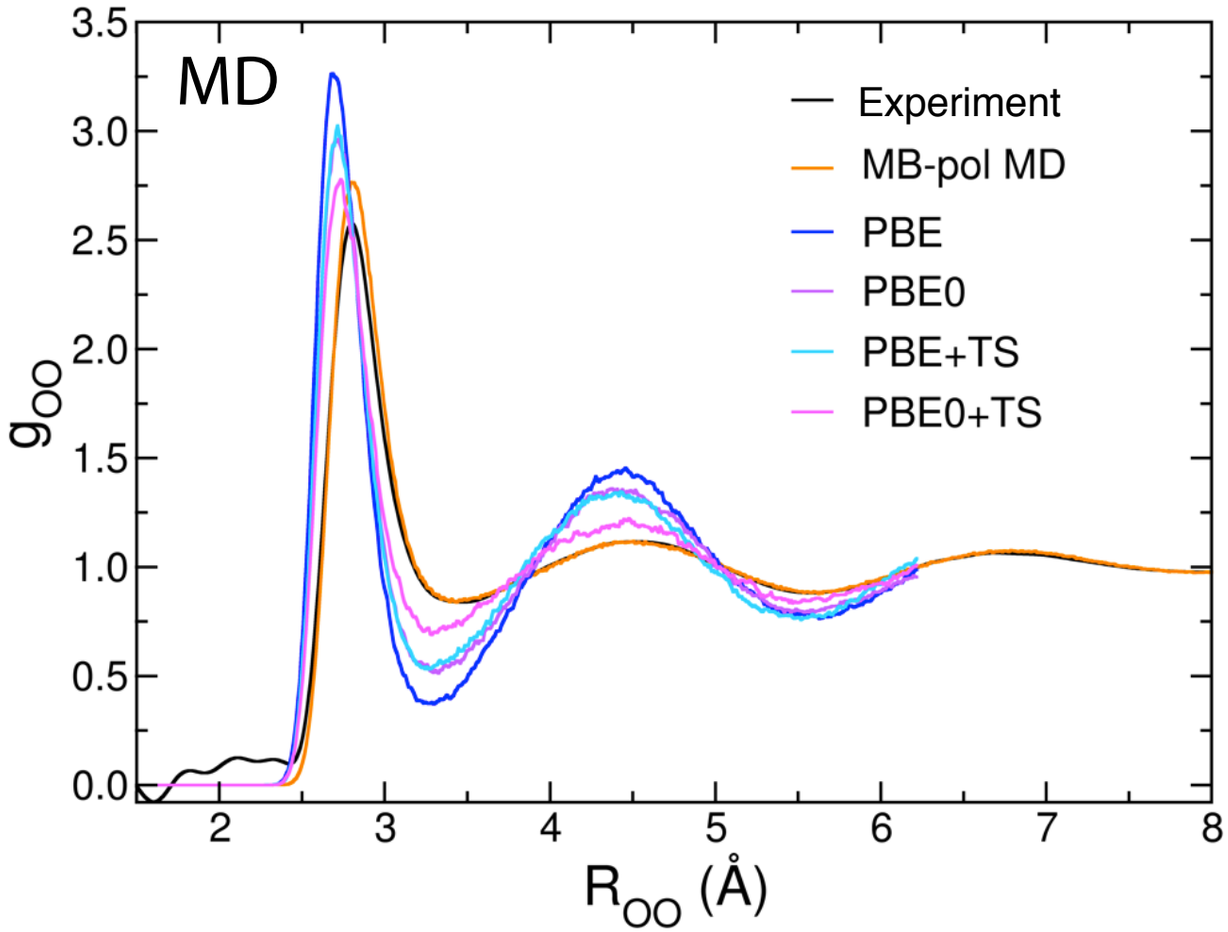


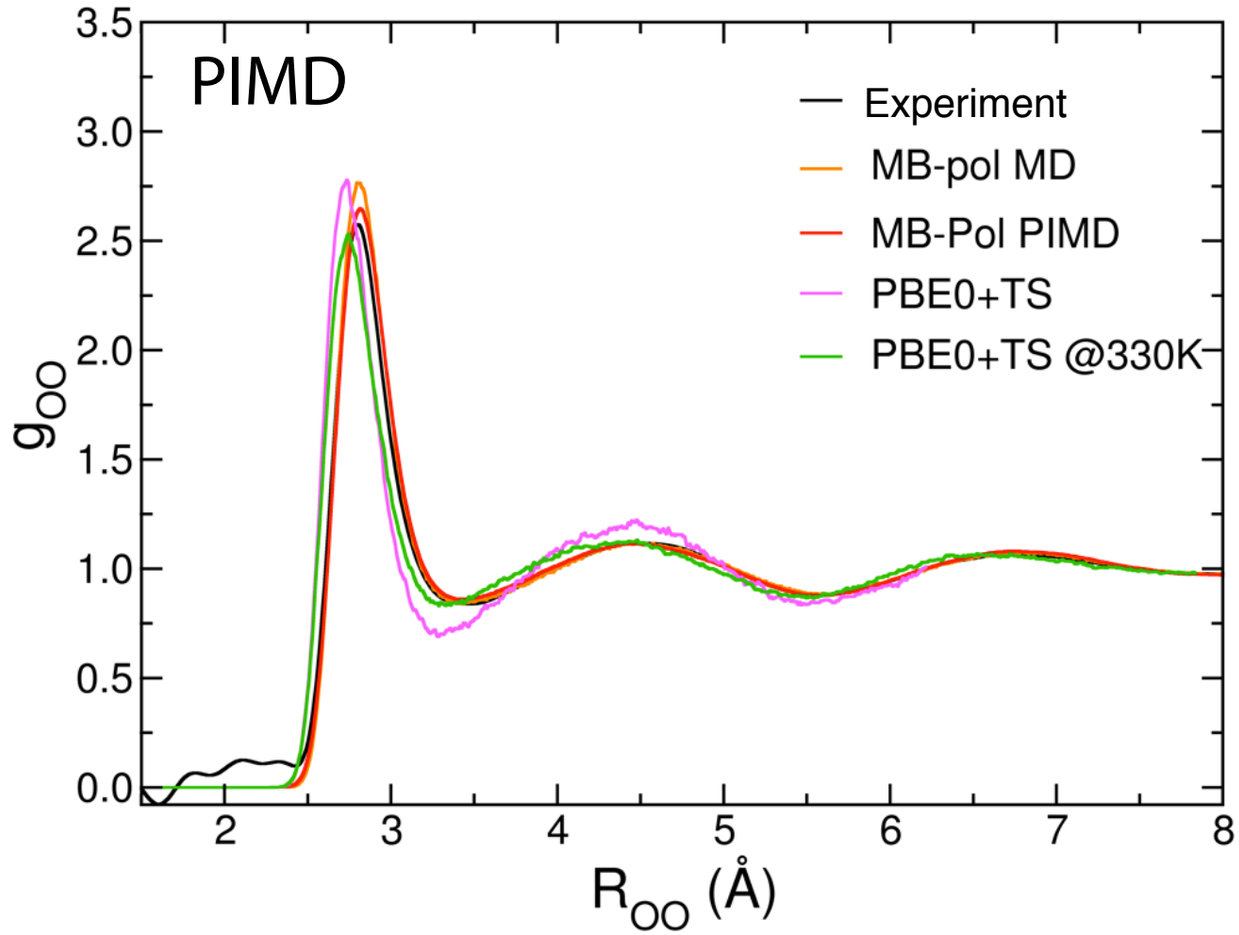
BLYP & BLYP-D3: *Wang, Ceriotti & Markland, J. Chem. Phys. 141, 104502 (2014)*

Liquid: Structure

Oxygen-oxygen radial distribution function

Nuclear quantum effects and model dependence





PBE & PBE0: *DiStasio, Santra, Li, Wu & Car, J. Chem. Phys. 141, 084502 (2014)*

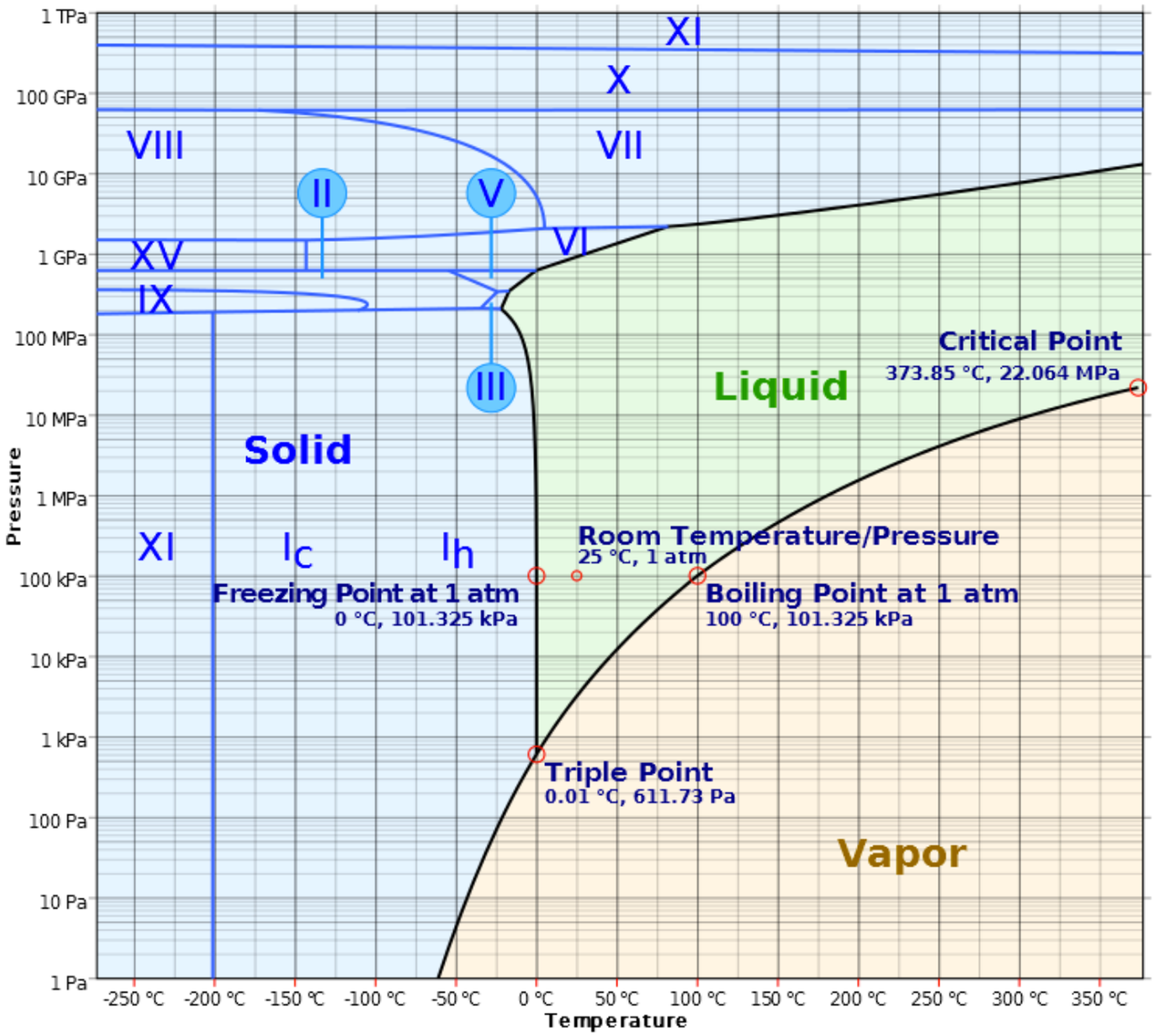
Courtesy of Robert DiStasio (Princeton University)

Looking at Ice to Learn about Water

15 different phases

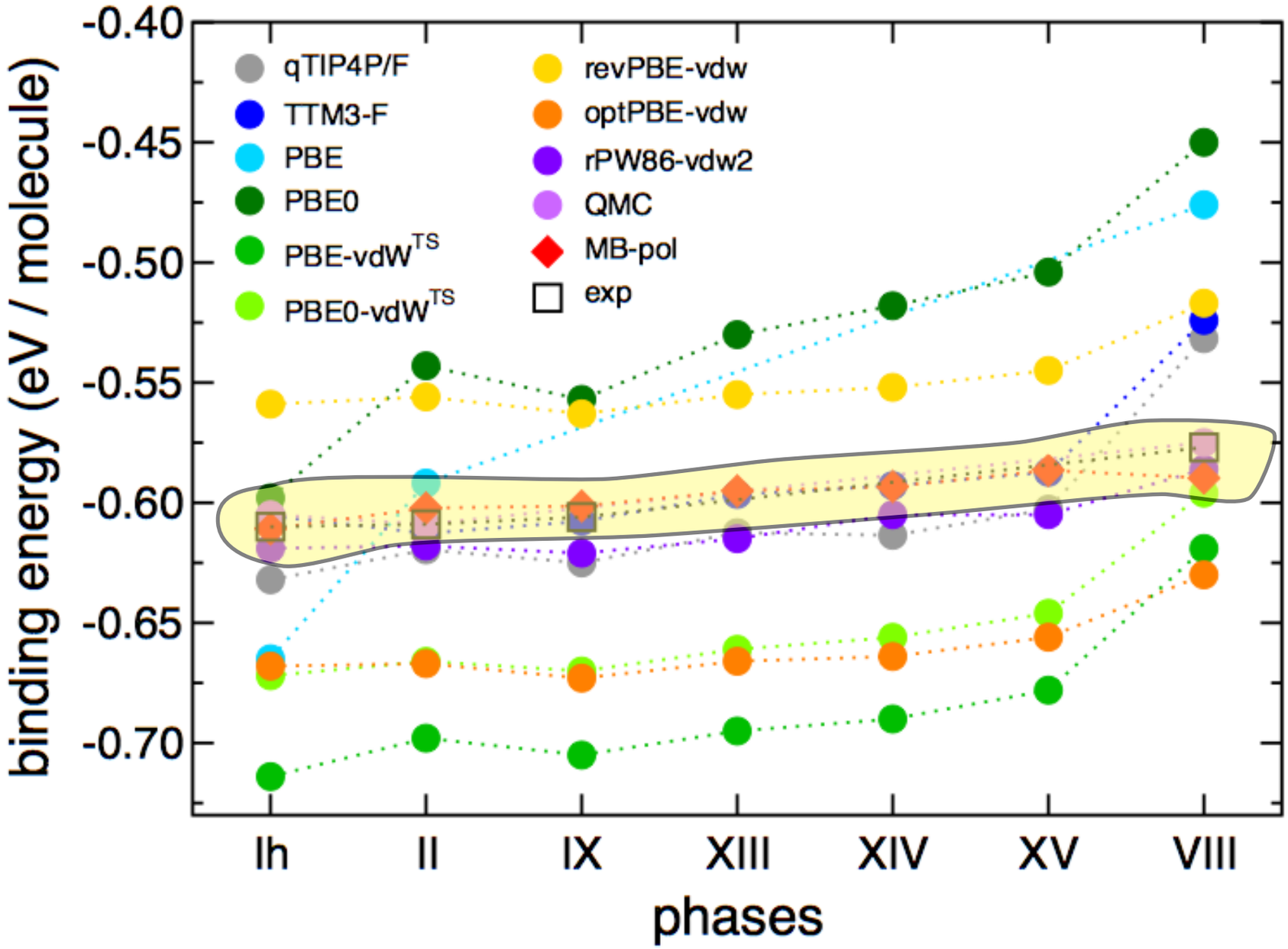
*"...**The structure of water is much less precisely known by experiment than the structures of the phases of ice**; for fluids, only radial distributions can be measured, whereas for crystals, accurate interatomic distances and angles can be determined. Consequently, **predicting a radial distribution of water is a less precise test of a water-water potential than predicting the structures of the crystalline phases**, and so also is predicting the energy because of the wide and imperfectly known range of intermolecular configurations in water. **It follows that effective potentials that are used to simulate water ought to be tested on the many phases of ice before being treated as serious representations of liquid water...**"*

Whalley, J. Chem. Phys. 81, 4087 (1984)



Sanchez & FP, to be submitted

Ice Phases: Binding Energies

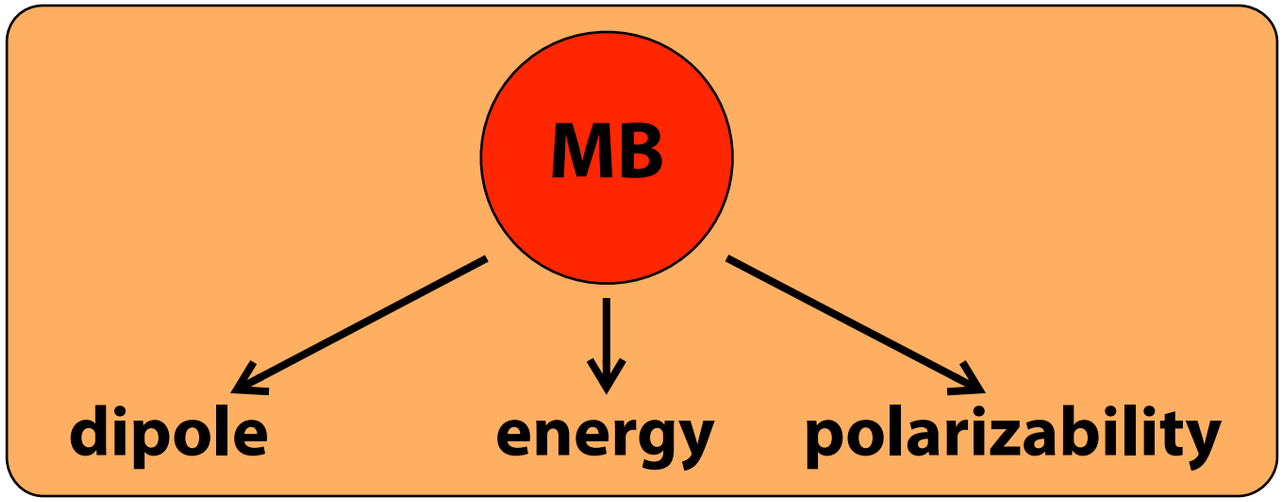


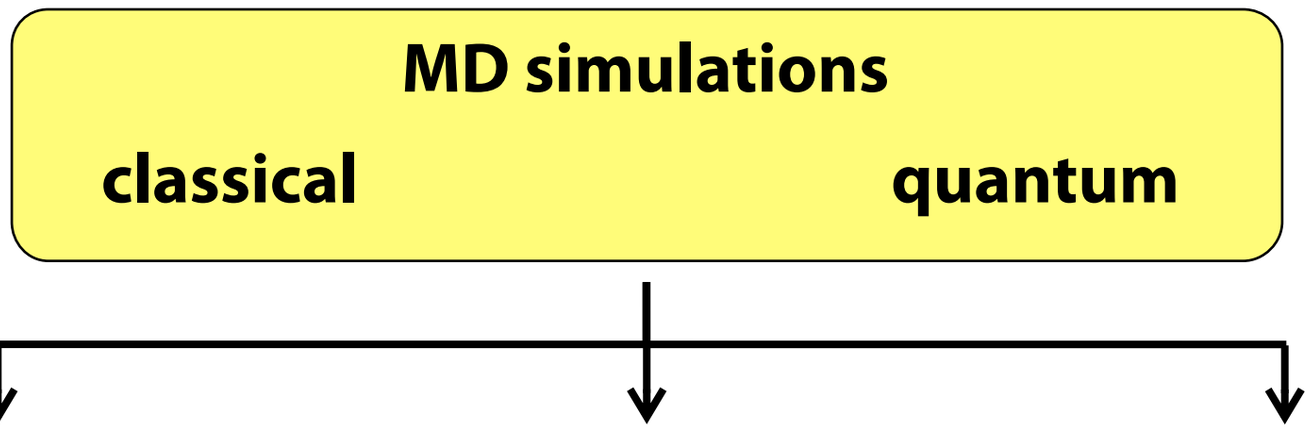
Experiment: *Whalley, J. Chem. Phys. 81, 4087 (1984)*

QMC and DFT: *Santra, Klimeš, Alfè, Tkatchenko, Slater, Michaelides, Car & Scheffler, Phys. Rev. Lett. 107, 185701 (2011)*

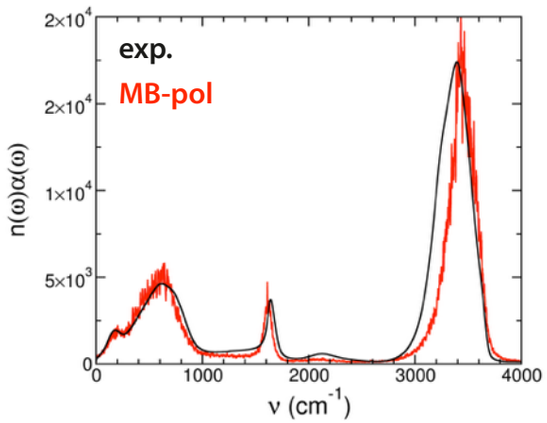
Sanchez & FP, to be submitted

MB-MD for Molecular Simulations

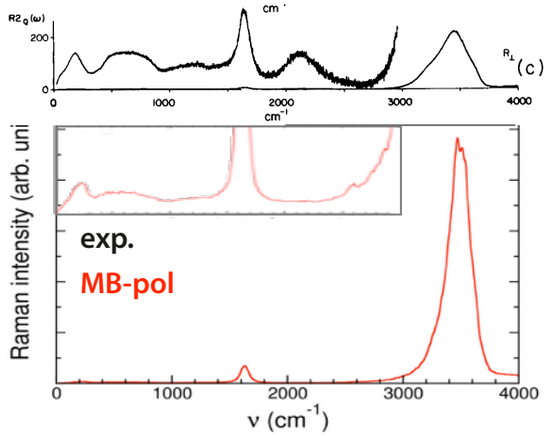




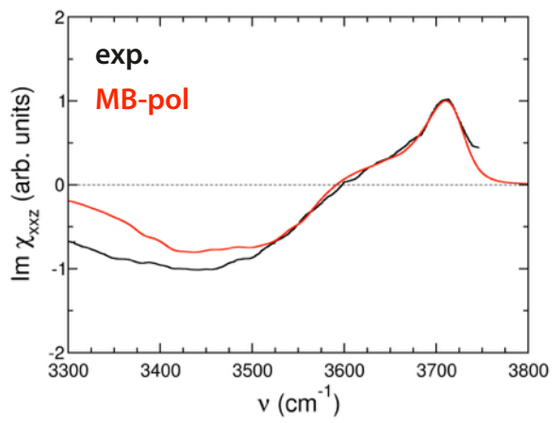
infrared



Raman



SFG



Medders & FP, J. Chem. Theory Comput., in press. DOI: 10.1021/ct501131j

Conclusions

Potential energy functions and **simulation approaches** that:

- are easily **computable** and **implementable** ✔
- **accurately** represent **both** molecular interactions and dynamics ✔
- are **transferable** across different phases ✔
- are **predictive** ✔
- enable **direct** comparisons with molecular-level **experiments** ✔

1) **Can** such a simulation approach **exist**?

Yes! MB-nrg provides a rigorous and systematically improvable framework.
Other approaches may exist as well.

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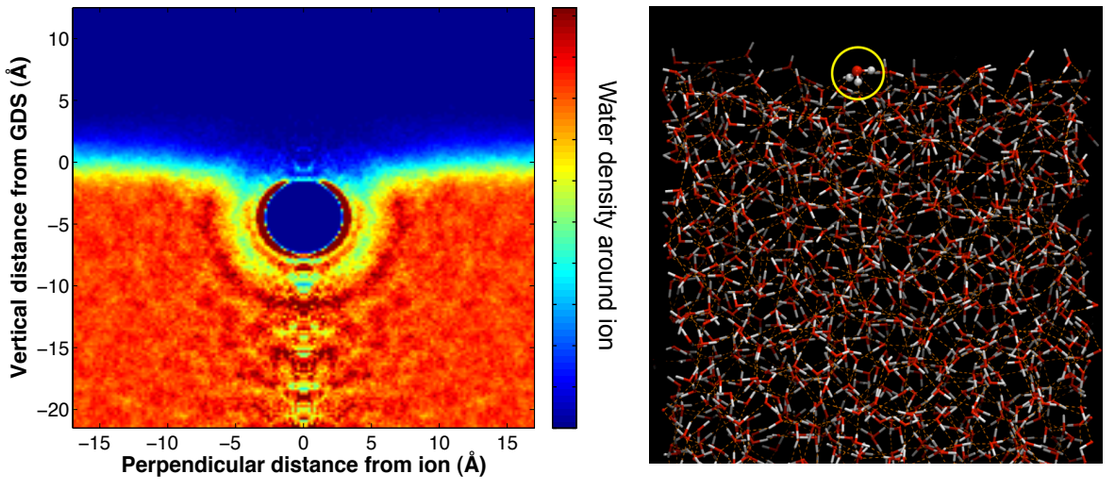
3) **Can** it be used for **complex systems**?

   Yes! It will likely require a "community effort" and synergistic collaborations with computer scientists and statisticians.

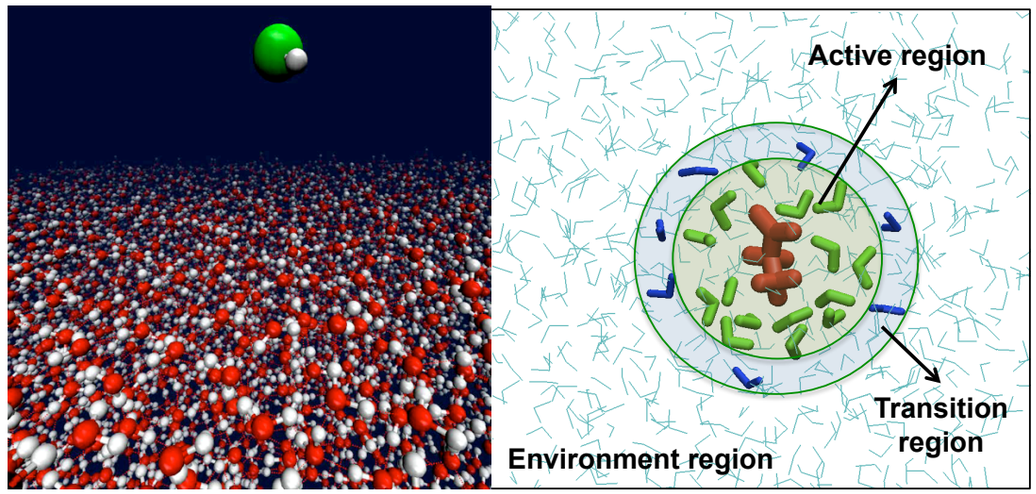
Looking Forward...

ion solvation and pH: bulk vs. interfaces



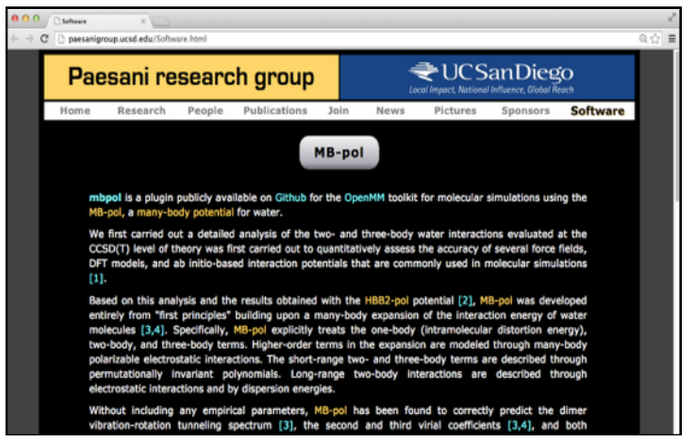
with Bajaj & Arismendi

chemical reactions: bulk vs. interfaces



with Riera-Riambau & Götz

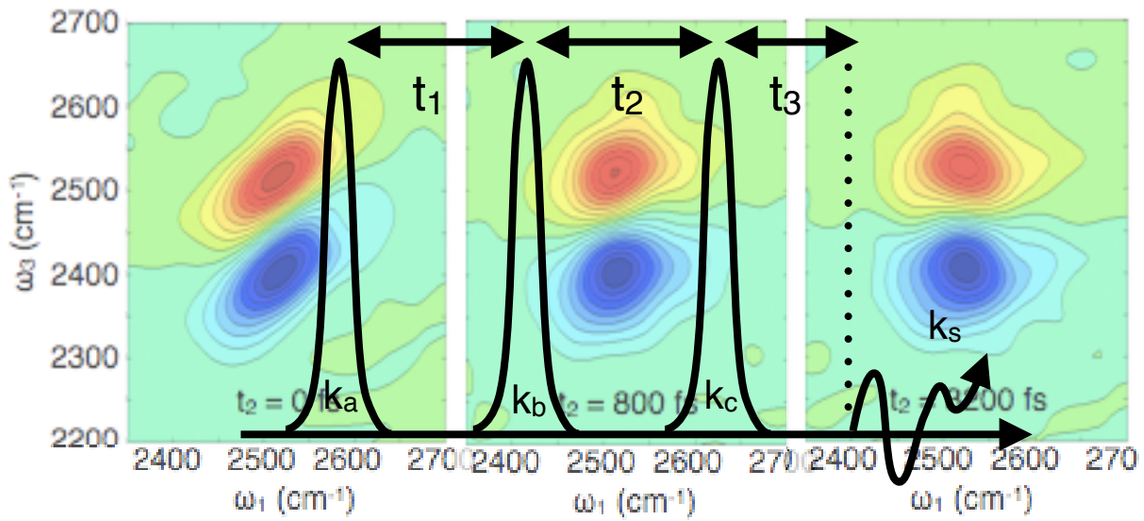
MB-MD as a new framework for molecular simulations



NVIDIA.

with Zonca & Sinkovits (SDSC), work in progress

multidimensional vibrational spectroscopy



collaboration with: Tokmakoff (Chicago) & Benderskii (USC)