An Illustrated and Illustrative Tour of Recent Work with CP2K

Ben Slater

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Elias Garcia Martinez (1930)
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Selected examples of work on porous materials and ice

Zeolites: Hybrid Functionals/ADMM
Ice: SS-NEB

MOFs: REPEAT scheme
SCAN functional
Ice: RPA/MP2
Elucidating framework aluminium distribution in catalytic zeolites

Zeolites

- Microporous, crystalline aluminosilicate solids

- Petrochemical processing
  - Cracking, isomerisation and alkylation

- Increasing concern for the environment has motivated development of sustainable and environmentally benign alternatives to traditional petrochemical methods

- The use of traditional zeolite catalysts in atypical processes
  - Pollution control
  - Hydrocarbon production

Chabazite (CHA)
Zeolites

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SSZ-13 (CHA)
Zeolites

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SSZ-13 (CHA)
Substituting tetravalent silica with trivalent alumina introduces a negative charge to the zeolite framework.

Charge-balancing counter cations (K\(^+\), Na\(^+\), Cu\(^{2+}\), H\(^+\))

Generally accepted that Al and associated cations play a crucial role in catalysis, particularly protonated zeolites, in which a Brønsted acidic site is formed.

Before we can begin to investigate catalytic mechanisms, and design new zeolite catalysts, we first need a full understanding of Al’s framework location.
Where is Al?

Löwenstein’s Rule – 1954

“There is a disinclination for T-O-T linkages of adjacent tetrahedral units to possess more than one aluminium atom, forbidding the formation of Al-O-Al bonds within the zeolite framework.”

Dempsey’s Rule – 1969

“On the basis of electrostatic arguments, framework Aluminium ions assume the furthest distance from one another.”

W. Löwenstein, American Mineralogist 39, (1954)
E. Dempsey et al., J. Phys. Chem. 73, no. 2 (1969)
Investigating Al distribution in SSZ-13

Previous investigations have invoked Lowenstein's rule to reduce computational expenditure.

2 Al per unit cell (Si/Al = 17)
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2 Al per unit cell (Si/Al = 17)
DFT data Na-SSZ-13 Si/Al = 17

‘Löwensteinian’ global minimum structure

2 Al per unit cell (Si/Al = 17)

\[ \Delta E_{(N\text{L}\text{global minimum} - L\text{global minimum})} = +44 \text{ kJ mol}^{-1} \text{ per U.C.} \]
DFT data H-SSZ-13 Si/Al = 17

‘non-Löwensteinian’ global minimum structure

2 Al per unit cell (Si/Al = 17)

\[ \Delta E(\text{NL}_{\text{global minimum}} - \text{L}_{\text{global minimum}}) = -14 \text{ kJ mol}^{-1} \text{ per U.C.} \]
DFT data H-SSZ-13 Si/Al = 17

‘non-Löwensteinian’ global minimum structure

CP2K, GGA – PBE functional, TZV2P basis

2 Al per unit cell (Si/Al = 17)

\[ \Delta E(\text{NL}_{\text{global minimum}} - L_{\text{global minimum}}) = -14 \text{ kJ mol}^{-1} \text{ per U.C.} \]
Other zeolites

**ΔE**(NL\textsubscript{global minimum} – L\textsubscript{global minimum})

-8.3 kJ mol\(^{-1}\) per U.C.

-9.2 kJ mol\(^{-1}\) per U.C.

-55.7 kJ mol\(^{-1}\) per U.C.

**LTA**

**RHO**

**ABW**

Density = 14·2 Tnm\(^{-1}\)

(CHA = 15·1 Tnm\(^{-1}\))
But why?

‘non-Löwensteinian’ global minimum structure

‘Löwensteinian’ global minimum structure

2 Al per unit cell (Si/Al = 17) H-S

+14 kJ mol⁻¹
But why?

‘non-Löwensteinian’ global minimum structure

\[(\text{O})_3\text{Si} - \text{O} - \text{Al} - \text{O} - \text{Al} - \text{O} - \text{Si(O)}_3\]

‘Löwensteinian’ global minimum structure

\[(\text{O})_3\text{Al} - \text{O} - \text{Si} - \text{O} - \text{Al} - \text{O} - \text{Si(O)}_3\]

+14 kJ mol\(^{-1}\)
But why?

‘non-Löwensteinian’ global minimum structure

\[(O)_3\text{Si} - \text{O} - \text{Al} - \text{O} - \text{Al} - \text{O} - \text{Si}(O)_3\]

3 Al-O(H) linkages

‘Löwensteinian’ global minimum structure

\[(O)_3\text{Al} - \text{O} - \text{Si} - \text{O} - \text{Al} - \text{O} - \text{Si}(O)_3\]

2 Al-O(H) linkages

\[\text{+14 kJ mol}^{-1}\]
But why?

'non-Löwensteinian' global minimum structure

3 Al-O(H) linkages
1 Si-O(H) linkage

(O)_3Si – O – Al – O – Al – O – Si(O)_3

'H'

(‘non-Löwensteinian’ global minimum structure)

'Łöwensteinian' global minimum structure

2 Al-O(H) linkages
2 Si-O(H) linkages

(O)_3Al – O – Si – O – Al – O – Si(O)_3

'H'

kT \approx 5 kJ/mol

Free energy difference is comparable to internal energy difference

Na-SSZ-13 \Delta E_{\text{NL_{global minimum} \rightarrow L_{global minimum}}} = +44 \text{ kJ mol}^{-1} \text{ per U.C.}
DFT data SSZ-13 Si/Al > 17

3 Al per unit cell (Si/Al = 11)

4 Al per unit cell (Si/Al = 8)
What does this mean?

- Potentially invaluable for understanding existing zeolite catalytic mechanisms and Brønsted acidity, to the development of new zeolite catalysts, and the synthesis of hierarchical materials.

But....

- How can we make these structures?
  
  Reverse dealumination

- What signatures could be used to unambiguously identify these -Al-O-Al-?
  
  $^{17}$O SS MAS NMR
Evidence for non-Löwensteinian ordering in protonated zeolite frameworks

Preference for the formation of discrete aluminium clusters in low silica frameworks.

Not the case for sodium-containing zeolites, where the global minimum structures are Löwensteinian ordered frameworks.

Demonstrates the influence of counter-cation identity on framework aluminium location.

We hope this work stimulates experimental investigation into the direct or post-synthesis of non-Löwensteinian ordered zeolites and further characterisation of existing materials.

MOF/ADMM example

Definitive Molecular Level Characterization of Defects in UiO-66 Crystals

Christopher A. Trickett, Kevin J. Gagnon, Seungkyu Lee, Felipe Gándara, Hans-Beat Bürgi, and Omar M. Yaghi*
Definitive Molecular Level Characterization of Defects in UiO-66 Crystals

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True defect structure?

Proton abstraction favourable

-114.1 kJ/mol

Proton *migration* favourable

Definitive defect structure?

63 configurations assessed from 30ps MD

34 configurations fall within 5kJ/mol of PBE0+D3 (ADMM)

S. Ling, B. Slater, Chem. Sci, 7, 4706, 2016
Defect structure is *fluxional*

30ps MD
PBE
NVT

OH- proton
localised

central water is
labile

rapid interchange
of protons

Where is the hydroxide?

Rapid exchange of protons

Static picture from XRD misses dynamic exchange

Proton migration barrier height?

Ea = 27.5 kJ/mol

PBE0+D3 (ADMM)

Ea = 6.5 kJ/mol

Source of proton tunnelling/intrinsic proton conduction

Possible frustrated Lewis acid site at high T (dehydrated)

S. Ling, B. Slater, Chem. Sci, 7, 4706, 2016
High throughput screening of MOFs

In collaboration with Dr Maciej Haranczyk (LBNL) and Prof Berend Smit (University of California, Berkeley and EPFL)

Variance in the ESP is fitted

Properties validation

Figure S1. The CP2K relaxed structure and REPEAT derived atomic partial charges were validated by comparison of the CO$_2$ adsorption isotherm in the original MOF-74 structure with the previously published results of Lin et al. The experimental isotherm of Mason et al.$^2$ is scaled due to 80% accessibility of the material.
Rational design of low-cost, high-performance MOFs for hydrogen storage and carbon capture

Cost

$$$$$
$

Volumetric Uptake of H₂

★★
★★★★★

Henry Coefficient of CO₂

★
★★★★★

CO₂:H₂O Selectivity

★★★
★★★★★

M₂(DOBDC)

M₂(DHFUMA)

Accurate first-principles structures and energies of diversely bonded systems from an efficient density functional

Jianwei Sun¹*, Richard C. Remsing²,³, Yubo Zhang¹, Zhaoru Sun¹, Adrienn Ruzsinszky¹, Haowei Peng¹, Zenghui Yang¹, Arpita Paul⁴, Umesh Waghmare⁴, Xifan Wu¹, Michael L. Klein¹,²,³ and John P. Perdew¹,²

One atom or molecule binds to another through various types of bond, the strengths of which range from several meV to several eV. Although some computational methods can provide accurate descriptions of all bond types, those methods are not efficient enough for many studies (for example, large systems, ab initio molecular dynamics and high-throughput searches for functional materials). Here, we show that the recently developed non-empirical strongly constrained and appropriately normed (SCAN) meta-generalized gradient approximation (meta-GGA) within the density functional theory framework predicts accurate geometries and energies of diversely bonded molecules and materials (including covalent, metallic, ionic, hydrogen and van der Waals bonds). This represents a significant improvement at comparable efficiency over its predecessors, the GGAs that currently dominate materials computation. Often, SCAN matches or improves on the accuracy of a computationally expensive hybrid functional, at almost-GGA cost. SCAN is therefore expected to have a broad impact on chemistry and materials science.

Sun et al. Nature Chemistry, 8, 831, 2016
The SCAN functional: the good
The SCAN functional: the good

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## The SCAN functional: the bad

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• In the presence of a guest (e.g. $p\text{CO}_2$), the cell volume $\sim$doubles
• In 2008, Brown et al., JACS, showed cell hysteresis in the absence of a guest.
• DFT+D and vdwDF approaches showed the dense phase is stabilised by dispersion. ($\sim$8-14 kJ/mol per Al) (Exp. 7.5 kJ/mol/Al - calorimetry)
• Vibrational entropy drives the expansion (low frequency modes)
## MIL-53-Al

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The SCAN functional: the ugly

**MIL-53-Al**

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The ice XV problem

see The polymorphism of ice: five unresolved questions, Salzmann et al., PCCP, 2011

Ice XV/VI have the largest variation in hydrogen bond angle of any phase.

Problem solved?
Ice VI/XV*

Interpenetrating lattices formed from hexameric chains

VI - SG 137

XV - SG 2

XRD data taken from Salzmann et al. PRL 2009
Key ice XV structures

Dense structure (~1 GPa)

2Cl

9A2
Varying HF and vdW does not change the order of stability.

18 structures
RI-MP2 results

1078s on 3840 processors (Archer)

9A2 = Cc most stable

Theory still predicts exptl (2C1) structure to be metastable

Full cell optimisation!
RI-MP2 vs RPA results

9A2 = Cc most stable 1078s on 3840 processors (Archer)

Theory still predicts exptl (2C1) structure to be metastable
Experiment and theory still in conflict

Theory still predicts wrong ground state
Experimentally, only about 70% of ice VI -> XV
Grains of ice XV in a matrix of VI

\[ U_{\text{corr}} = \frac{2\pi}{V_f} M^2 \]
Solid state NEB - ice Xlc-IV

(a) ice Ic network

(b) ice IV network

ice I layer

ice IV layer

$X_{lc}$ (0.93) to IV (1.27 g/cm$^3$)
Acknowledgements

Dr. Sanliang Ling       Miss Rachel Fletcher

**MOF-74**
Matthew Whitman (Berkeley)
Liangheng Tong (formerly KCL)
Dr Maciej Haranczyk (LBNL)
Prof Berend Smit (University of California, Berkeley and EPFL)

**Ice XV - MP2/RPA**
Mauro del Ben (LBNL)
Joost VandeVondele (Formerly ETH, now ?)

**Unpublished work - SS-NEB**
Jacob Shephard (Edinburgh)
Christoph Salzmann (UCL)