How to Ensure the Accuracy of Polarizable Force Fields?

Toon Verstraelen (a), Steven Vandenbrande (a), and Paul W. Ayers (b)

(a) Center for Molecular Modeling, Ghent University, Belgium
(b) Department of Chemistry, McMaster University, Hamilton, Ontario, CA

Toon.Verstraelen@UGent.be

Workshop on Force Fields: From Atoms to Materials
Jülich, Germany, November 3-5, 2014

Center for Molecular Modeling

Belgian Science Policy Office belspo

fwo

UNIVERSITEIT GENT

How to Ensure the Accuracy of Polarizable Force Fields?

Introduction

Generalized ACKS2

Numerical Validation

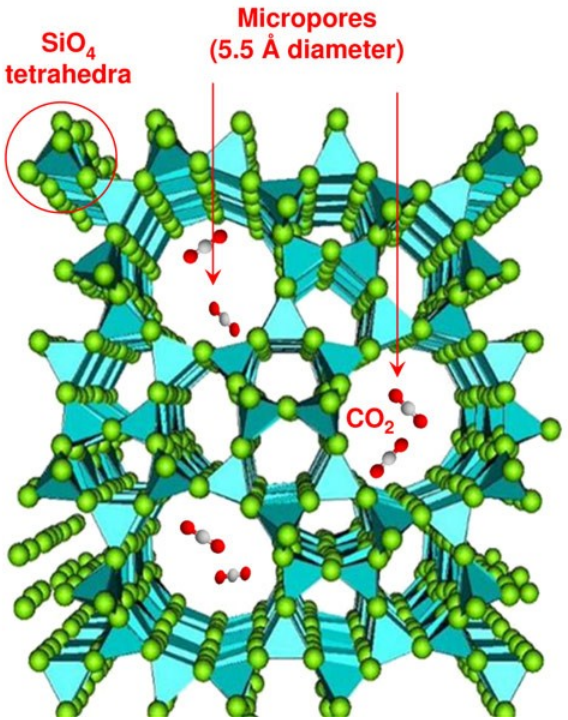
Conclusions

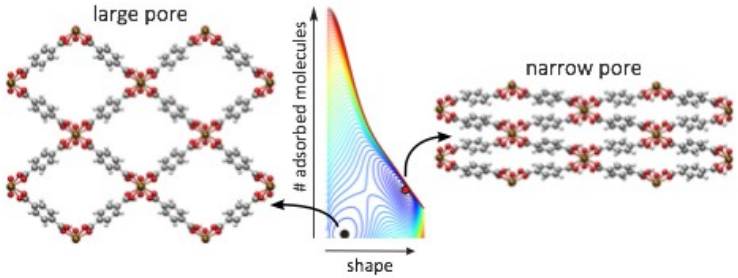
Many-body potentials

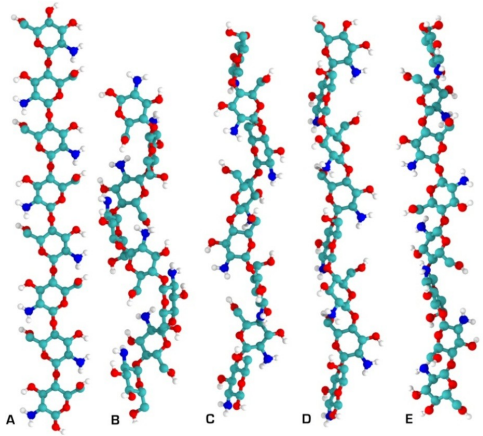
In the simplest case:

$V(R_1, ..R_N)$ = sum of *few-body* terms of nuclear positions (no e^-)

Many useful materials applications:







Yet, not all interactions are simply additive:

- Metallic bonds -> EAM, ...
- Induction, polarization, charge-transfer -> PFF
- Exchange repulsion
- Higher order dispersion
- ...

Polarizable force field (PFF) = fluctuating charges, dipoles, ...

Conventional approach

- Born-Oppenheimer
- Approximate e^- model ... with classical physics (?)

$$V_{\mathrm{PFF}}(\boldsymbol{R}_1,\ldots,\boldsymbol{R}_N,q_1,\ldots,q_N,\boldsymbol{p}_1,\ldots,\boldsymbol{p}_N) =$$
$$\sum_i^N q_i\,\chi_i^q + \frac{1}{2}\sum_{ij}^N q_i\,\eta_{ij}^{qq}(\boldsymbol{R}_i-\boldsymbol{R}_j)\,q_j$$
$$+\sum_{ij}^N \boldsymbol{p}_j^{\intercal}\,\boldsymbol{\eta}_{ij}^{qp}(\boldsymbol{R}_i-\boldsymbol{R}_j)\,q_i + \frac{1}{2}\sum_{ij}^N \boldsymbol{p}_i^{\intercal}\,\overline{\overline{\eta}}_{ij}^{pp}(\boldsymbol{R}_i-\boldsymbol{R}_j)\,\boldsymbol{p}_j + \ldots$$

Widely used:

- ReaxFF, COMB, ...
- Bio: variants of CHARMM, AMBER, OPLS, ...
- many oxide FFs
- ...

An odd observation ...

Charges are often kept fixed in a PFF!

Why should one include variable charges?

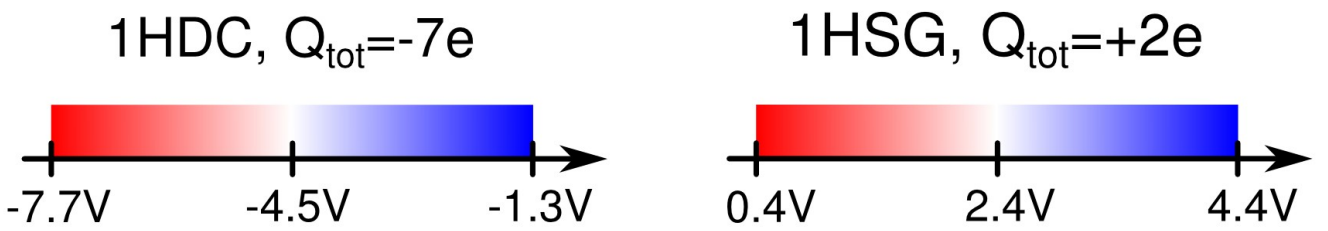
- Leading term in atomic multipole
- Charge-transfer in bonding, e.g. H-bond
- Non-local polarizability, e.g. π-bonds
- ...

Why are variable charges avoided?

- Metallic polarizability scaling
- Fractional charges in dissociation limit

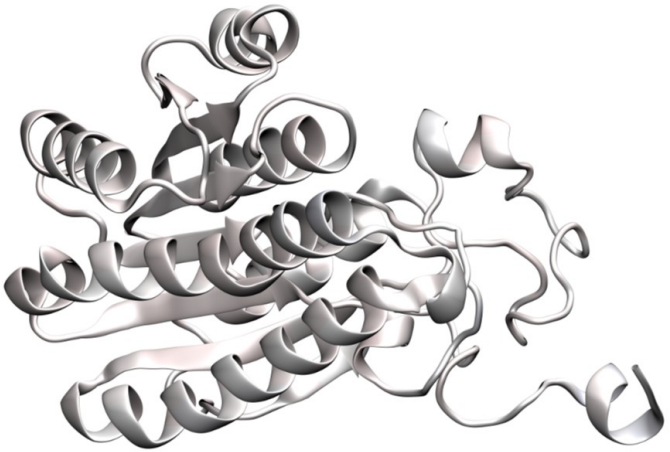
First challenge: *how to include fluctuating charges properly?*

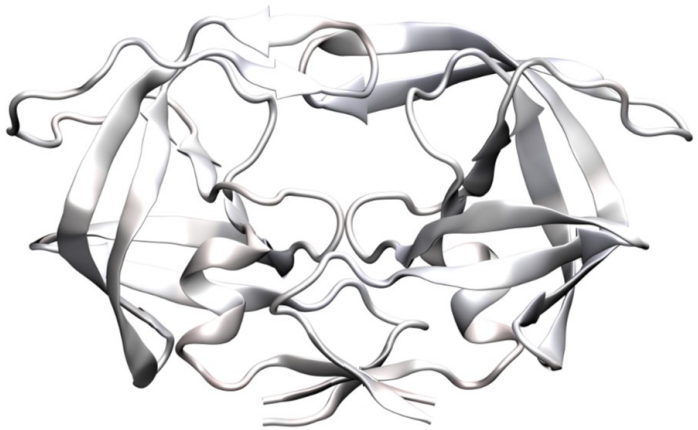
Charge-transfer must be localized ...



Conventional fluctuating charges

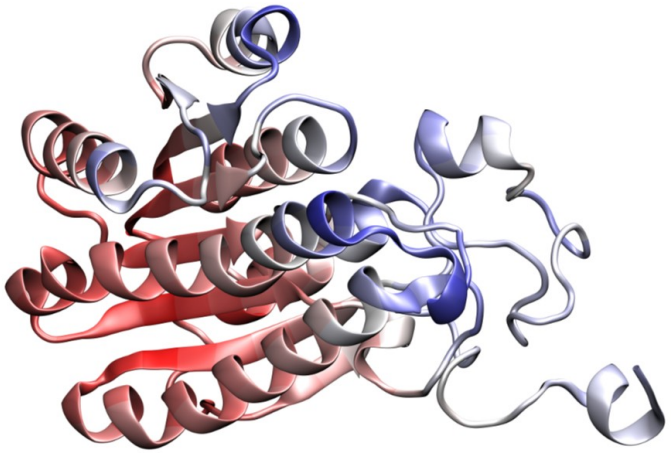
EEM, QEq, FlucQ, ...
[Mortier JACS v108 p4315 y1986]

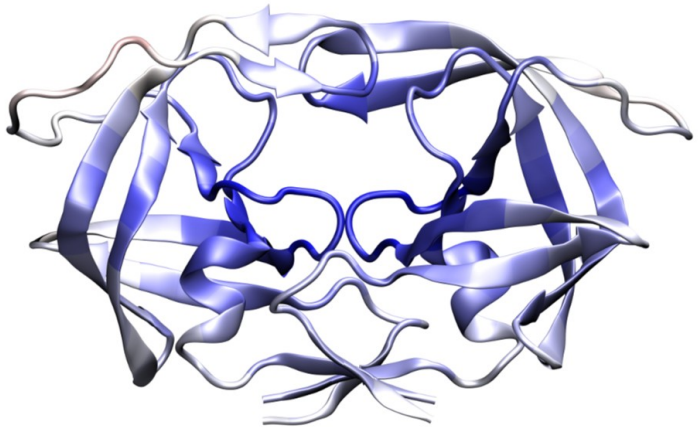




Split-Charge Equilibration

SQE = AACT+EEM
[Nistor JCP v125 p094108 y2006]





[Verstraelen JCTC v8 p661 y2011]

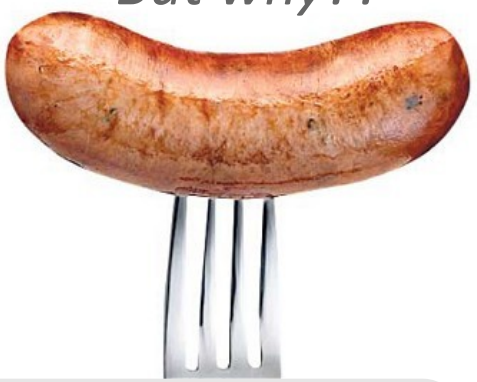
Quantitative models: a sausage?

Too many PFF parameters

At least (per atom type) ...

- Fluctuating charge models:
  - **Atomic hardness**
  - **Width s-type function**
- Inducible dipole models:
  - **Atomic dipole polarizability**
  - **Width p-type function**
- Improved models (to fix first challenge)
  - **Even more parameters...**

Tastes so good!!
But why??



Second challenge: *how to fix all parameters?*

How to Ensure the Accuracy of Polarizable Force Fields?

Introduction

Generalized ACKS2

Numerical Validation

Conclusions

Foundation: DFT with auxiliary wavefunction

[Verstraelen JCP v138 p074108 y2013; JCP in press]

ACKS2 = Atom-Condensed Kohn-Sham DFT approximated to 2nd order

Generalized = Multipoles, beyond Kohn-Sham

Starting point:

$$E_v[\rho] = E^{\mathrm{exp}}[\rho] + E^{\mathrm{imp}}[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}$$

$$E^{\mathrm{imp}}[\rho] = \min_{\Psi \to \rho} W[\Psi]$$

Explicit part: classical $e^- e^-$ repulsion (+ GGA XC)

Implicit part: **kinetic energy**, HF exchange, ...

In green: **classical PFF**

Chemical Potential Equalization *[York & Yang JCP **1996**, 104, 159]*

After several approximations (linear response, ...)

[Verstraelen JCP v138 p074108 y2013; JCP in press]

Variables:

$$\Delta\rho(\mathbf{r}) = \sum_k C_k f_k(\mathbf{r}) \qquad \Delta u(\mathbf{r}) = \sum_k U_k g_k(\mathbf{r})$$

PFF Equations:

$$\sum_\ell \eta_{k\ell} C_\ell + V_k - \sum_\ell O_{k\ell} U_\ell = \Delta\mu\, D_k \quad \forall\, k$$

$$-\sum_\ell C_k O_{k\ell} + \sum_\ell \chi_{k\ell} U_\ell = 0 \quad \forall\, k$$

$$\sum_\ell D_\ell C_\ell = 0$$

"Parameters":

$$\eta_{k\ell} = \iint \eta^{\mathrm{exp}}(\mathbf{r},\mathbf{r}') f_k(\mathbf{r}) f_\ell(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

$$\chi_{k\ell} = \iint \chi^{\mathrm{imp}}(\mathbf{r},\mathbf{r}') g_k(\mathbf{r}) g_\ell(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

$$O_{k\ell} = \int f_k(\mathbf{r}) g_l(\mathbf{r}) d\mathbf{r}$$

$$V_k = \int f_k(\mathbf{r}) \Delta v(\mathbf{r}) d\mathbf{r}$$

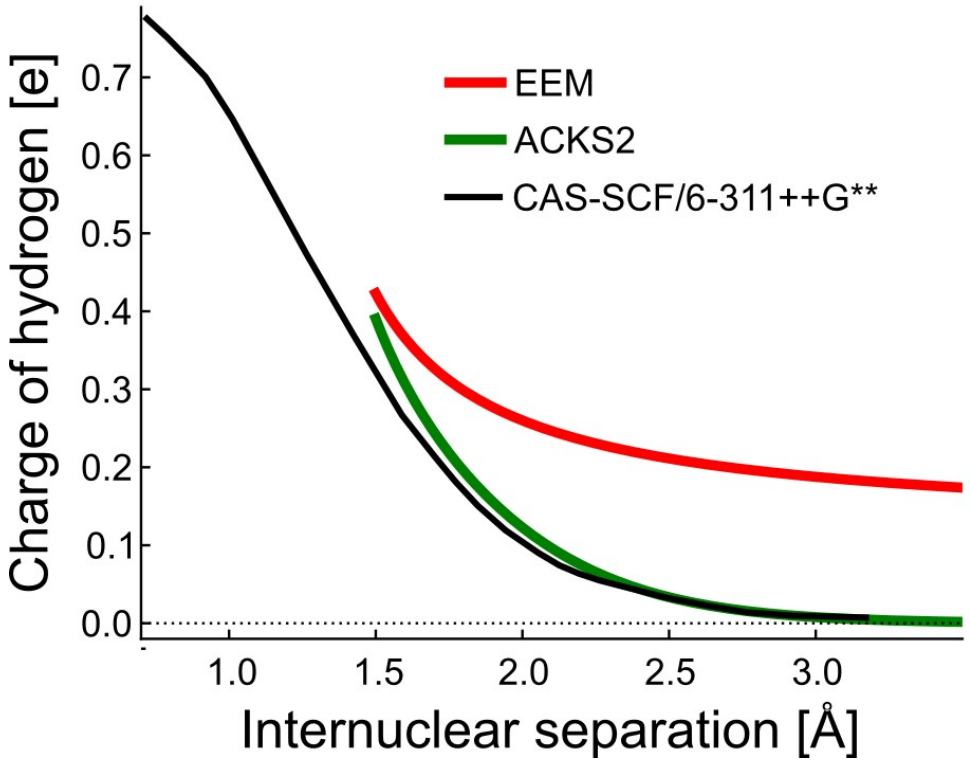
$$D_k = \int f_k(\mathbf{r}) d\mathbf{r}$$

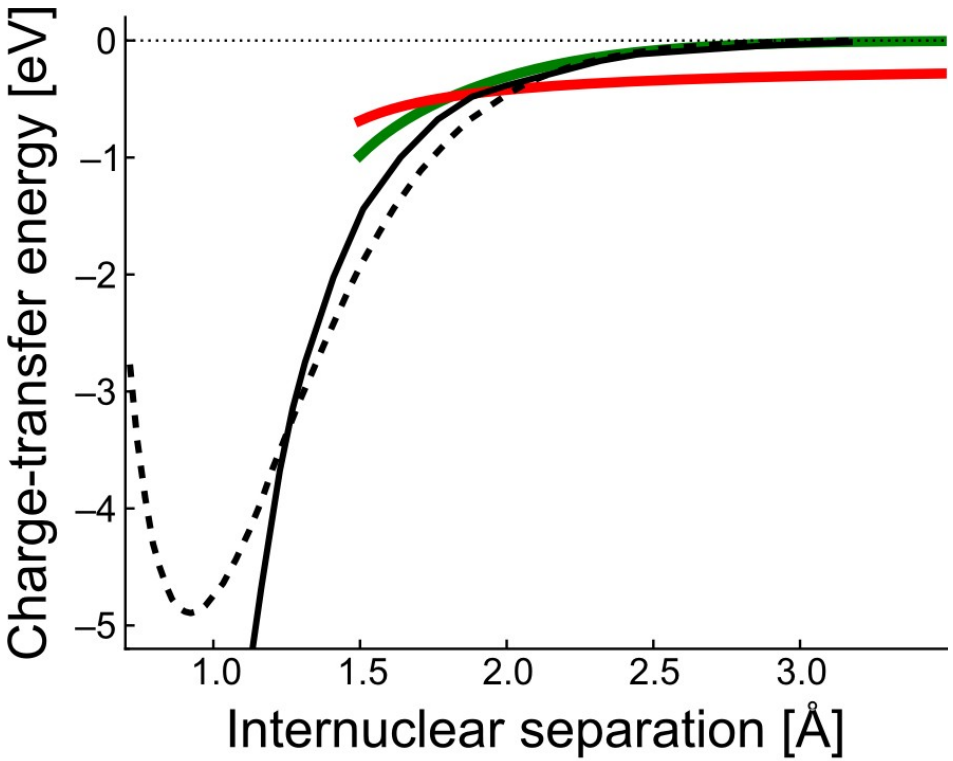
In green: **classical PFF**

Chemical Potential Equalization *[York & Yang JCP **1996**, 104, 159]*

ACKS2 solves important issues

- Dielectric polarizability scaling: isomorphic to SQE
- Dissociation with integer charges: HF dissociation





[CAS-SCF: Cioslowski JCP v99 p5151 y1993]
[ACKS2: Verstraelen JCP v138 p074108 y2013]

How to Ensure the Accuracy of Polarizable Force Fields?

Introduction

Generalized ACKS2

Numerical Validation

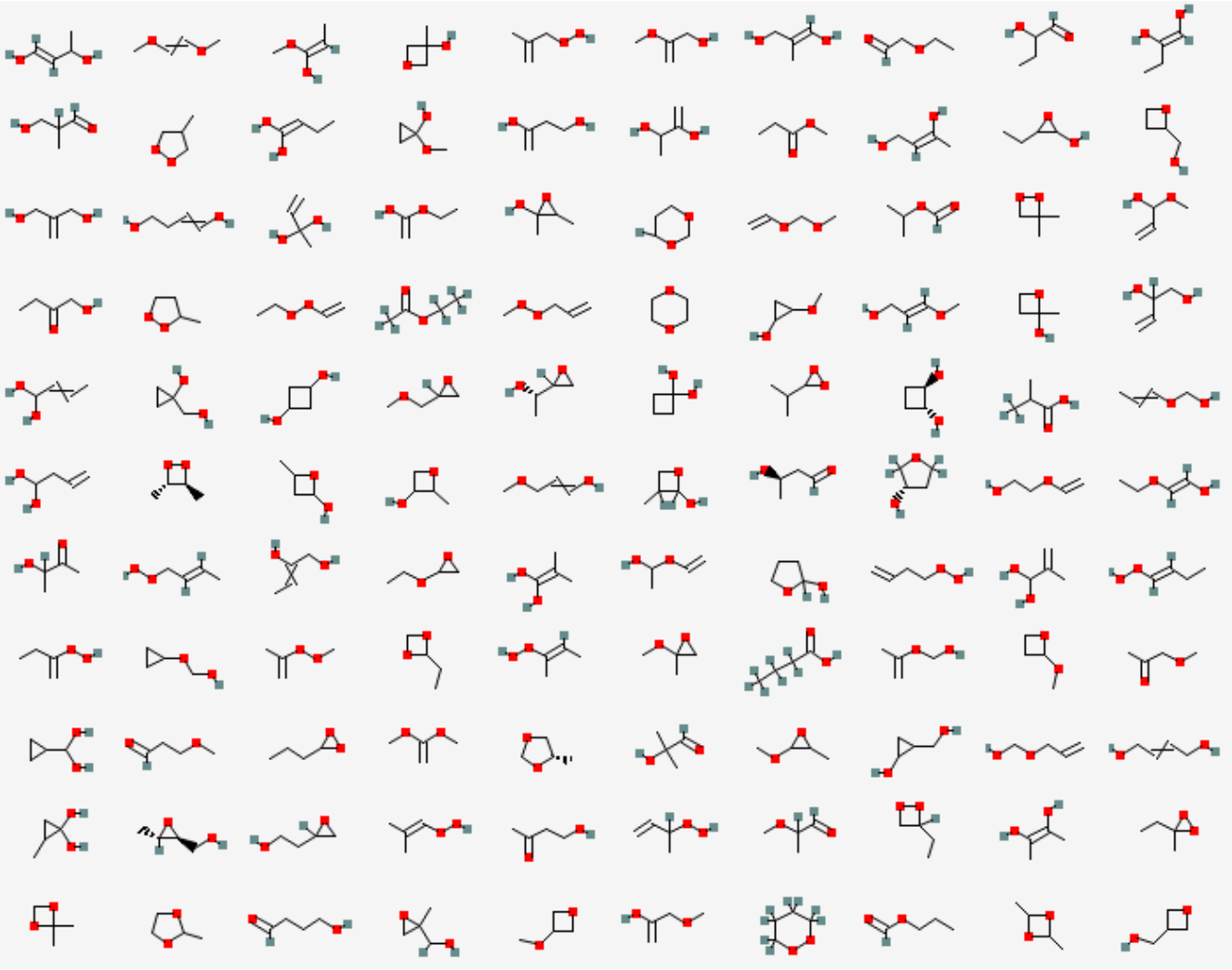
Conclusions

Molecular test set

110 isomers of $C_4O_2H_8$ from PubChem

Computation details:
- BLYP/6-311++G(3df,2p)
- geometry optimization
- dipole polarizability (CPKS)

Diversity:
- Chemical groups
- Charges
- Polarizability
- Heats of formation
- Dipole moments



[Verstraelen JCP in press]

Basis sets and accuracy

Potential basis set

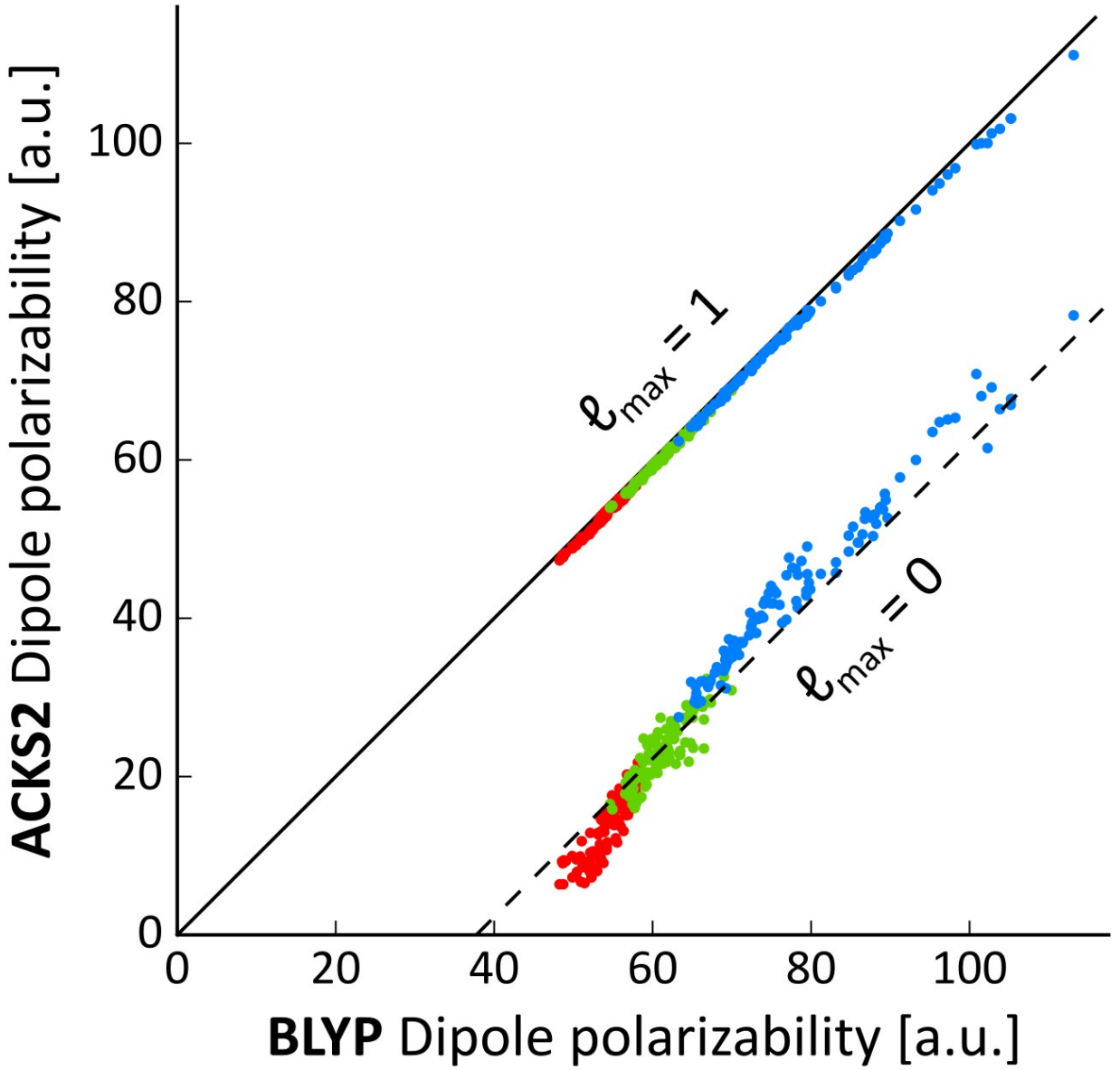
AIM operators
Hirshfeld-E
[Verstraelen JCTC v9 p2221 y2013]

Density basis set

Response to AIM operators

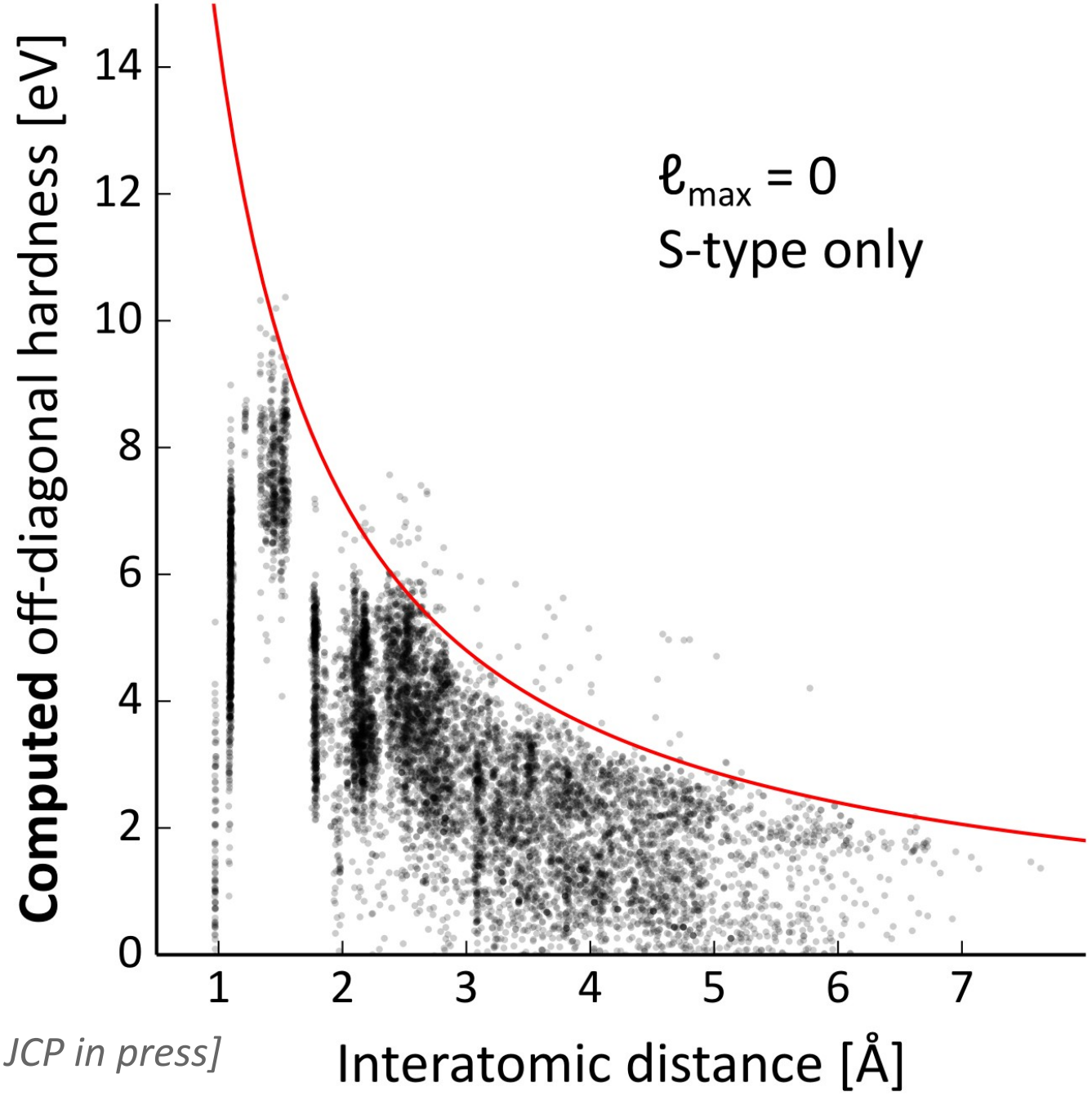
Series: ℓ_{max} = 0 ... 5

0 = charges
1 = charges + dipoles
2 = ...



[Verstraelen JCP in press]

(Lack of) parameter robustness: η(A,B)



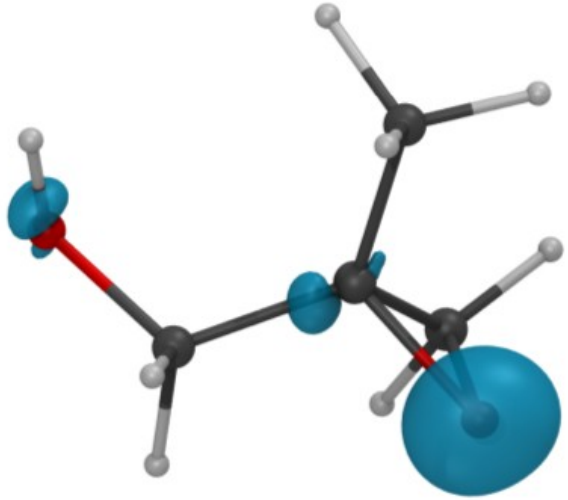
[Verstraelen JCP in press]

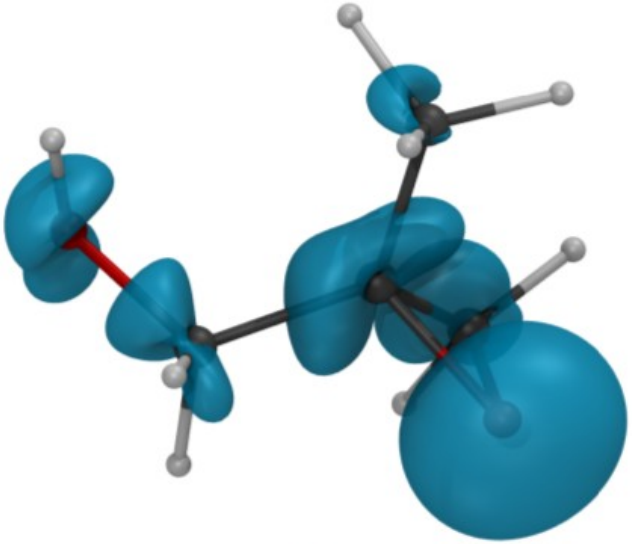
Response = Non-local basis = Non-transferable parameters

(a)
isovalue = 0.05 a.u.

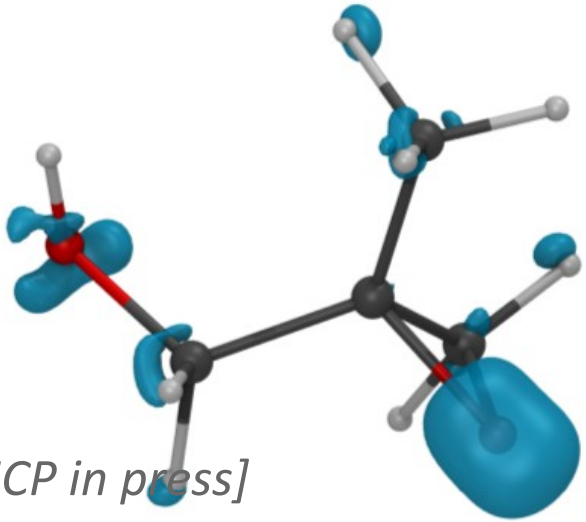
(b)
isovalue = 0.01 a.u.

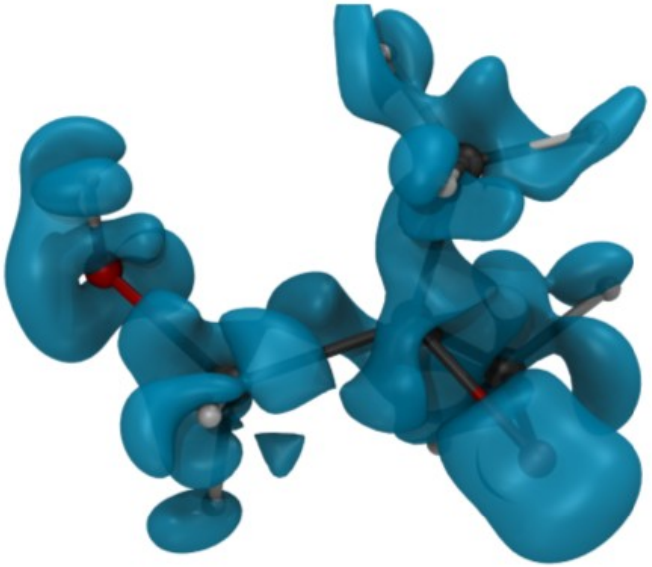
$\ell_{max} = 0$





$\ell_{max} = 5$





[Verstraelen JCP in press]

Intermediate conclusion

Generalized ACKS2 formalism works.

Parameters are not robust (geo dependence).

How to derive a computationally feasible PFF?

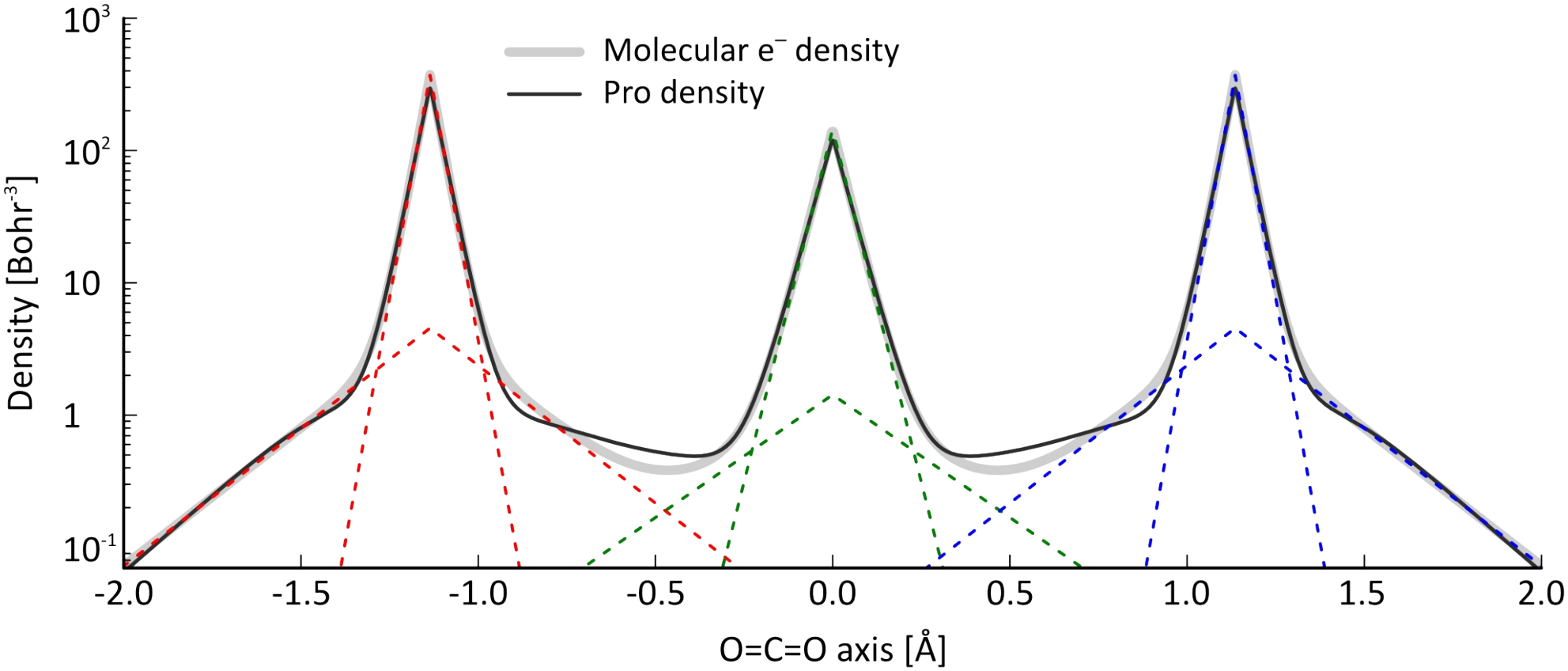
[Verstraelen JCP in press]

A more robust density basis (1)

$$\rho(\mathbf{r}) \approx \sum_{i=1}^{M} \frac{N_i}{8\pi\beta_i^3} \exp(-|\mathbf{r} - \mathbf{R}_i|/\beta_i)$$

[Savin IJQC vS22 p59 y1988, Hu JCTC v3 p1004 y2007, ...]

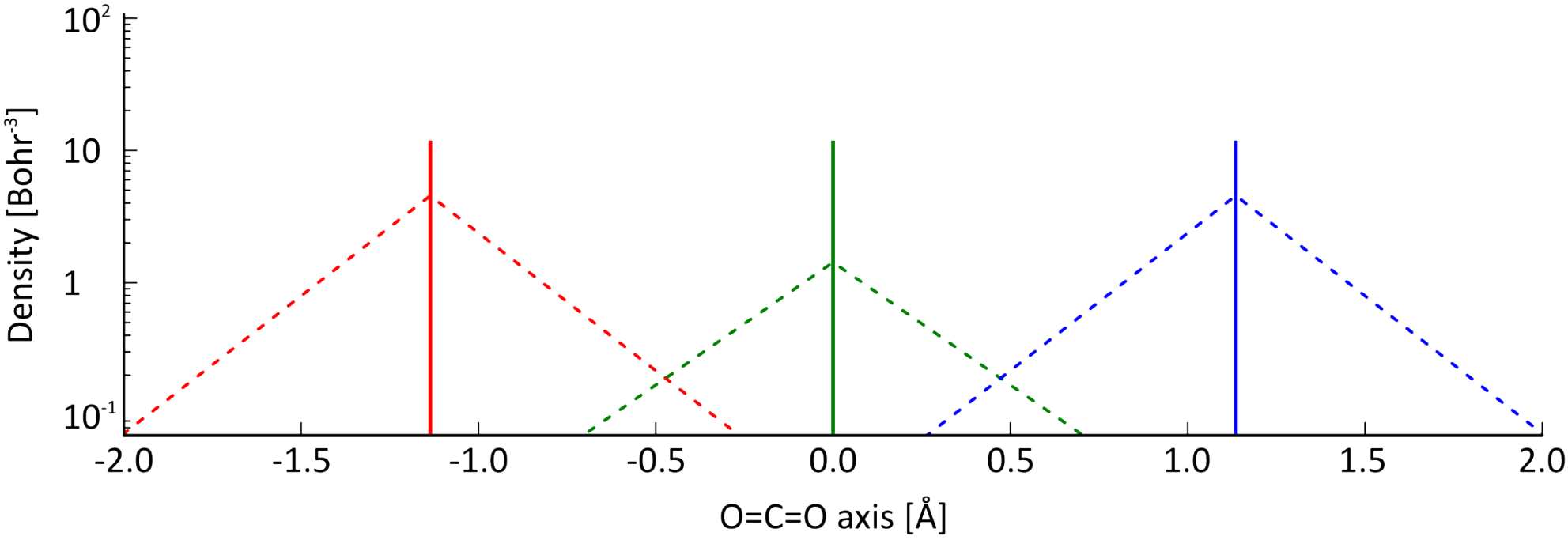
[new fitting method: paper in preparation]



A more robust density basis (2)

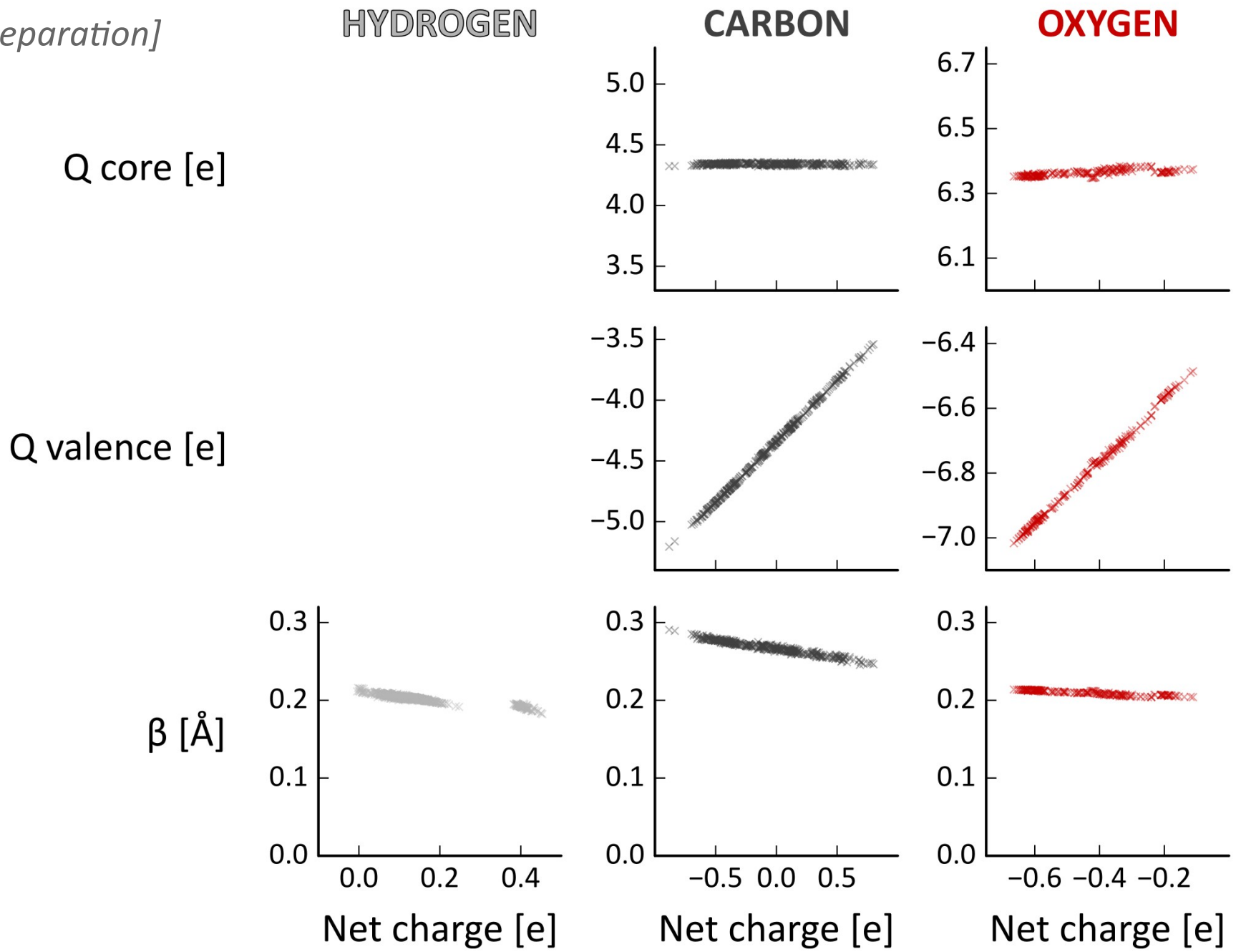
In force-field applications:

- Core e^- + nucleus ≈ point charge
- Valence e^- ≈ Slater function



A more robust density basis (3)

[in preparation]



Basis sets and accuracy

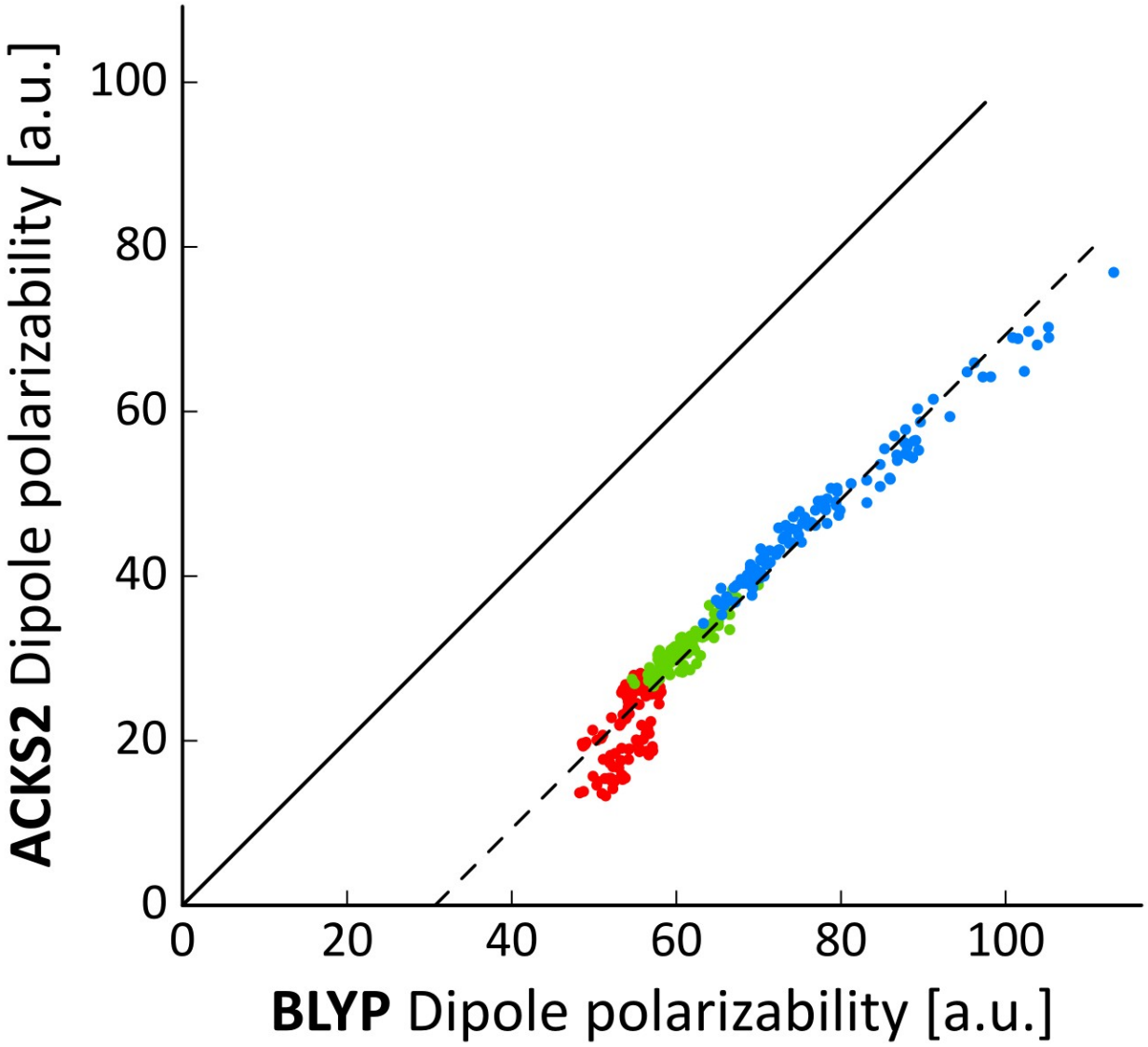
Potential basis set

AIM operators
MBIS
[in preparation]

Density basis set

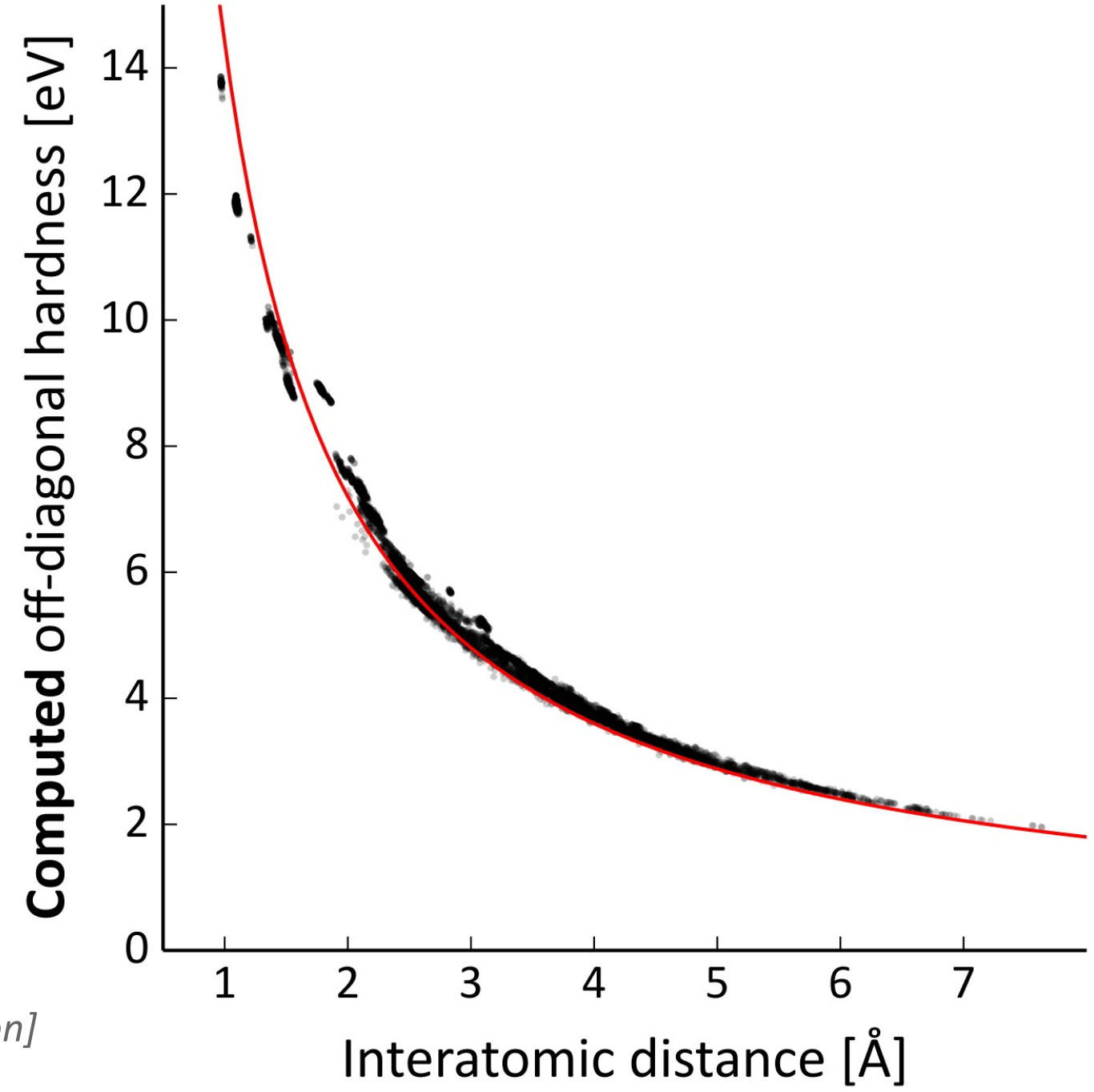
Valence Slater functions

S-type only (charges)



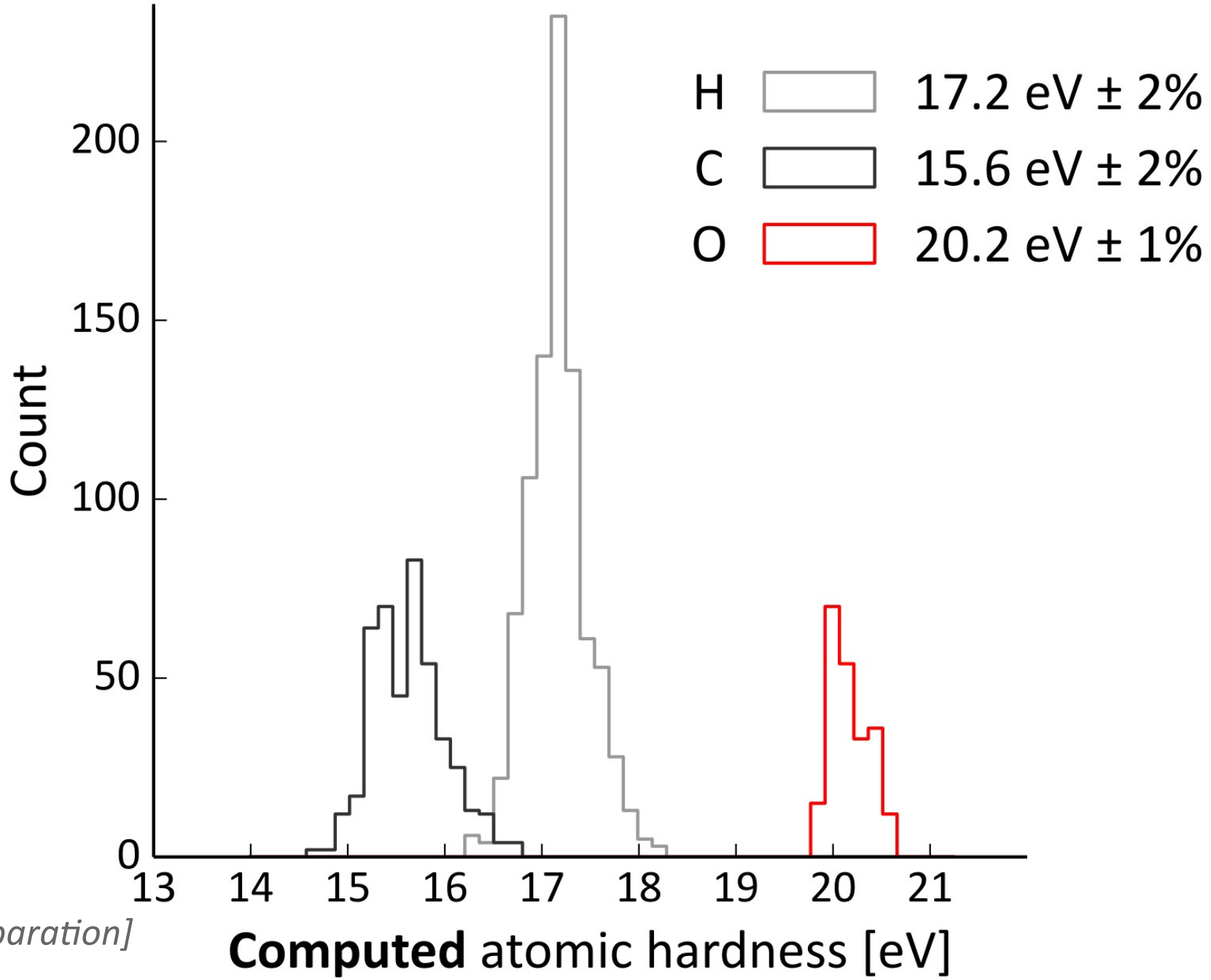
[in preparation]

Parameter robustness: η(A,B)



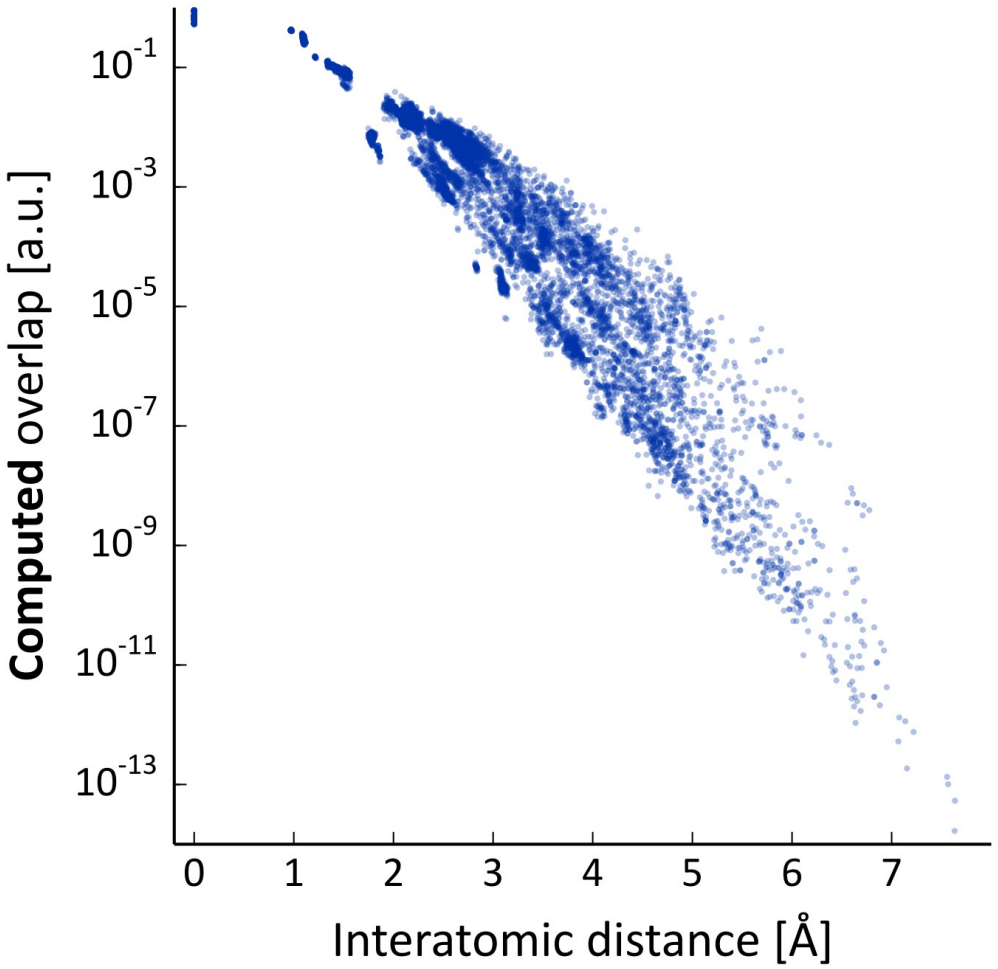
[in preparation]

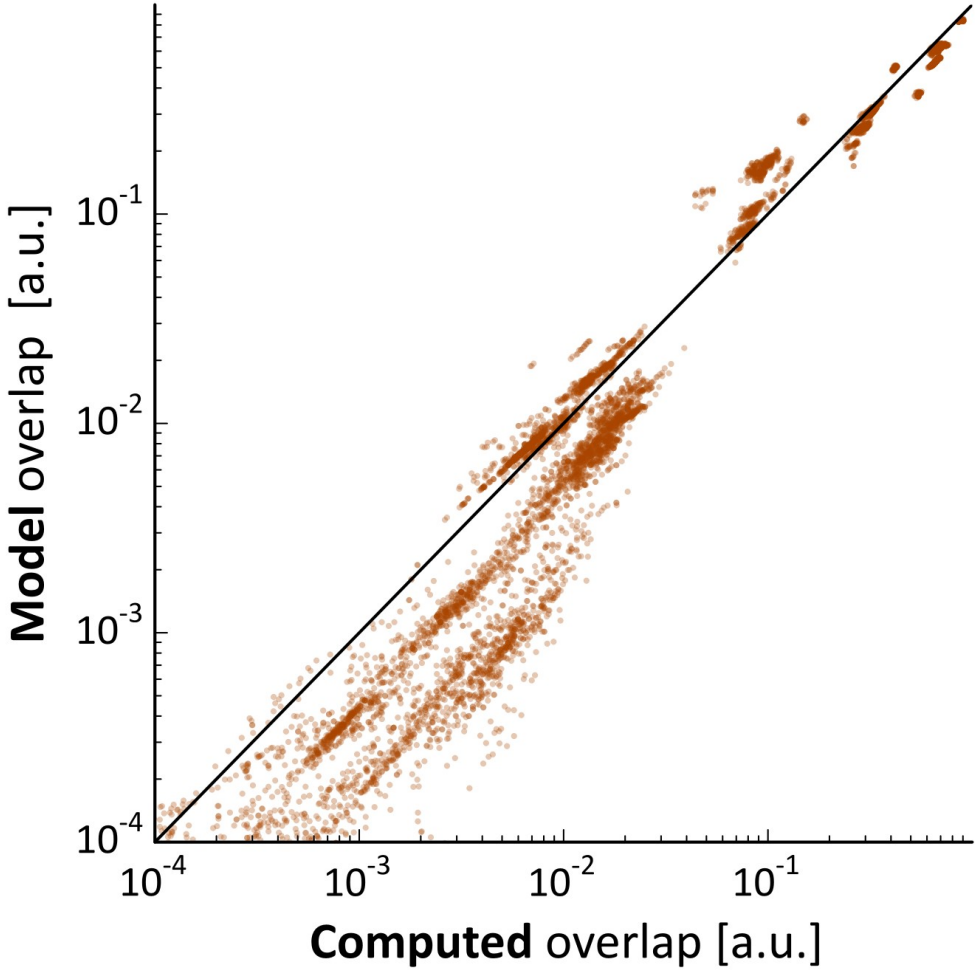
Parameter robustness: η(A,A)



[in preparation]

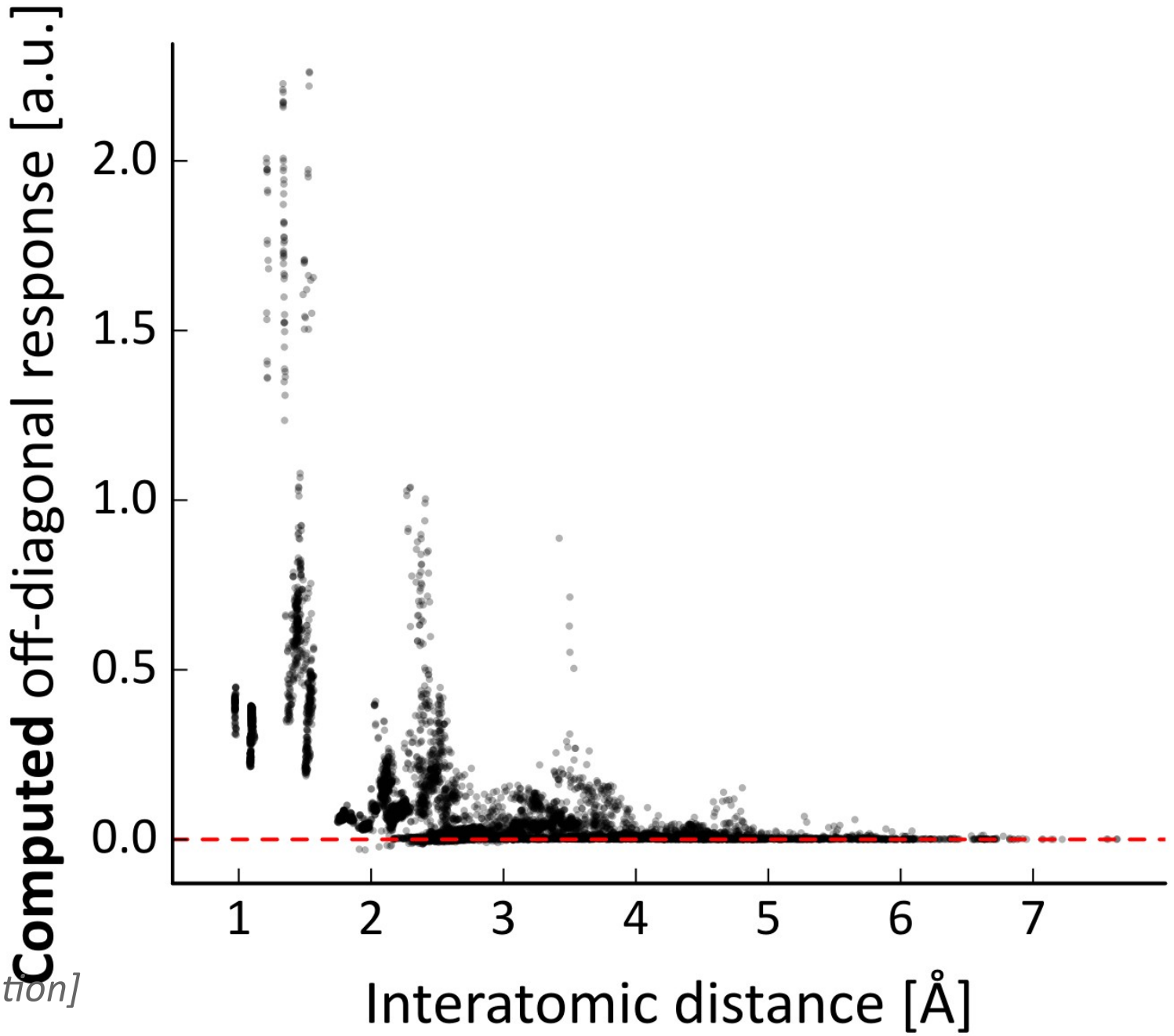
Parameter robustness: O(A,A) & O(A,B)





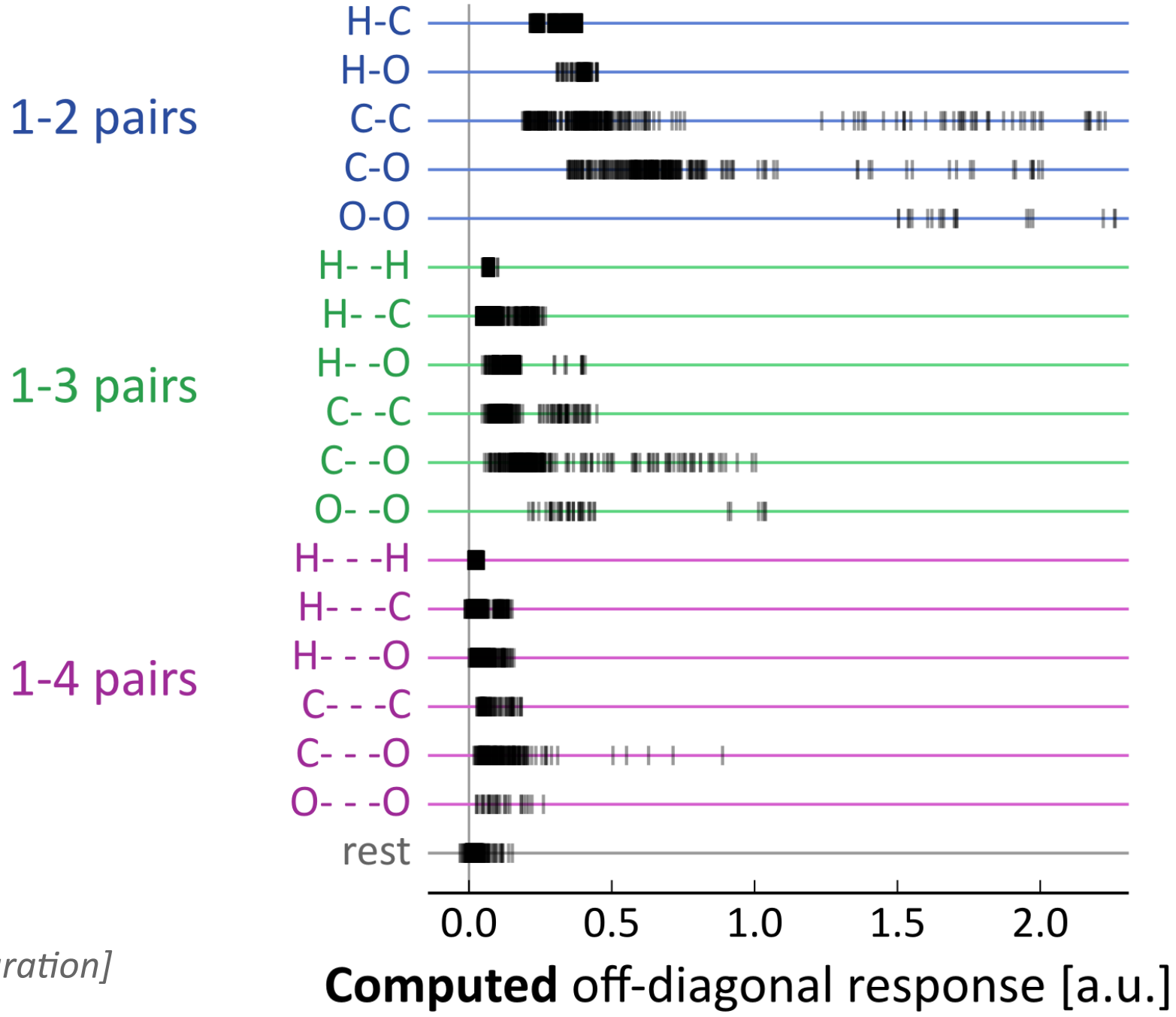
[in preparation]

Parameter robustness: χ(A,B)



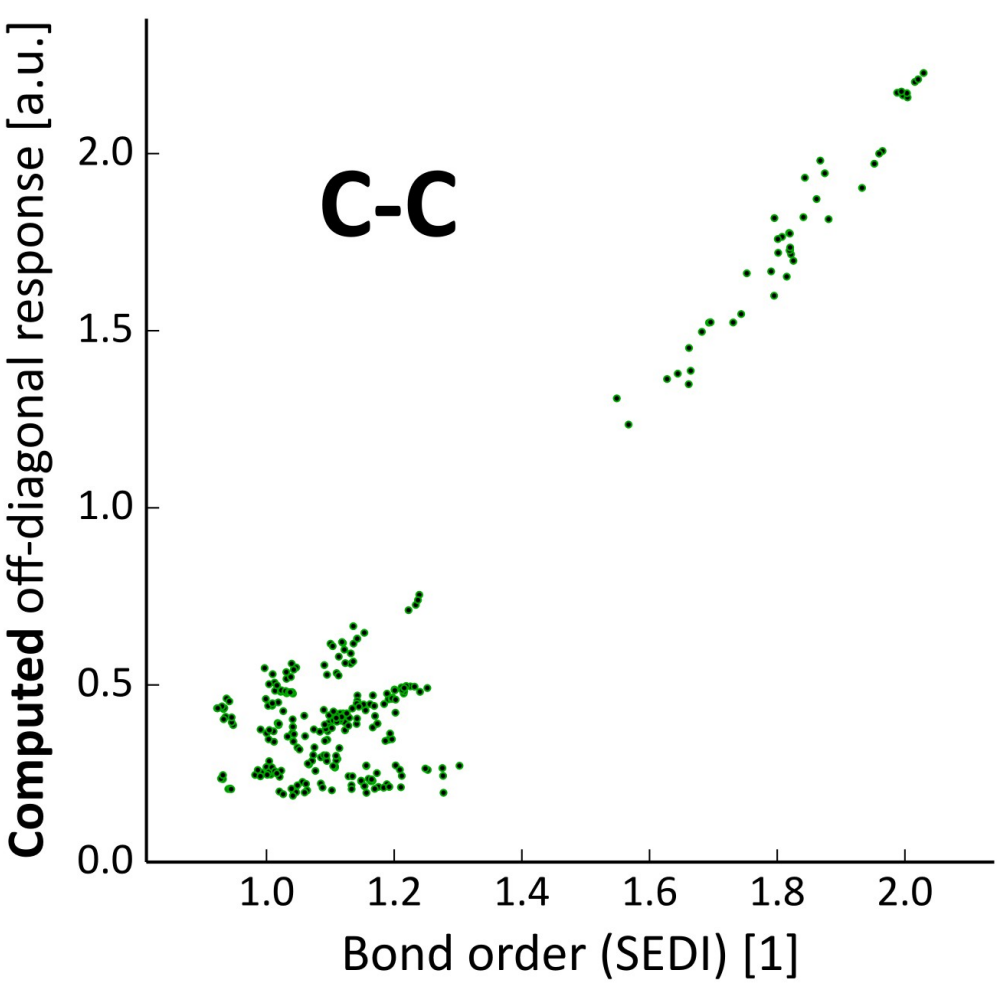
[in preparation]

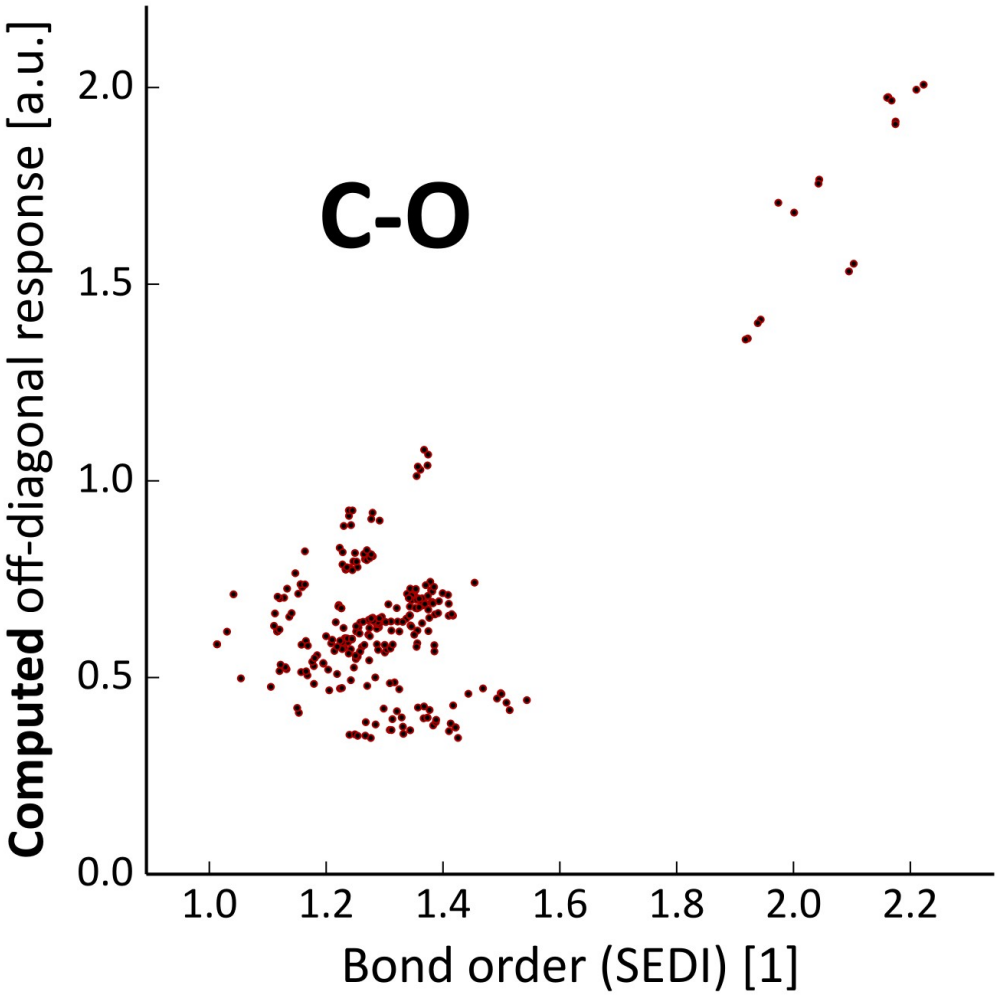
Parameter robustness: χ(A,B)



[in preparation]

Parameter robustness: χ(A,B)





[in preparation]

How to Ensure the Accuracy of Polarizable Force Fields?

Introduction

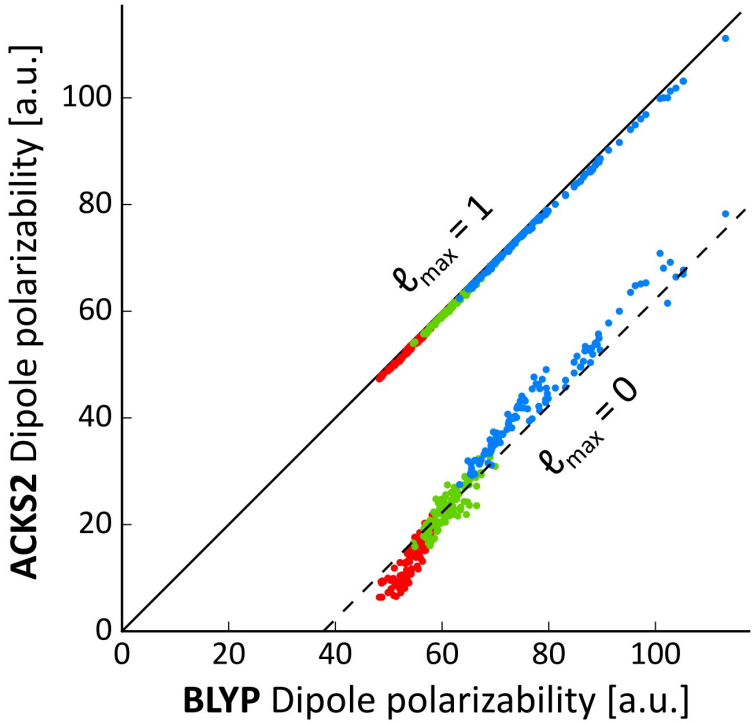
Generalized ACKS2

Numerical Validation

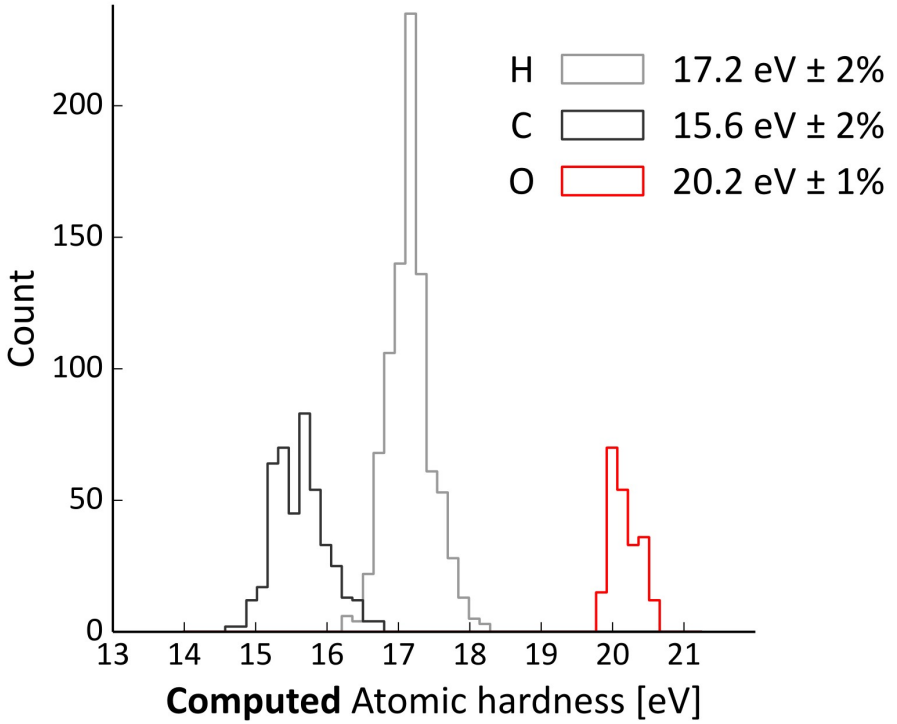
Conclusions

Summary

ACKS2 reproduces DFT response



Parameters ≈ robust



- Chemical insight required
- To be extended with dipoles

Acknowledgments

At CMM (UGent, Belgium)

- Sven Rogge
- Steven Vandenbrande
- Louis Vanduyfhuys
- Veronique Van Speybroeck
- Michel Waroquier

At McMaster (Canada)

- Paul Ayers

Computing facilities

Stevin Supercomputer Center at UGent (VSCentrum)

HPC UGENT

Funding

fwo

Belgian Science Policy Office belspo

Horton

http://theochem.github.io/horton/

In this work

- Atoms-in-molecules partitioning + derived quantities
- Interfacing with different codes (Gaussian, MOLPRO, PSI4, ORCA, GAMESS, ...)
- Derivation of polarizable FF parameters from e^- theory

Beyond

- Geminal methods
- Constrained DFT
- ....