Fall 10-1-2012

Atomis'c Materials Design Using the Computa'onal Materials Repository

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Atomistic Materials Design Using the Computational Materials Repository

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CAMd
Center for Atomic-scale Materials Design

CASE
Catalysis for Sustainable Energy

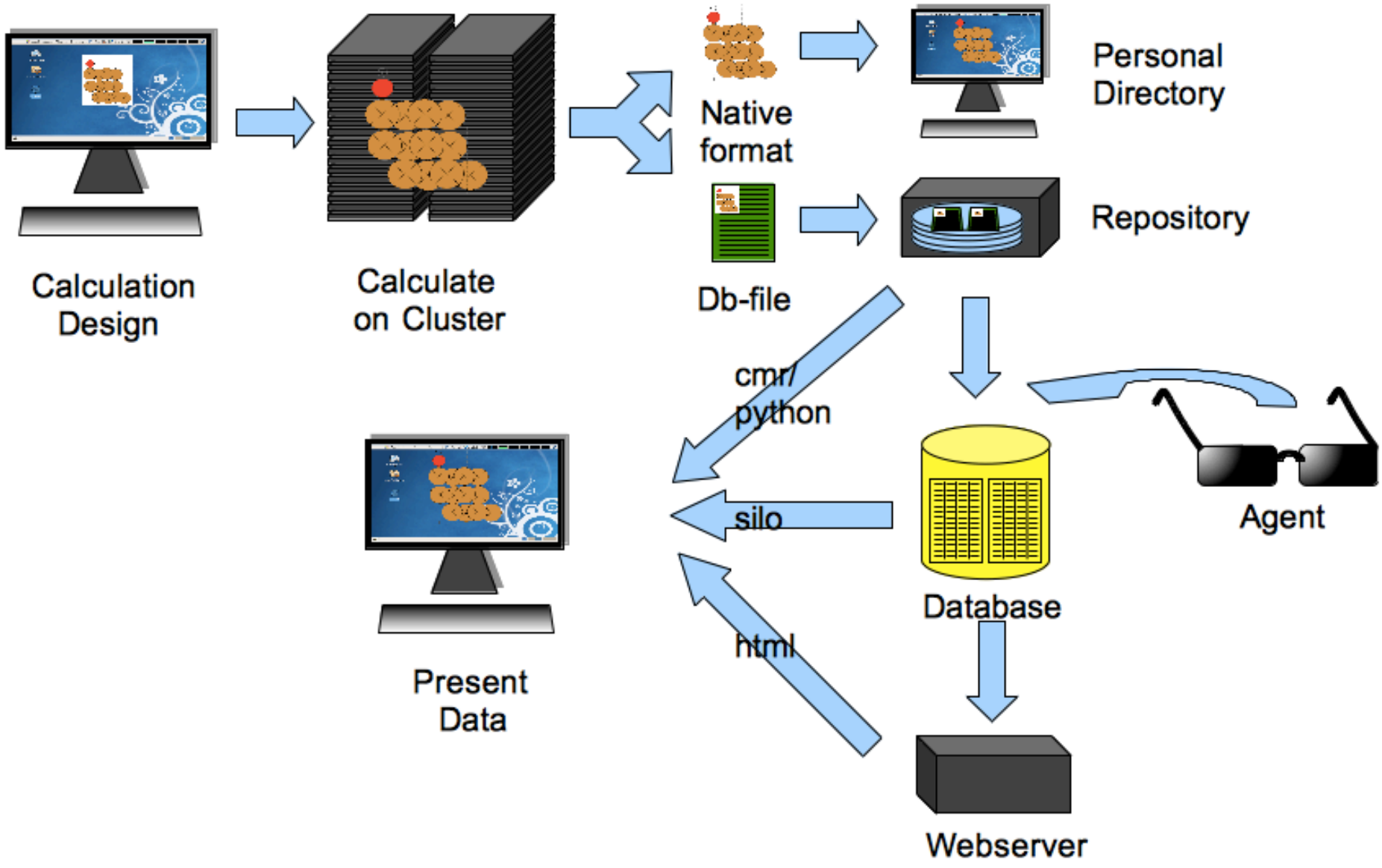
Outline

- Computational Materials Repository
- Perovskites for water splitting
- New optimized exchange-correlation density functionals

Computational Materials Repository

- A system for storing/uploading, analyzing, retrieving, and sharing computational data.
- Some ideas:
  - Many interfaces (sql, python, web, ”silo”)
  - Agents – small pieces of code automatically performing calculations in the database
  - Taxonomy/folksonomy
  - Data identification – publication
- Software at http://wiki.fysik.dtu.dk/cmr
- Data at htts://cmr.fysik.dtu.dk

Computational Materials Repository



Generic data view

related keyword

Found 2704 results (0.470712s)

« 1 2 3 4 5 ... 271»

Fields

link

Restrict keywords:

O2 +(2704)
mox +(2704)
10.1039/C1EE02717D +(2704)
perovskite +(2704)
O +(2704)
ABO3 +(2704)
Re +(103)
As +(103)
Sr +(103)
Rb +(103)
Cu +(103)

Download information:

- ase: a python script that retrieves this item from the database and creates an ase atoms object
- csv: a csv spread sheet with all the data
- CMR: a python script that retrieves this item from the database
- json: all the data in json format

id_ref	jmol	A	B	anion	heat_of_formation	gllbsc_dir-gap	gllbsc_ind-gap	CB_dir	CB_ind	VB_dir	VB_ind	atoms	db_keywords	doi	ingredients	downloads
8926	Jmol	Rh	Re	O3	1.0400	0	0	5.9347	5.9347	5.9347	5.9347	O Rh Re (3O, 1Rh, 1Re)	10.1039/C1EE02717D ABO3 mox O O3 perovskite Re Rh RhReO3	10.1039/C1EE02717D	0.50 Re2 + 0.25 Rh4 + 3.00 O	ase CMR json XYZ
8935	Jmol	Rh	Ag	O3	2.3700	0	0	6.0569	6.0569	6.0569	6.0569	O Rh Ag (3O, 1Rh, 1Ag)	10.1039/C1EE02717D ABO3 Ag mox O O3 perovskite Rh RhAgO3	10.1039/C1EE02717D	0.25 Rh4 + 3.00 O + 0.25 Ag4	ase CMR json XYZ
8938	Jmol	Rh	Co	O3	1.5200	0	0	6.0182	6.0182	6.0182	6.0182	O Co Rh (3O, 1Co, 1Rh)	10.1039/C1EE02717D ABO3 Co mox O O3 perovskite Rh RhCoO3	10.1039/C1EE02717D	0.50 Co2 + 0.25 Rh4 + 3.00 O	ase CMR json XYZ
8945	Jmol	Rh	Cu	O3	1.9100	0	0	6.0677	6.0677	6.0677	6.0677	O Cu Rh (3O, 1Cu, 1Rh)	10.1039/C1EE02717D ABO3 Cu mox O O3 perovskite Rh RhCuO3	10.1039/C1EE02717D	0.25 Rh4 + 3.00 O + 0.25 Cu4	ase CMR json XYZ
8946		Rh	Si	O3	1.1400	0	0	6.1417	6.1417	6.1417	6.1417	O Si Rh (3O, 1Si, 1Rh)	10.1039/C1EE02717D ABO3 mox O O3 perovskite Rh RhSiO3 Si	10.1039/C1EE02717D	0.25 O8Si4 + 0.25 Rh4 + 1.00 O	ase CMR json XYZ

keywords

atoms

Project specific interface: Light absorbing materials for water splitting

Computational Materials Repository

Hide search box

Link to image

Do not forget to press **update matrix** after changing the selection!
If there is an error - it means that the dataset is already being calculated! Please wait a moments and try again.

Chose a data set:	ABO3 (2704)
Width:	800
Height:	1200
X axis ticks:	B
Y axis ticks:	automatically selected
X sort order:	Electronegativity (Paulin
Y sort order:	Electronegativity (Paulin
Action on Click:	show band edges

References:
- ABN (3)
- ABO (20)
- AN (50)
- AO (52)
- AON (35)
- default (3)
- mbulk (52)

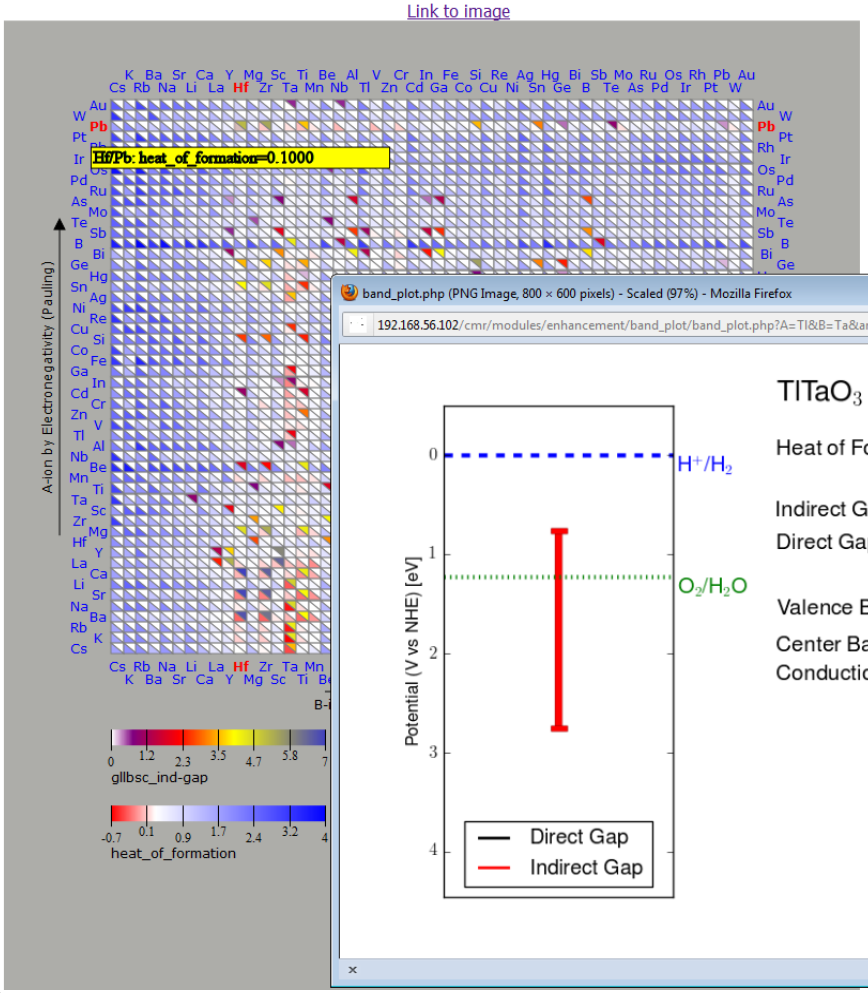
	Value field:	Colors:
Triangle 1: (top-right)	gllbsc_ind-gap (eV)	0->white,0.7->purple,2.2->re
Triangle 2: (bottom-left)	heat_of_formation (eV)	min->red,0.3->white,4->blue
Triangle 3:		
Triangle 4:		

Examples for the color choice:

```
0->white,1->red,7->blue

0->white,0.9->red,2.2->green,4->yellow,8->blue

-100->blue,100->red
```

Valid color names are black, blue, cyan, green, gray, green, lightblue, pink, red, purple, white, yellow. Please note that the values must be in **increasing** order.

Update matrix



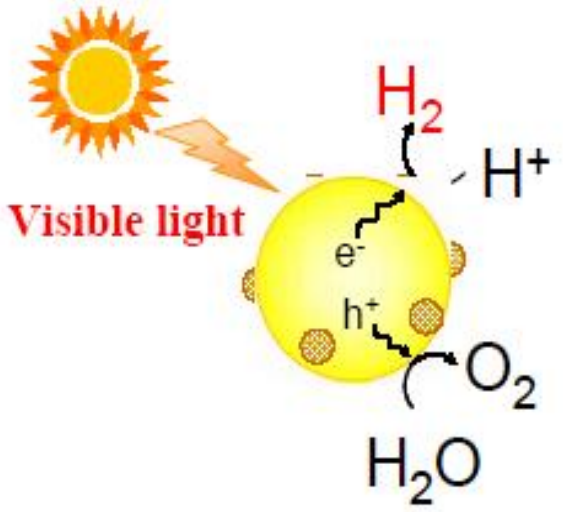
http://cmr.fysik.dtu.dk - the database

http://wiki.fysik.dtu.dk/cmr - the software, publication to appear in Comp. Sci. Eng.

Water splitting

Complicated process:

- Light absorption
- Electron-hole motion
- Induce reactions



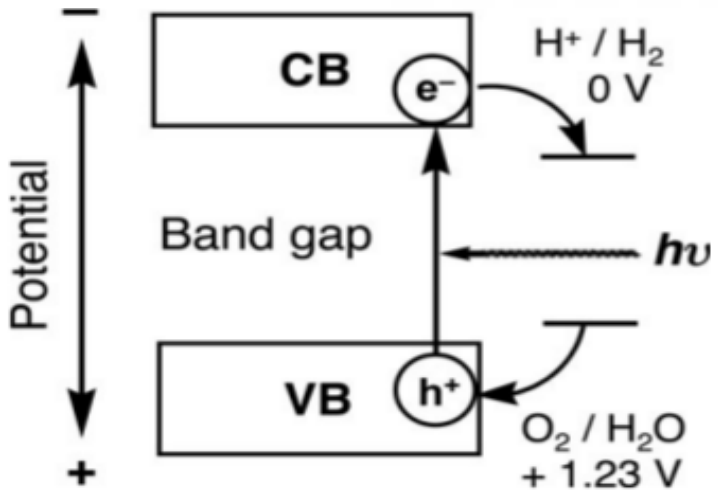
Examples: TiO_2, GaN:ZnO, $ZnGeN_2$:ZnO

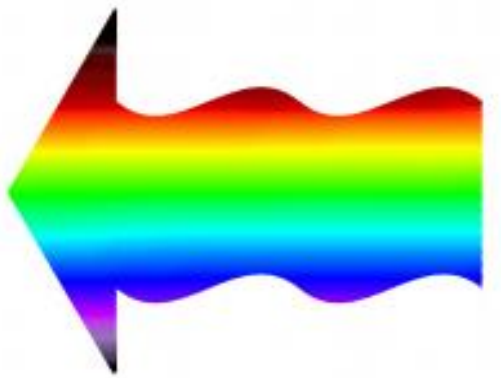
(Fujishima and Honda, Nature 1972)

(Maeda et al., JACS, **127**, 8286 (2005))

Materials for water splitting

- **Chemical/structural stability**
- **Band gap of 1.5-3 eV (overpotentials, losses)**
- **Band edge positions straddle the water redox potentials**
- Good electron/hole mobilities
- Low cost, non-toxicity
- Good catalytic properties





Principle of water splitting using semiconductor photocatalysts.

Methodology – density functional theory + friends

GPAW – projector augmented wave method in real space

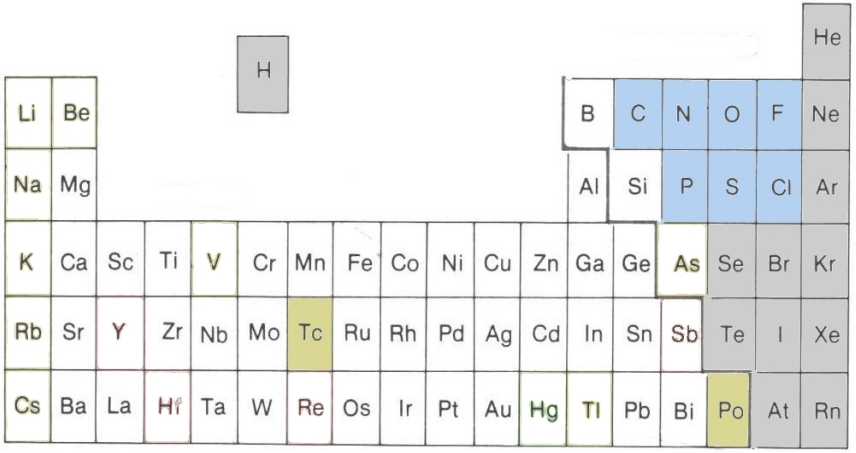
J. Enkovaara *et al.* J. Phys.:Cond. Mat. **22** (2010) ← **Review article**

https://wiki.fysik.dtu.dk/gpaw/ ← **Free download, GPL**

- High accuracy: Wave functions expanded on real space grids or plane waves
- High efficiency: Wave functions expanded in atomic-like orbitals (LCAO)
- Efficient parallelization (good scalability up to > 32.000 CPUs)
- Xc-functionals: LDA, GGAs, meta-GGA, LDA+U, EXX, vdWDF, GLLB, BEEF
- Time-dependent DFT (including “Bootstrap”)
- Many-body perturbation theory (GW and Bethe-Salpeter equation)
- Phonons and electron-phonon coupling
- Quantum electron transport
- Atomic Simulation Environment (ASE) python scripting interface

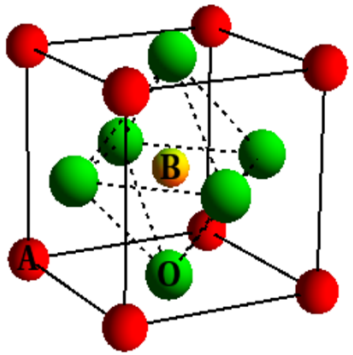
Materials – cubic perovskites

- Perovskite, common stable structure, 50% are quasi-cubic
- Variety of properties: ferroelectricity, magnetism, superconductivity and (photo)catalytic activity
- 52 different metallic elements
- Different anions (O, N, S, F, Cl, ...)



Excluded elements:

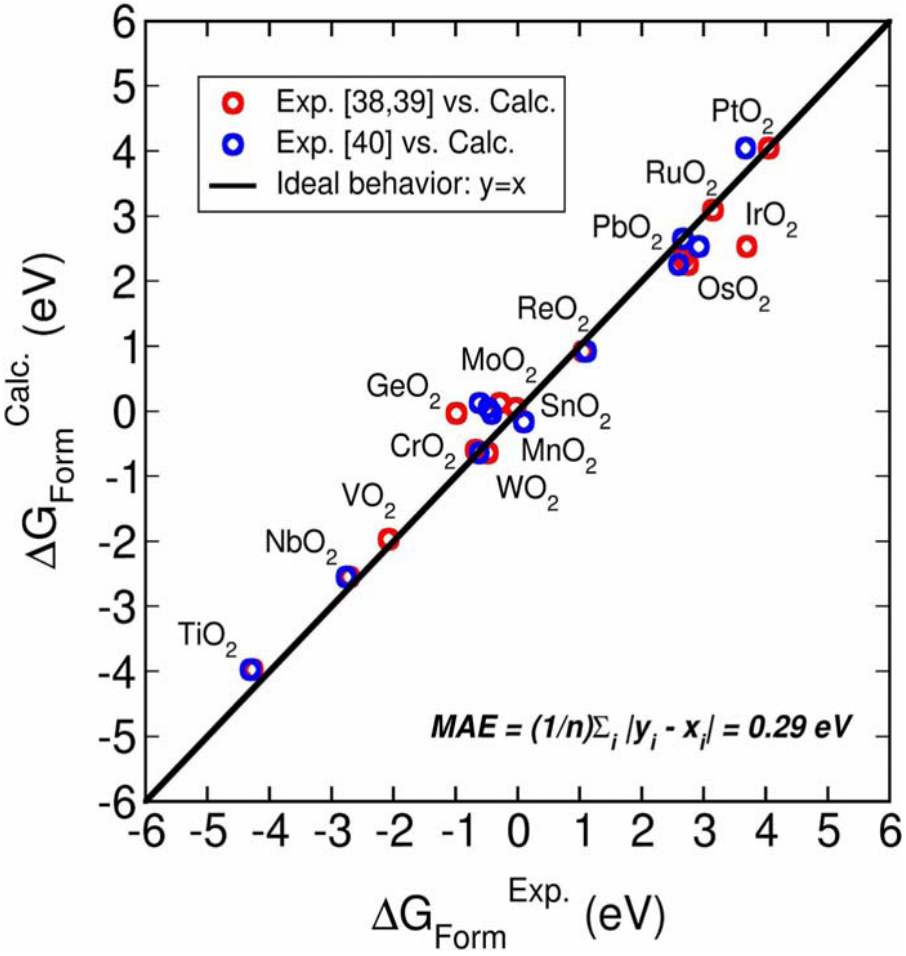
- Non Metals;
- Radioactive, toxic.



ABO_3

Predicting stability of oxides – Heat of formation

- Focus on oxides because of high stability (towards oxidation!)
- DFT-RPBE calculated formation energy for rutile dioxides.
- Similar results obtained for perovskite structures.



J I Martínez, H A Hansen, J. Rossmeisl, and J. K. Nørskov , Phys. Rev B 2009

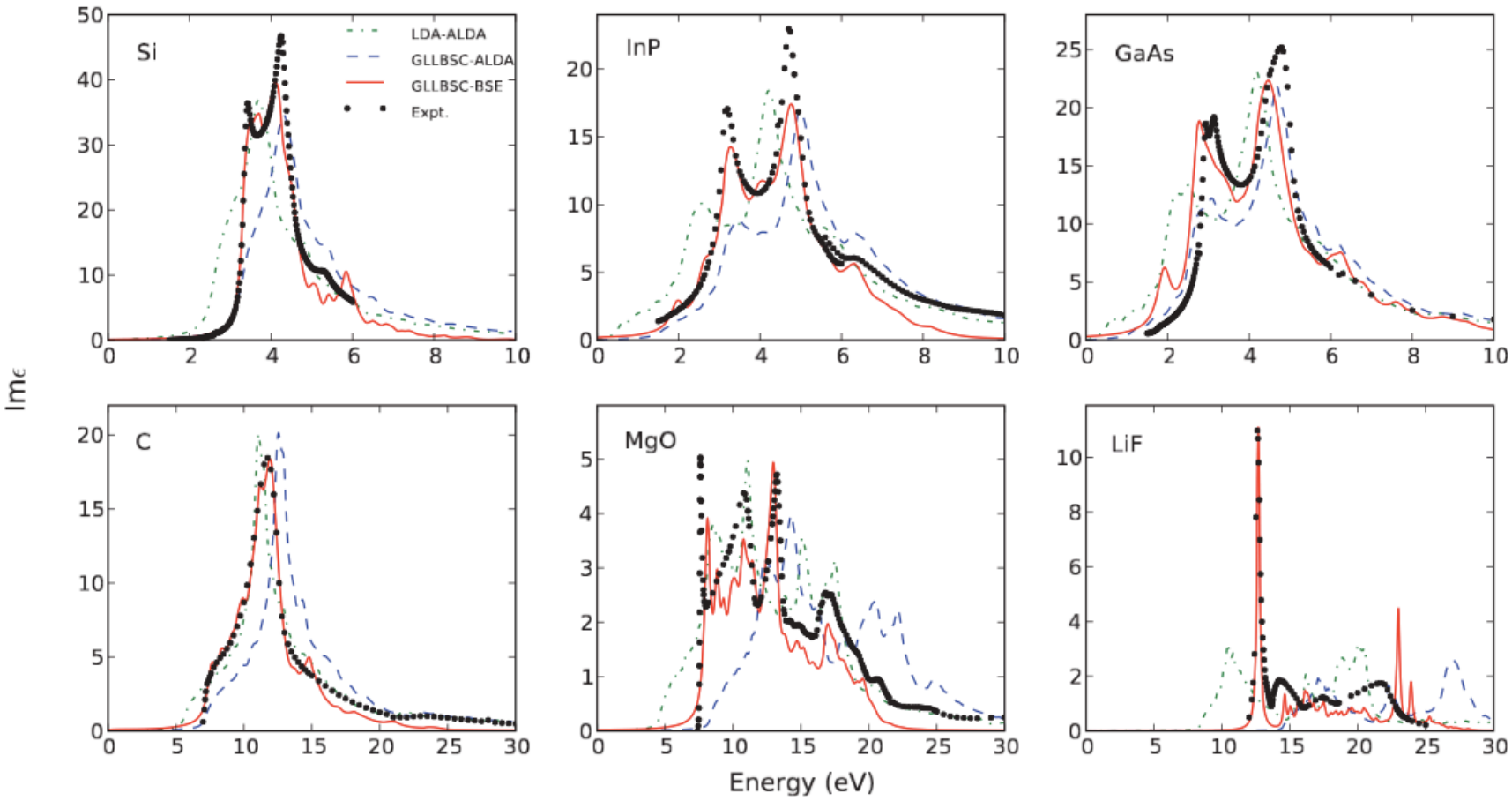
Calculation of bandgaps

- DFT is aimed at calculating ground state total energies – does not provide bandgap
- Bandgaps particularly bad for (semi-)local approximations
- GLLB approximation
  - Improved xc-potential compared to LDA/GGA
  - Explicit evaluation of derivative discontinuity

$$E_g^{QP} = E_g^{KS} + \Delta_{xc}$$

First description: Gritsenko *et al.*, *Phys. Rev. A* **51**, 1944 (1995).
Implemented in GPAW: Kuisma *et al.*, *Phys. Rev. B* **82**, 115106 (2010).

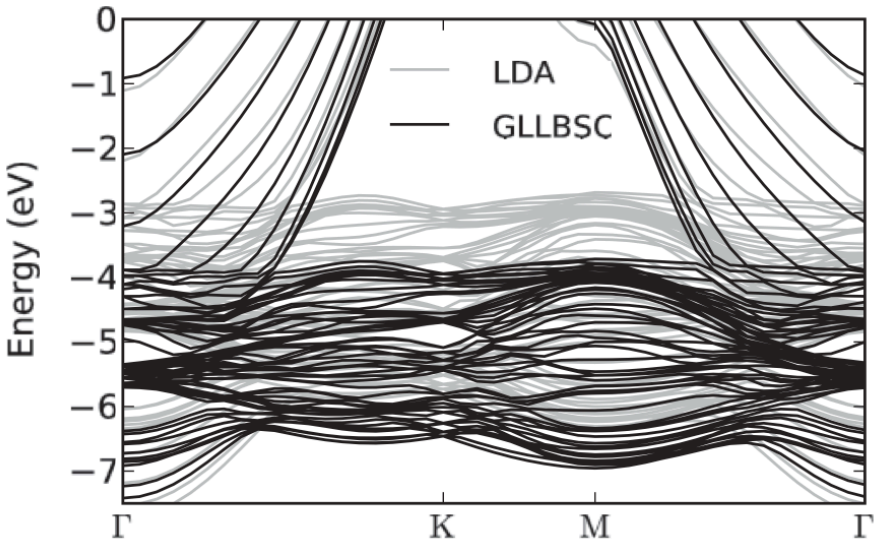
Optical absorption spectra with GLLB-SC

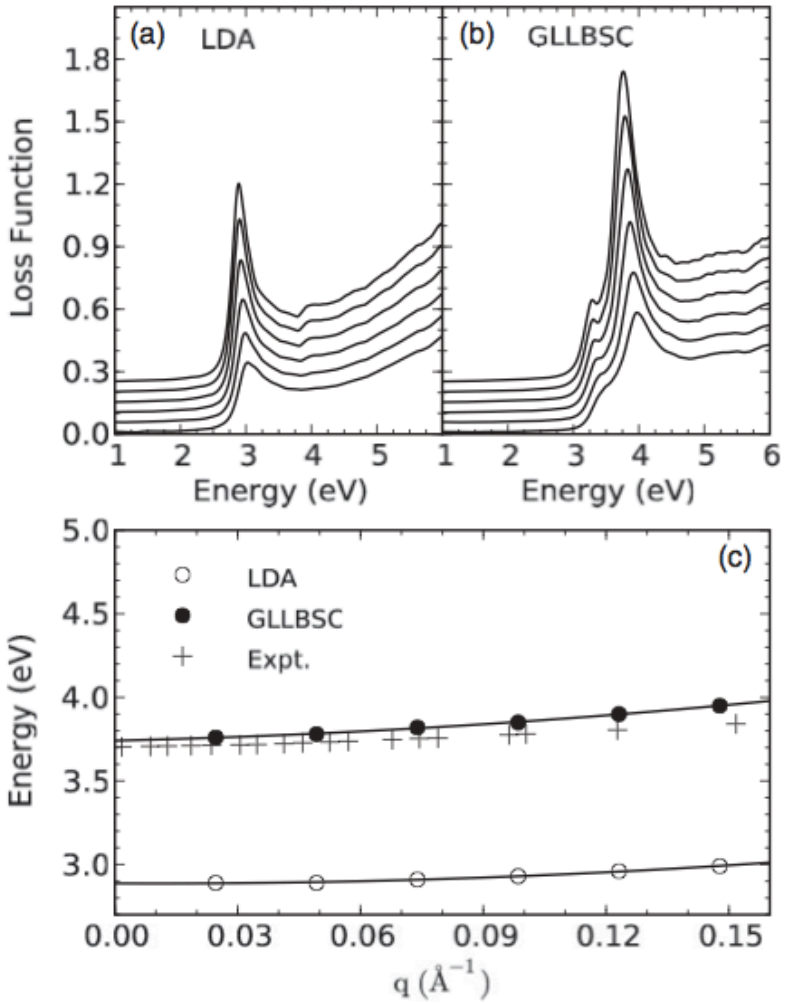


Derivative discontinuity used in spectrum for TDDFT, but not for W in BSE.

Jun Yan, K. W. Jacobsen, and K. S. Thygesen, PRB **86**, 45208 (2012)

Ag surface plasmon with GLLB-SC





J. Yan, K. W. Jacobsen, and K. S. Thygesen, PRB **84**, 235430 (2011)

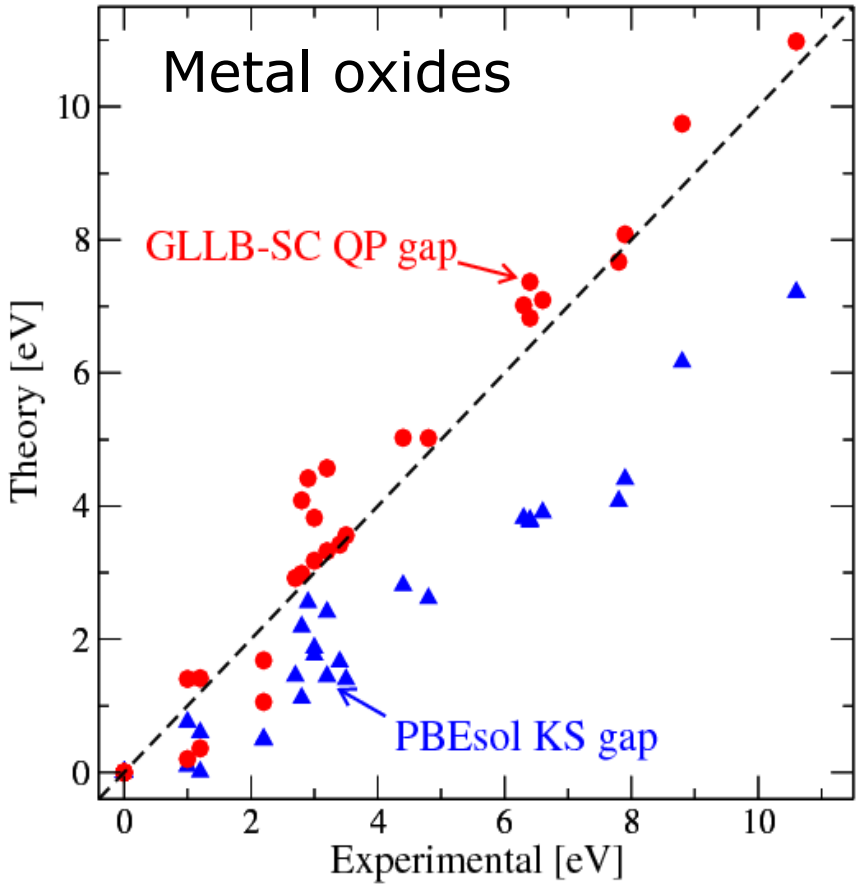
Predicting bandgaps of oxides with GLLB-SC

The GLLB-SC (solid-correlation) xc-functional:

$$E_g^{QP} = E_g^{KS} + \Delta_{xc}$$

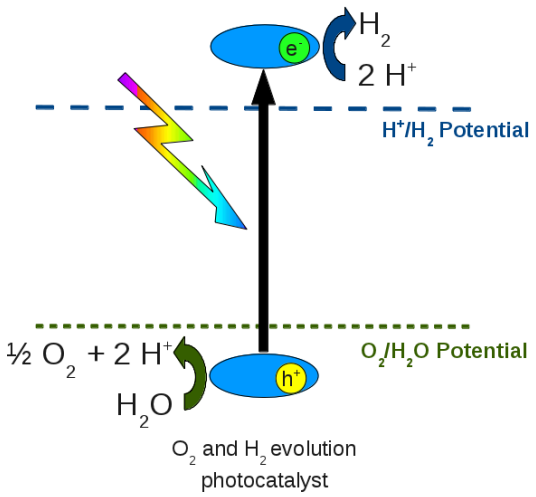
Derivative discontinuity

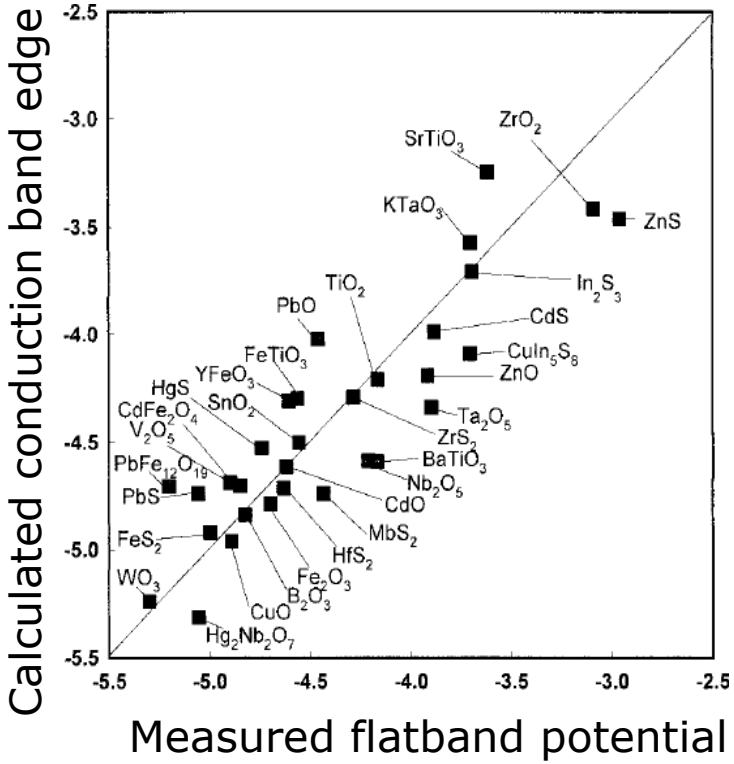
- Bandgaps within ~0.5 eV of exp.
- Minimal computational cost
- Neglect of electron-hole interaction – excitons



Band edge positions

Empirical formula: $E_C = (\chi_A \chi_B \chi_O{}^3)^{1/5} - 1/2E_{gap} + E_0$





X = 1/2(A+I_1) = Absolute electronegativity (Mulliken scale)

A=Affinity level

I_1=Ionization level

E_{gap}= Band gap

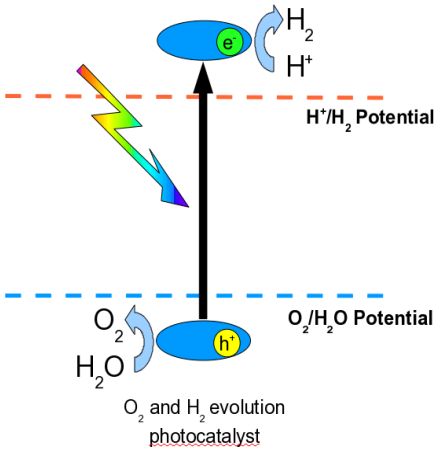
E_0 = Difference between NHE and vacuum ~ -4.5 eV

M. A. Butler and D. S. Ginley, Journal of The Electrochemical Society (1978)

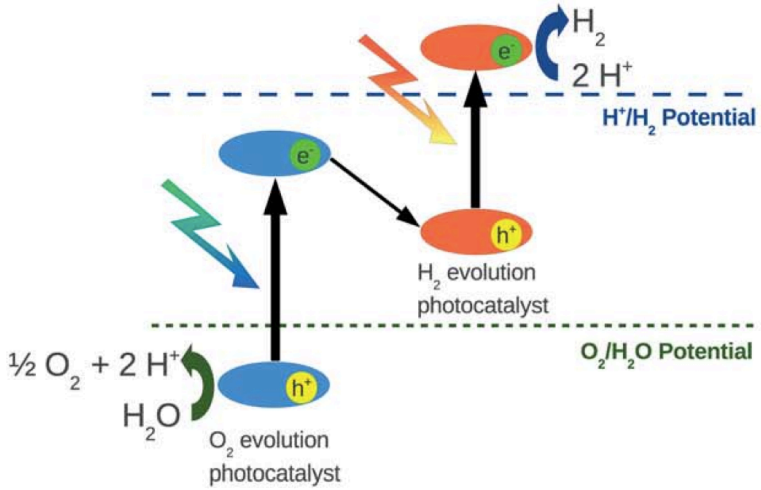
Y Xu and MAA Schoonen, American Mineralogist (2000)

One- and two-photon water splitting

One-photon



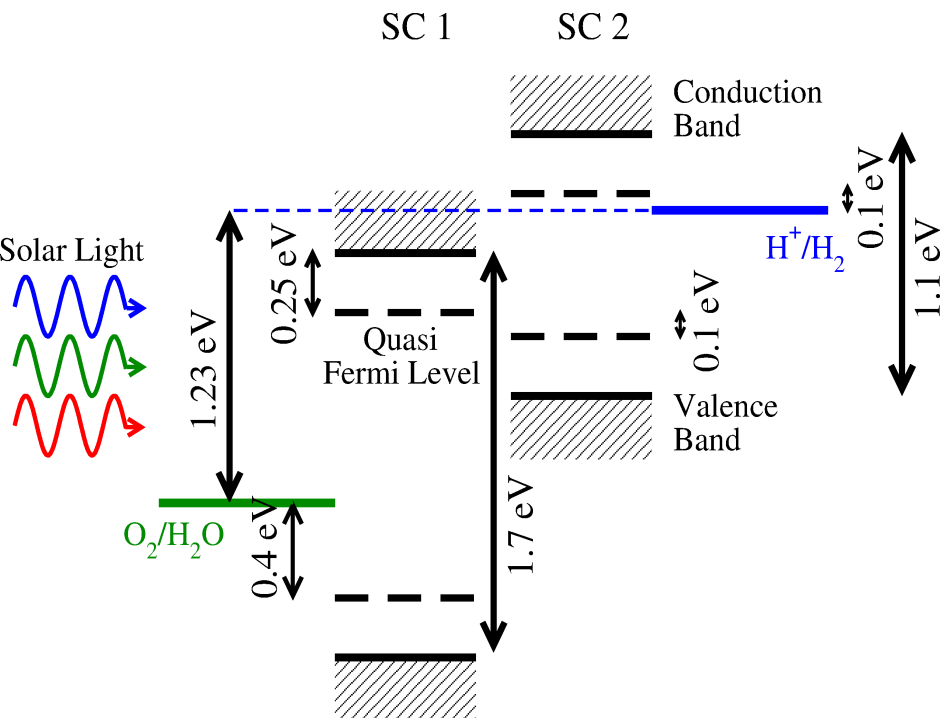
Two-photon

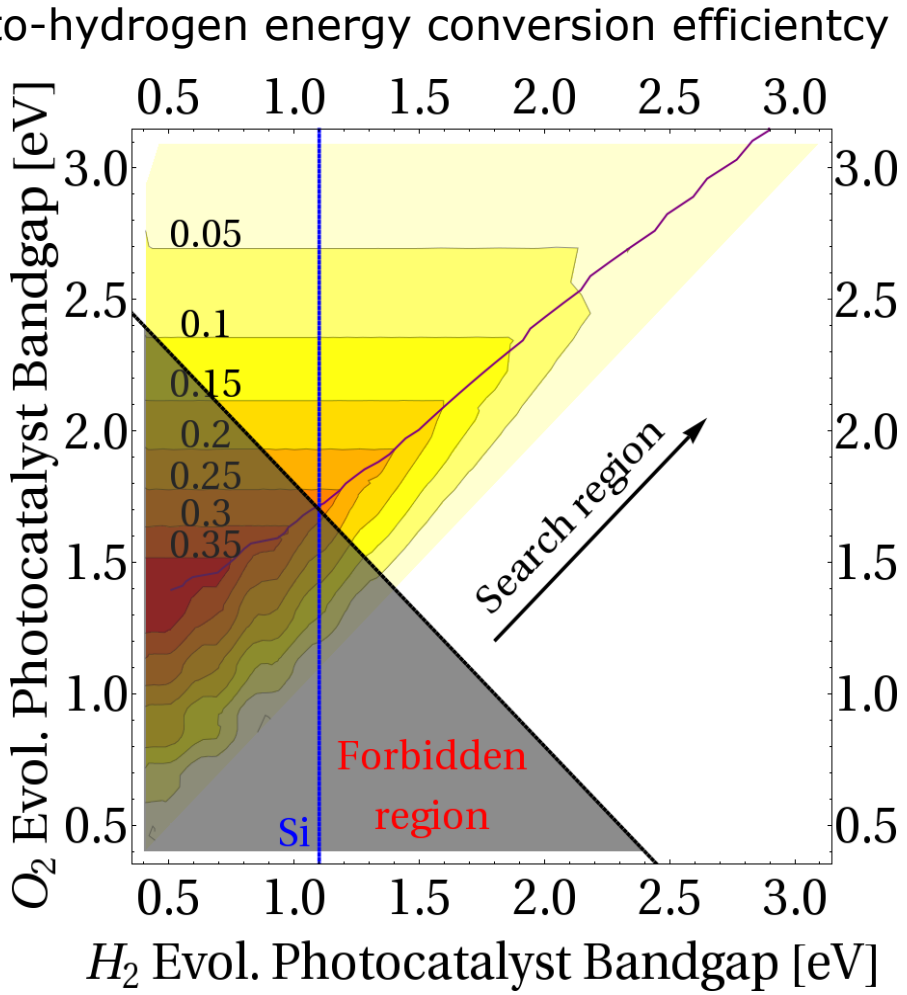


H_2 photocatalyst: Si
O_2 photocatalyst: screening

Screening parameters	One-photon WS	Two-photon WS
Chemical/structural stability (ΔE)	$\Delta E \leq 0.2$ eV	$\Delta E \leq 0.2$ eV
Bandgap (E_{gap})	$1.5 \leq E_{gap} \leq 3$ eV	$1.3 \leq E_{gap} \leq 3$ eV
Band edges (VB_{edge}, CB_{edge})	$VB_{edge} > 1.23$ eV $CB_{edge} < 0$ eV	$VB_{edge}^{anode} > 1.23$ eV $CB_{edge}^{cathode} < 0$ eV $VB_{edge}^{cathode} > CB_{edge}^{anode}$

Tandem cell efficiency



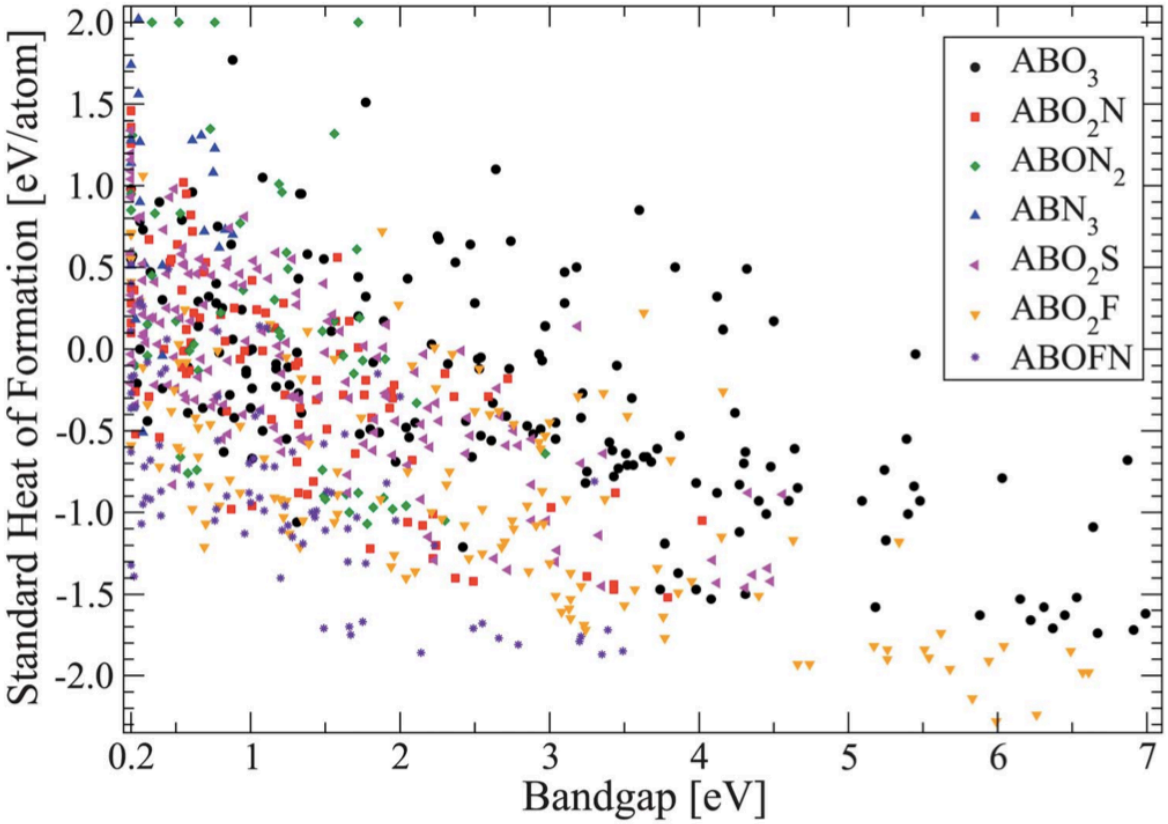


(J. R. Bolton et al., *Nature* 1985.)

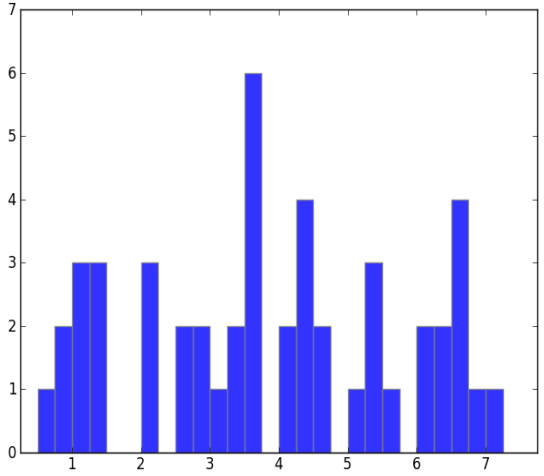
(M. G. Walter et al., *Chem Rev* **110**, 6446, 2010)

(I.E. Castelli, D.D. Landis, K.S. Thygesen, S. Dahl, I. Chorkendorff, T.F. Jaramillo, and K.W. Jacobsen, *Energy & Environmental Science*, doi: 10.1039/c2ee22341d)

Perovskites: Stability vs. band gap



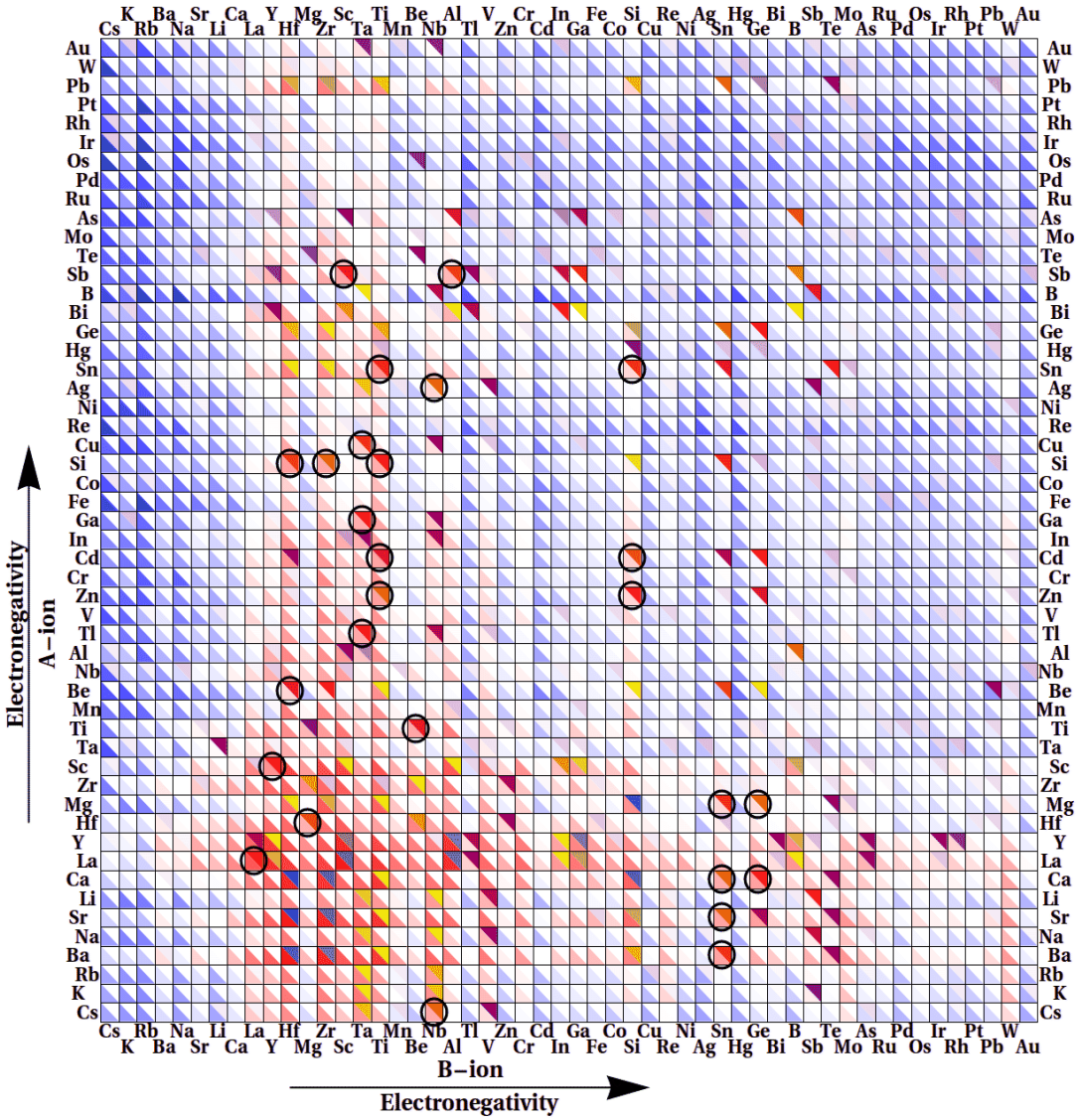
~19000 materials



Bandgap distribution for ABO_3

\+ many highly stable metallic systems

Perovskites: ABO_3 candidates



Stability:
formation energy < 0.2 eV;
Light absorption:
1.5 eV < band gap < 3 eV.

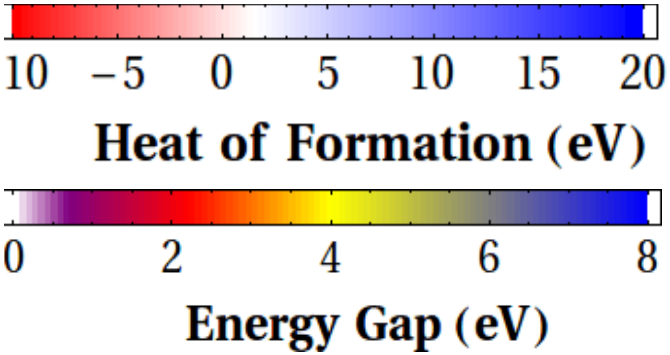
43 oxides

↓ Extended stability

13 oxides

↓ Level alignment

10 oxides

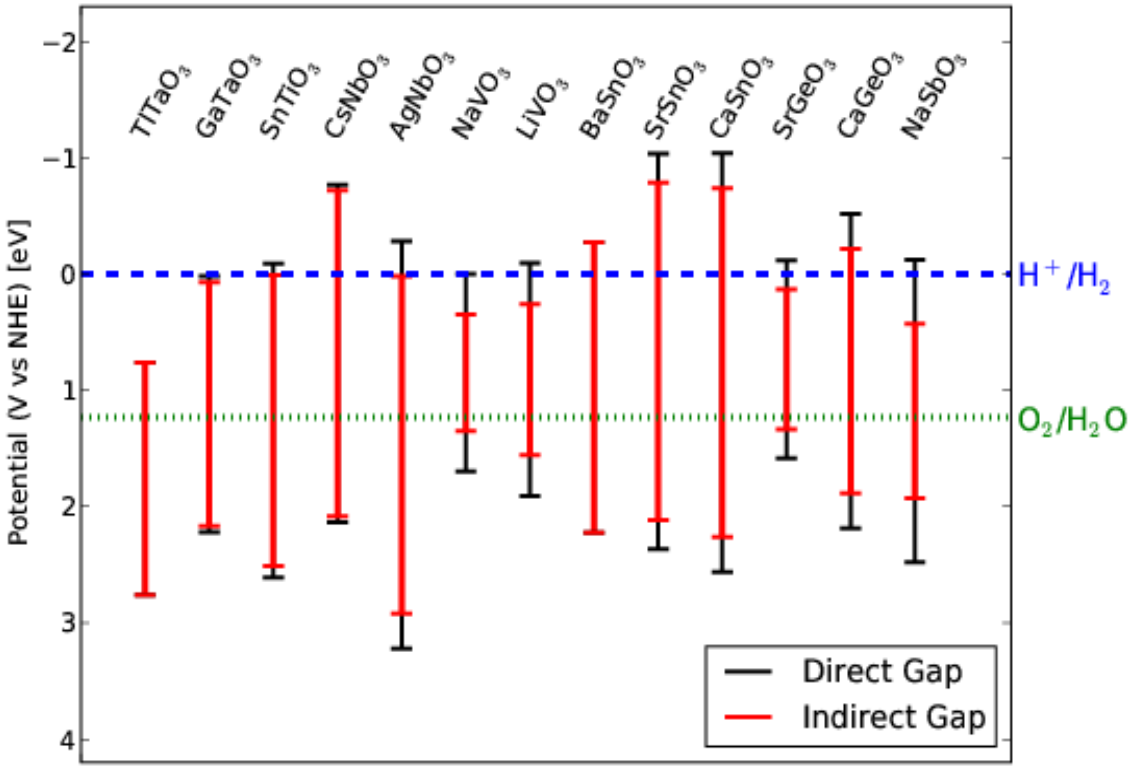


One-photon water splitting – oxide candidates

Empirical formula for the conduction band relative to NHE:

Butler and Ginley (1978)

$$E_C = (\chi_A \chi_B \chi_O{}^3)^{1/5} - 1/2 E_{gap} + E_0$$



$AgNbO_3$ and **$BaSnO_3$** known.

$AgNbO_3$ works!

$BaSnO_3$ defect-induced recombination

$SrSnO_3$ and **$CaSnO_3$**:

known in orthorhombic perovskite

→ too large gaps

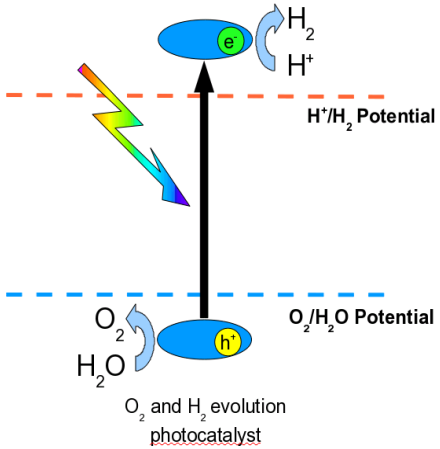
10 materials identified

Oxides, oxynitrides, oxysulfides, oxyfluorides, oxyfluornitrides

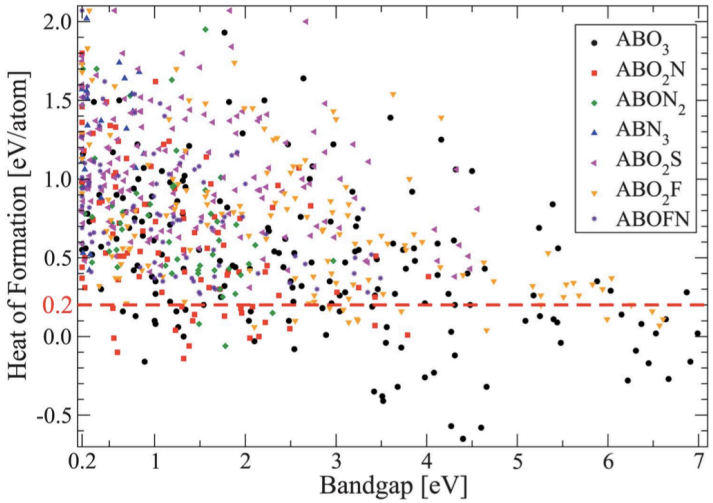
Materials candidates:

- ABO_3 :10
- ABO_2N :5 — $BaTaO_2N$, $SrTaO_2N$, $CaTaO_2N$, $LaTiO_2N$ (known); $MgTaO_2N$ (unknown)
- $ABON_2$:2 — $LaTaON_2$ (known); $YTaON_2$ (unknown)
- ABN_3 :0
- ABO_2S :0
- ABO_2F :3
- ABOFN :0

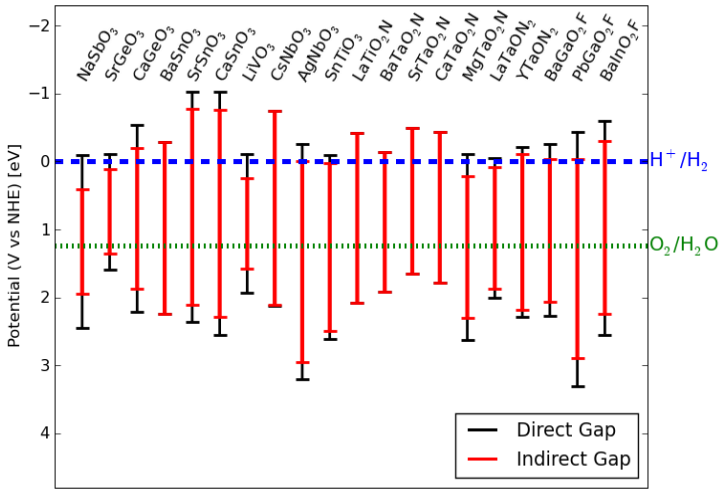
One-photon water splitting



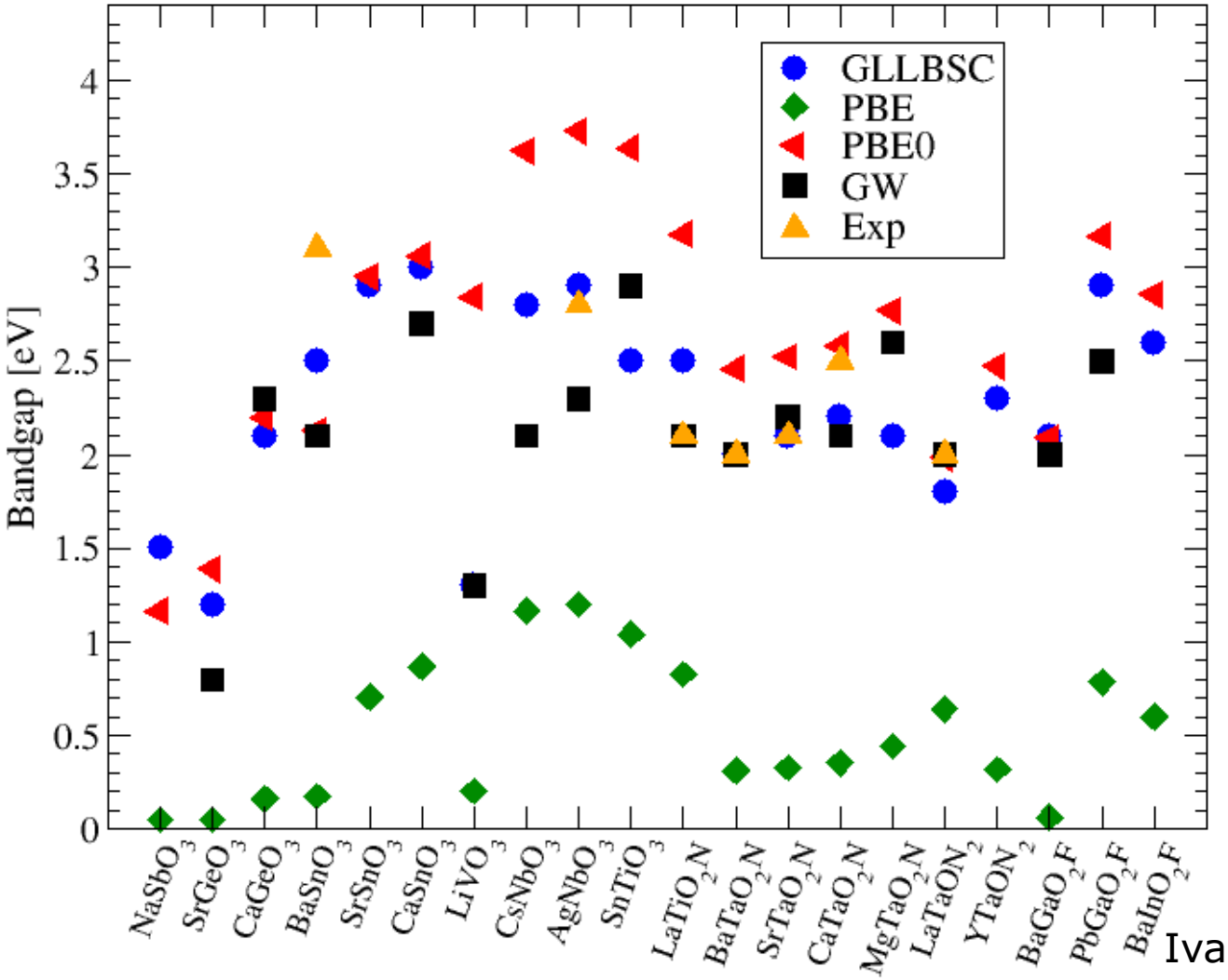
~19000 materials



20 candidate materials



Further analysis of candidate materials: bandgap calculations



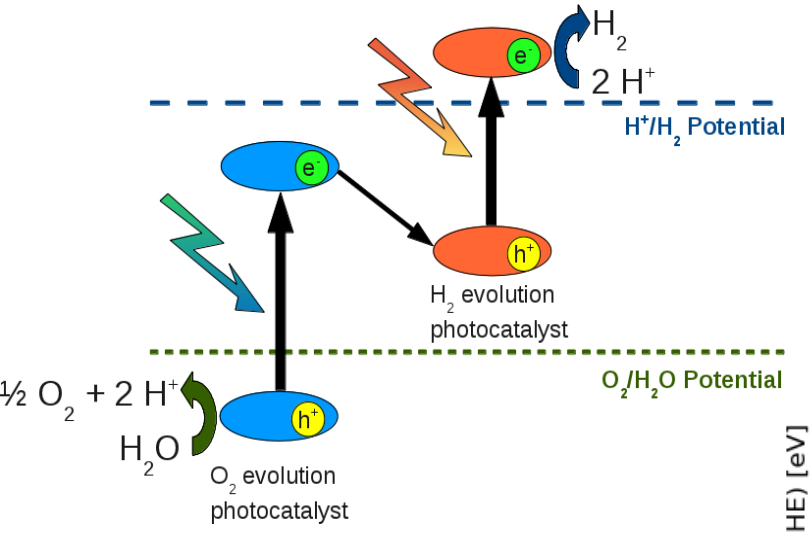
PBE0: hybrid

GW: G_0W_0 +plasmon pole

In the future: Absorption spectra

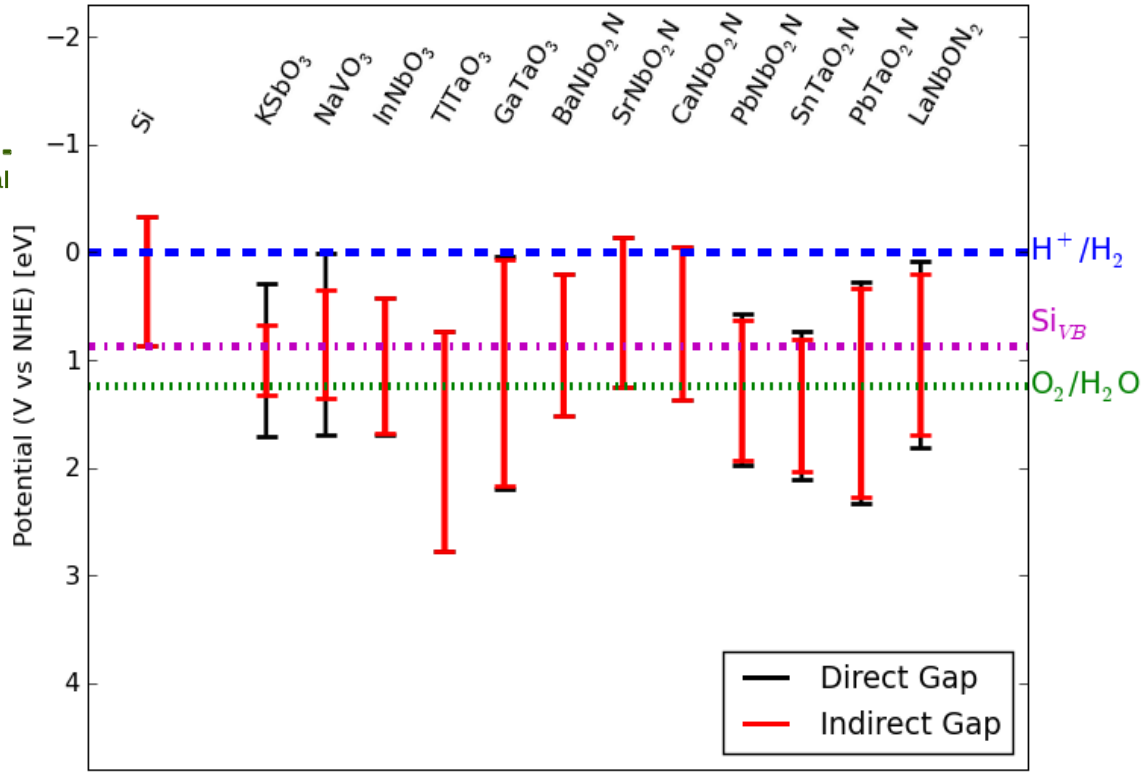
Ivano Castelli, Falco Hüser

Tandem cell water splitting: Screening results



$E_{form} < 0.2$

$1.3 < E_{gap} < 3$ eV



12 candidates

+ 20 from overall WS

I.E. Castelli, D.D. Landis, K.S. Thygesen, S. Dahl, I. Chorkendorff, T.F. Jaramillo, and K.W. Jacobsen, *Energy & Environmental Science*, **5**, 9034 (2012).

$LaTiO_2N$ now under experimental investigation at CINF/CASE/DTU.

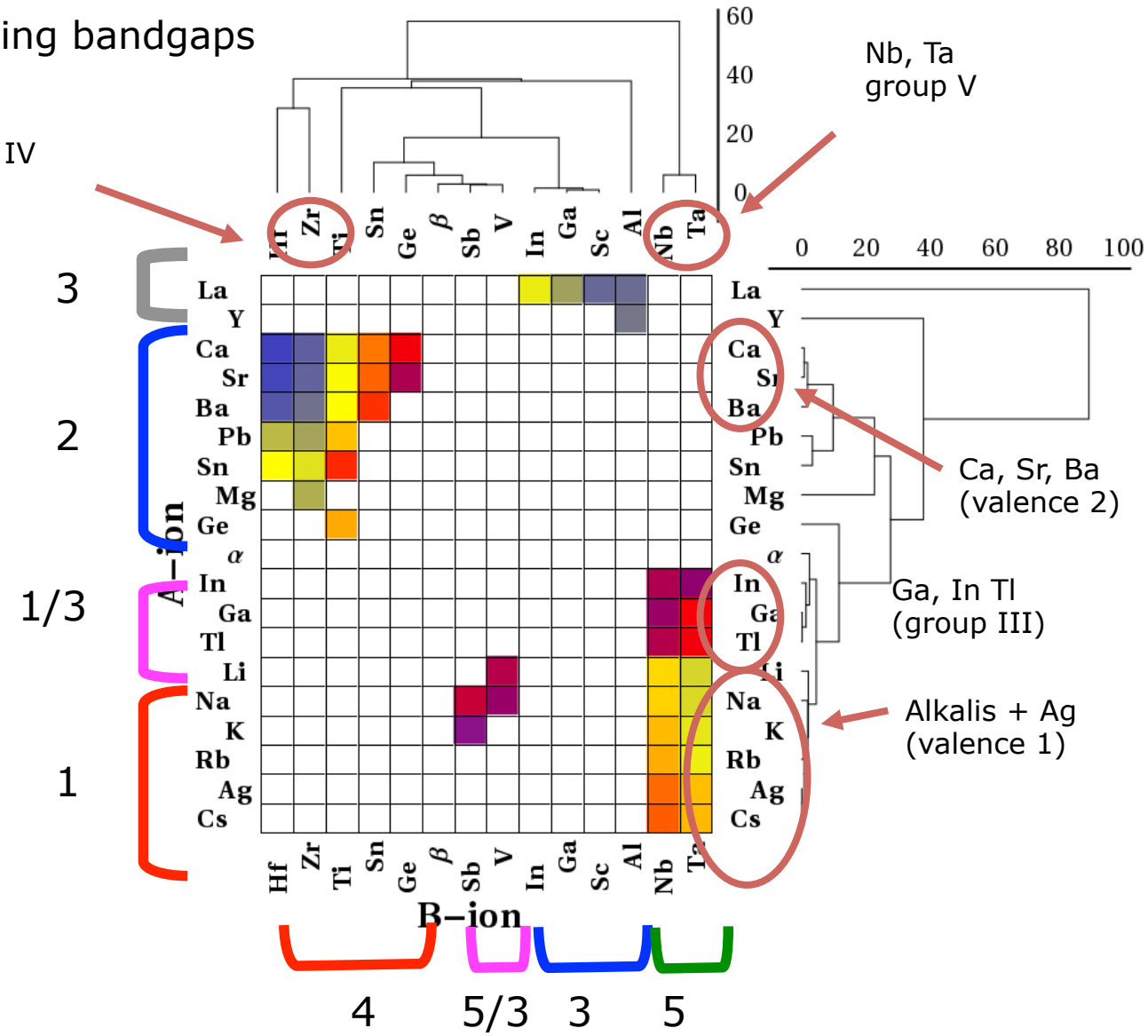
Data mining

- Understanding
  - Wealth of information available
  - Many (and identifying new) chemical concepts and rules unused
    - Valence
    - Metal, if odd number of electrons in unit cell
    - Stability size rule: tolerance factor ~ 1
- Prediction
  - Use information from one screening to make subsequent ones more efficient
    - Maybe based on understanding
    - Maybe not – “machine learning”

Clustering based on bandgap for ABO_3: rediscovering valence

46 stable ABO_3 showing bandgaps

Clusters follow the valences of the elements.



Learning on ABO_3 – predicting for ABO_2N

Probability for a perovskite with a given A-ion (or B-ion) to be stable and have a bandgap considering only systems obeying the two rules:

Odd/even rule: only a system with even number of electrons in the unit cell can form a semiconductor/insulator.

Valence rule: the sum of the possible valences of the two metals and of the anions have to be equal in absolute value for a semiconductor to be possible.

ABO_3

A-ion	Probability [%]	B-ion	Probability [%]
Na	60.0	Ta	34.6
Sr	50.0	Nb	34.6
Ca	50.0	Zr	33.3
Li	50.0	Hf	27.8
K	50.0	Ti	26.1
Ba	40.0	Sn	13.6
Cs	33.3	Al	10.5
Rb	33.3	Ge	9.1
Ag	33.3	Sb	7.7
La	21.1	V	7.4
Sn	13.6	Sc	5.2
Pb	13.6	Ga	5.2
Tl	10.5	In	5.2
In	10.5		
Ga	10.5		
Mg	10.0		
Y	5.3		
Ge	4.5		

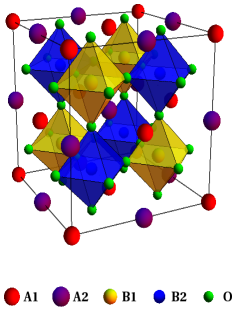
Prediction →

ABO_2N

A-ion	B-ion	Stable?	Bandgap [eV]
Ca	Ta	✓	2.2
Sr	Ta	✓	2.1
Ca	Nb	✓	1.4
Sr	Nb	✓	1.4
Ba	Ta	✓	2.0
La	Ti	✓	2.5
Ba	Nb	✓	1.3
Pb	Ta	✓	2.0
La	Zr	✓	3.4
Pb	Nb	✓	1.3
La	Hf	✓	3.8
Mg	Ta	✓	2.1
Mg	Nb		1.5
Ca	V		0
Sr	V		0
La	V		0
La	Sn		1.8
Ga	Ti		0
Y	Ti		2.4
In	Ti		0.2
Tl	Ti		0
Ba	V		0
La	Si		3.0
La	Ge		0.2
Ge	Ta		1.8
Sn	Ta	✓	1.2

Towards bandgap engineering: double perovskites

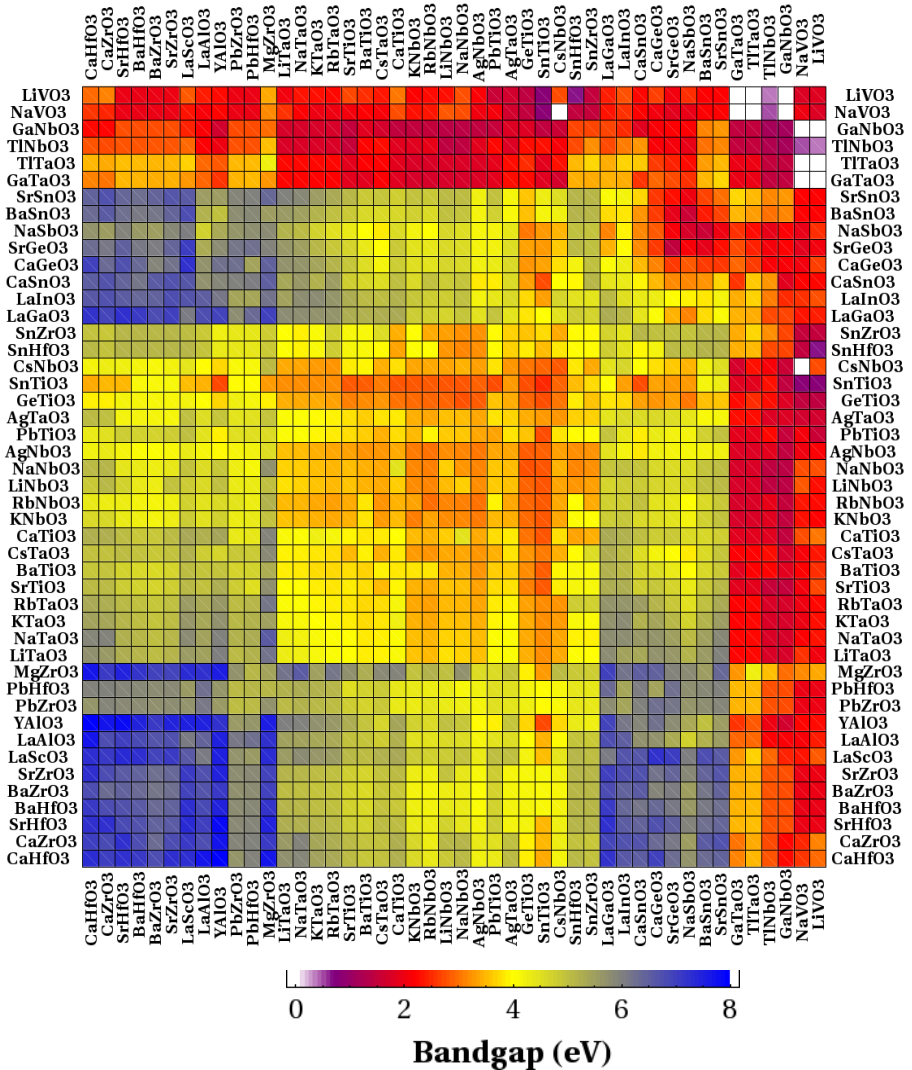
Double perovskite: obtained combining two stable cubic perovskites with a bandgap.



New "design rules":

- Double perovskite has average of perovskite gaps
- But, for B1 p-metal and B2 d-metal gap is significantly increased (but typically > 4 eV)
- Several hundred new potential water splitting materials discovered

Calculated bandgaps



Towards bandgap engineering: layered perovskites + ICSD

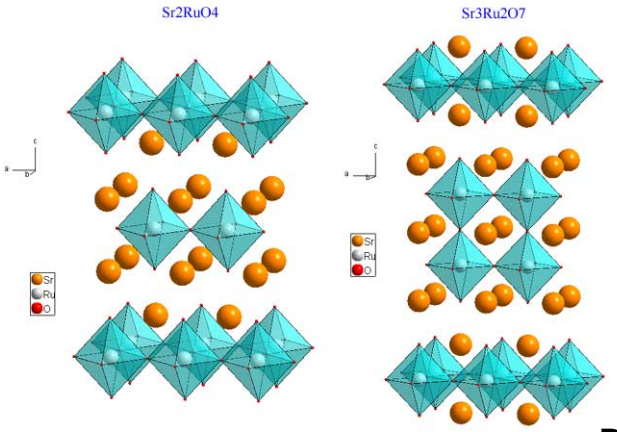
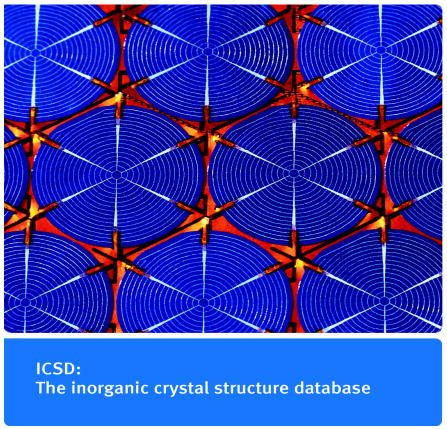
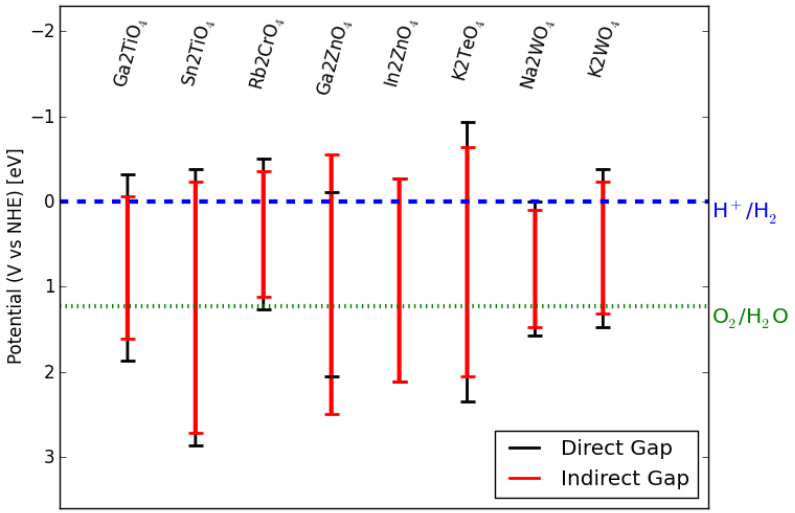
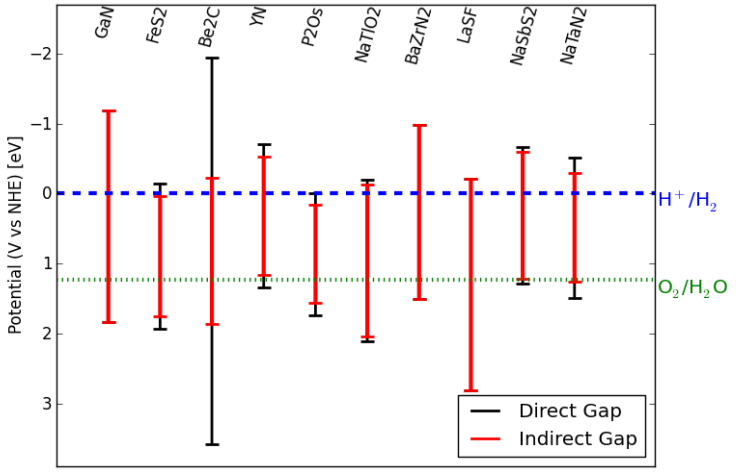


Figure from Cava lab, Princeton



Preliminary screenings:





Collaboration with Materials Project, Anubhav Jain, Gerbrand Ceder, Bandgaps calculated for pre-optimized structures

CMR website for perovskites

Computational Materials Repository

Hide search box

Do not forget to press **update matrix** after changing the selection!
If there is an error - it means that the dataset is already being calculated! Please wait a moments and try again.

Chose a data set:	ABO3 (2704)
Width:	800
Height:	1200
X axis ticks:	B
Y axis ticks:	automatically selected
X sort order:	Electronegativity (Paulin
Y sort order:	Electronegativity (Paulin
Action on Click:	show band edges

References:
- ABN (3)
- ABO (20)
- AN (50)
- AO (52)
- AON (35)
- default (3)
- mbulk (52)

	Value field:	Colors:
Triangle 1: (top-right)	gllbsc_ind-gap (eV)	0->white,0.7->purple,2.2->re
Triangle 2: (bottom-left)	heat_of_formation (eV)	min->red,0.3->white,4->blue
Triangle 3:		
Triangle 4:		

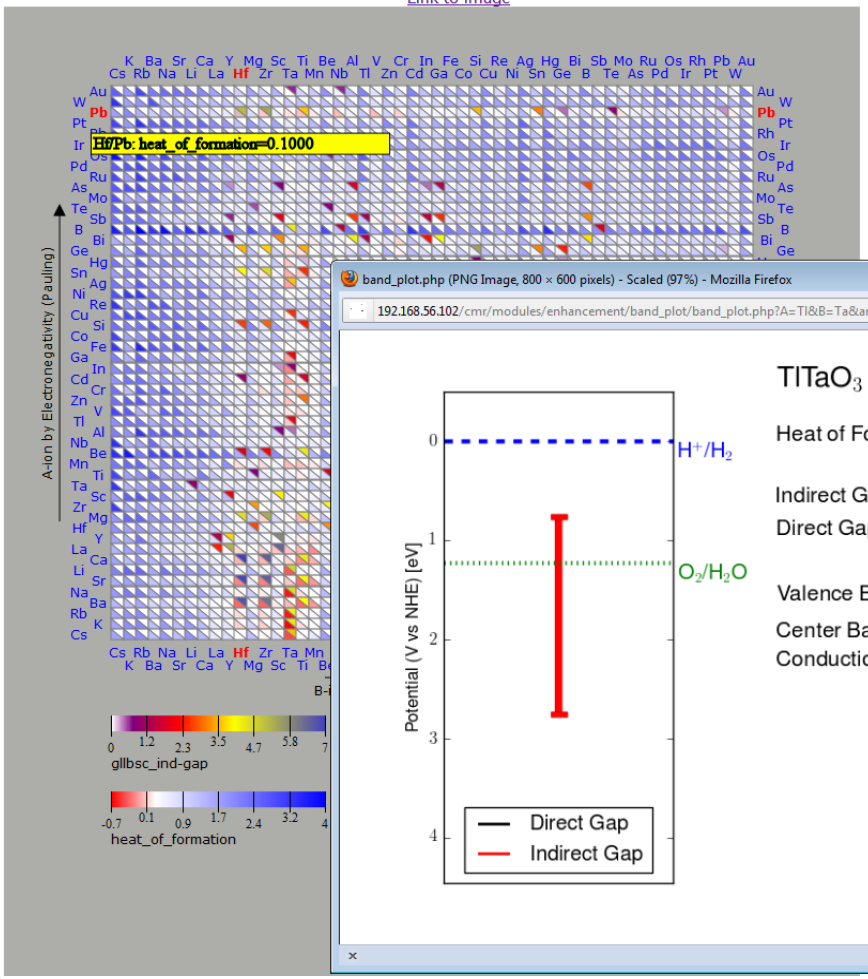
Examples for the color choice:

```
0->white,1->red,7->blue

0->white,0.9->red,2.2->green,4->yellow,8->blue

-100->blue,100->red
```

Valid color names are black, blue, cyan, green, gray, green, lightblue, pink, red, purple, white, yellow. Please note that the values must be in **increasing** order.

Update matrix

Link to image



http://cmr.fysik.dtu.dk - the database

http://wiki.fysik.dtu.dk/cmr - the software, publication to appear in Comp. Sci. Eng.

Optimized Bayesian Error Estimation xc-Functional: BEEF-vdW

$$E_{xc} = \sum_{m=0} a_m E_m^{\text{GGA-x}} + \alpha_c E^{\text{LDA-c}} + (1-\alpha_c) E^{\text{PBE-c}} + E^{\text{nl-c}}$$

- Linear model
  - GGA exchange expanded on orthogonal Legendre polynomials
  - Non-local correlation included as in vdW-DF2
- Databases
  - Molecules (fragmentation, reaction energies and barriers)
  - Solids (cohesive energies, lattice constants)
  - Chemisorption energies
  - Binding energies for non-covalently bonded systems
- Important issues
  - Avoid overfitting – Tikhonov regularization, bootstrapping
  - Balancing relative importance of datasets

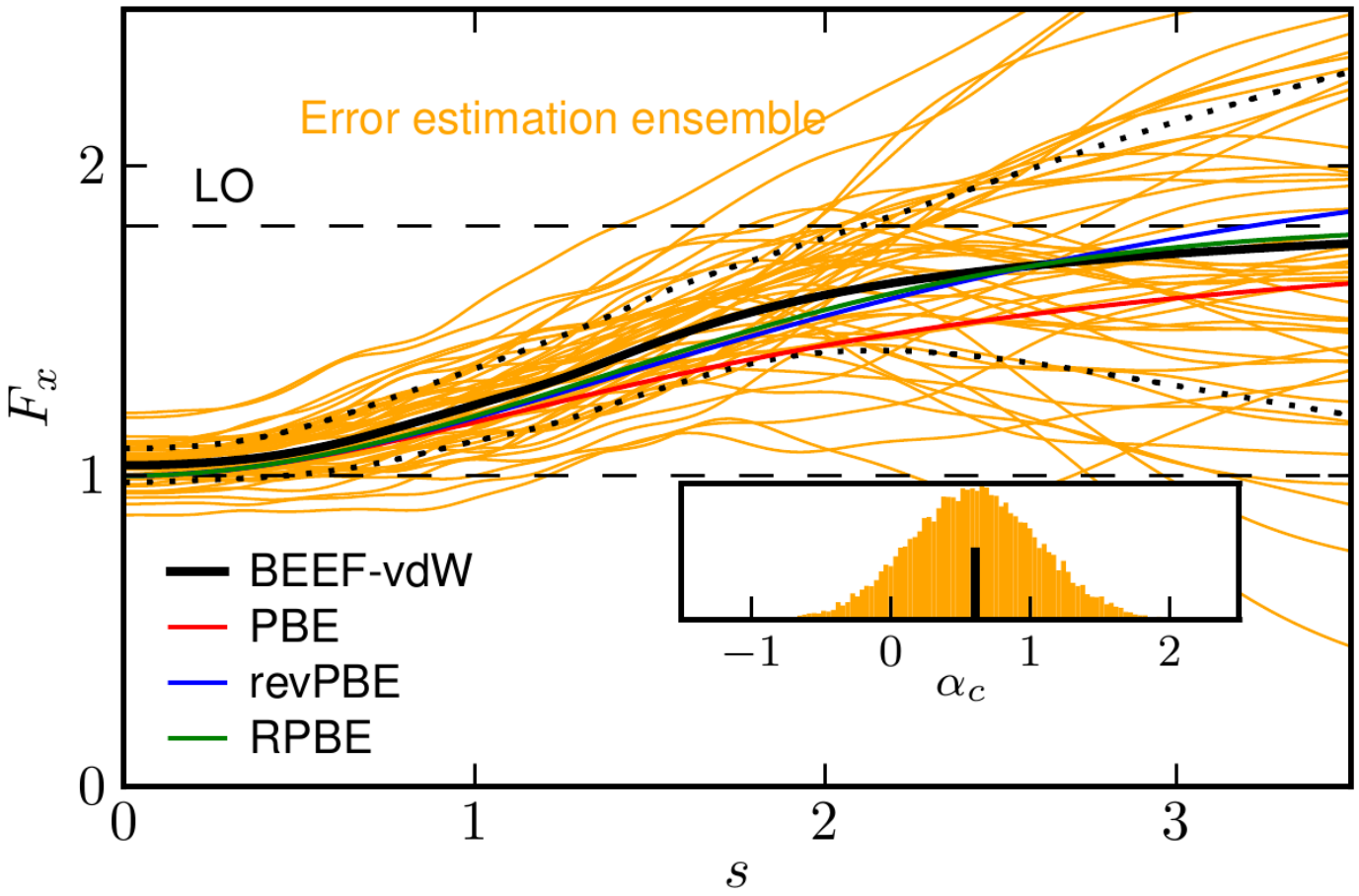
BEEF-vdW:

Jess Wellendorff, Keld Lundgaard, A. Møgelhøj, V. Petzold, D. D. Landis, J. K. Nørskov, T. Bligaard, and K. W. Jacobsen, Physical Review B (Condensed Matter) **85**, (2012).

V. Petzold, T. Bligaard, and K. W. Jacobsen, Top Catal **55**, 402 (2012).

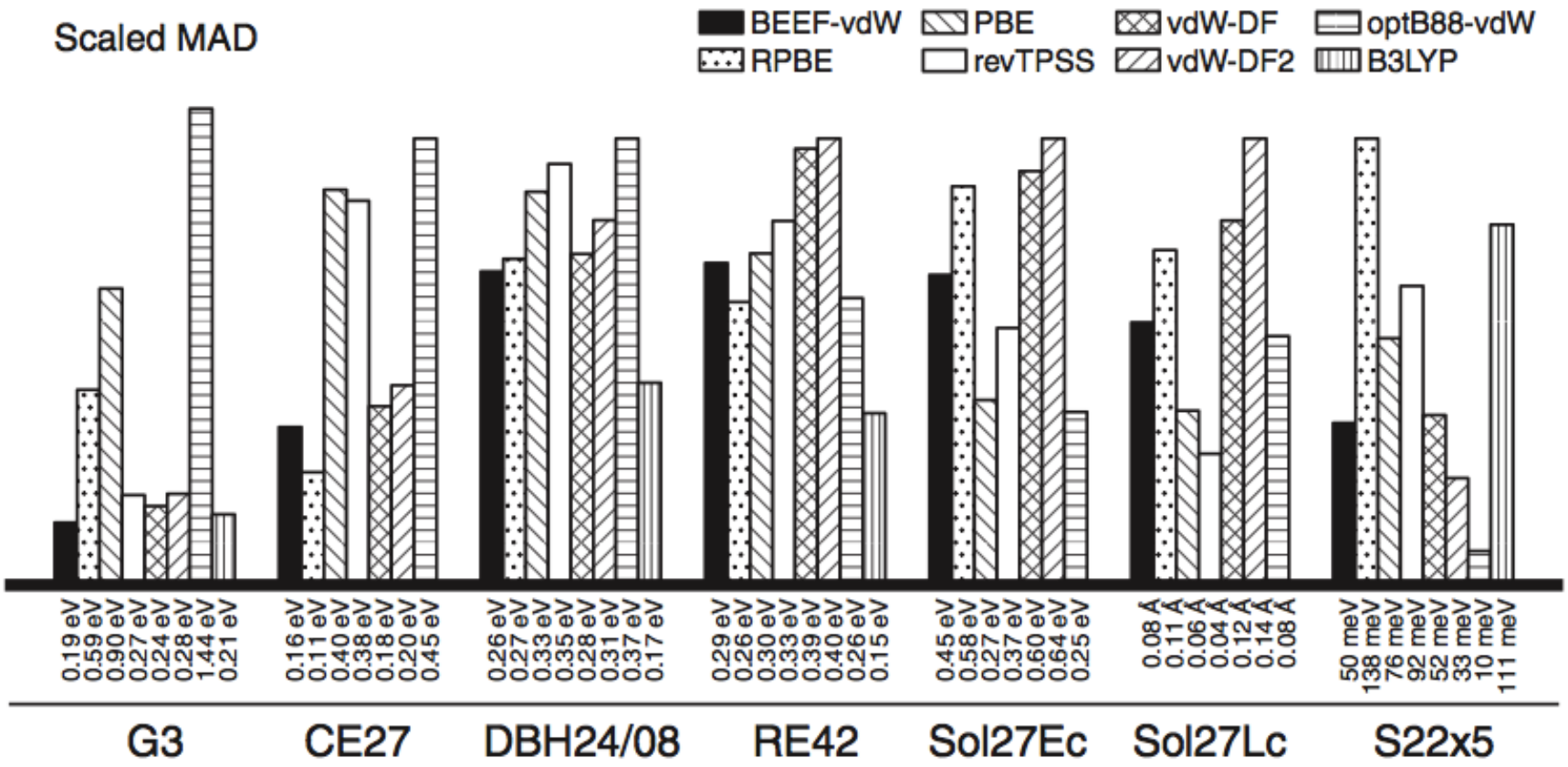
Here is the BEEF(-vdW)

Exchange enhancement factor



Available in the GPAW code including error estimation

Mean Absolute Deviation



G3: molecular formation energies

CE27: chemisorption on TM surfaces

DBH24: gas-phase reaction barriers

RE42: gas-phase reaction energies

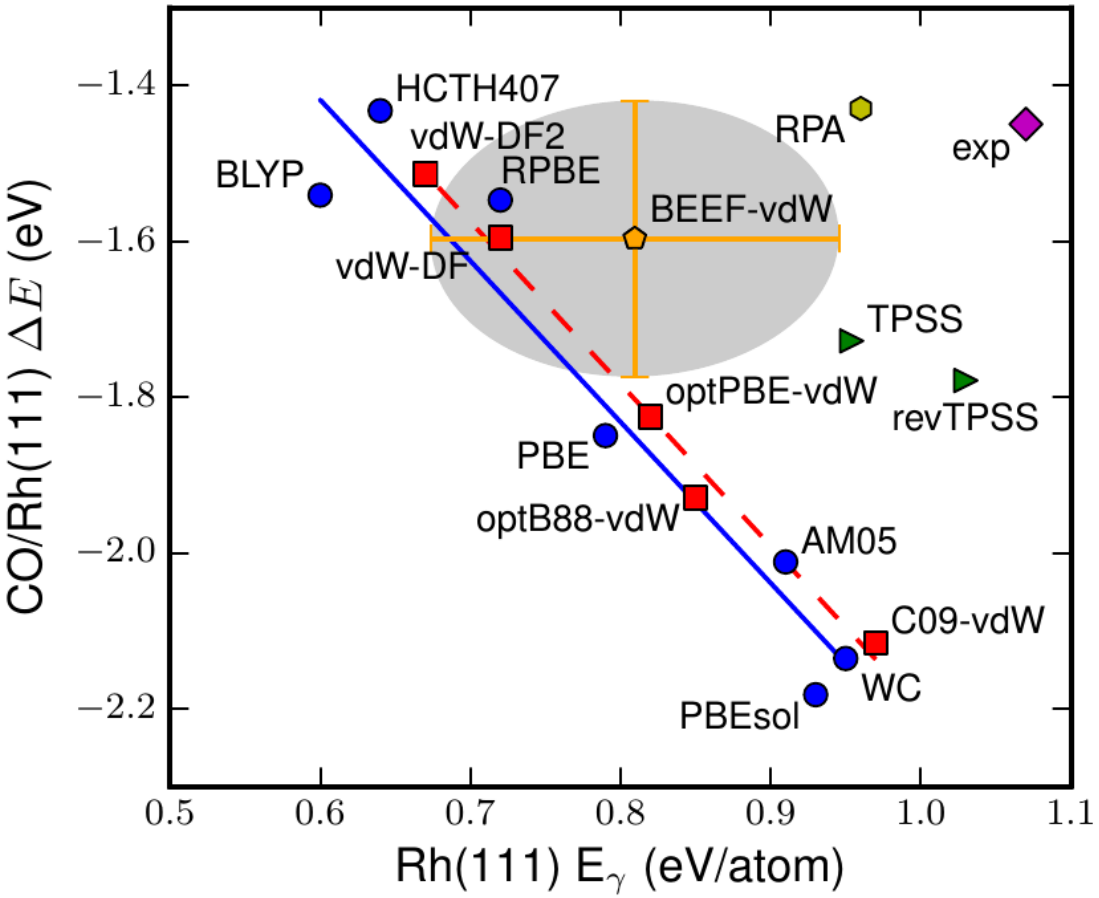
Sol27Ec: solid cohesive energies

Sol27Lc: solid lattice constants

S22x5: non-covalent (vdW) binding

Overall very good performance. “Robust”.

Breaking the "GGA-line"?



CO/Rh(111) adsorption energy vs. the Rh(111) surface energy.

Error bars indicate BEEF-vdW ensemble error estimates.

Purple diamond indicates experimental result.

Coming up: Functional at meta-GGA level.

Original plot from:
L. Schimka, J. Harl, A. Stroppa, A. Grüneis, M. Marsman, F. Mittendorfer, and G. Kresse, Nat. Mater. 9, 741 (2010).

Data available in CMR

COMPUTATIONAL MATERIALS REPOSITORY

CAMd
Center for Atomic-scale Materials Design

Access to data from the study:
Density functionals for surface science: Exchange-correlation model development with Bayesian error estimation

DTU
Danmarks Tekniske Universitet

HOME | Project description | Details on data

Hide search box

Database: CE27
Sub database:
System name:
Show atomic structure

Functionals:

LDA	PBEsol	optB88-vdW
PBE	WC	optPBE-vdW
BLYP	TPSS	C09-vdW
HCTH407	revTPSS	BEEF-vdW
RPBE	vdW-DF	
AM05	vdW-DF2	

Restrict the result to contain ALL selected atoms:
(If none are chosen all atoms are allowed.)
The maximum number of atoms allowed is limited to 4.

H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar

« 1 2 3 » 10 download as csv

name	atoms	ref_energy	PBE	RPBE	PBEsol	revTPSS	vdW-DF	vdW-DF2	optB88-vdW	BEEF-vdW
H2/Pt(111)	H Pt (1H, 20Pt)	-0.410	-0.976	-0.652	-1.348	-0.816	-0.330	-0.316	-0.777	-0.462
H2/Ni(111)	H Ni (1H, 20Ni)	-0.980	-1.131	-0.786	-1.526	-1.108	-0.581	-0.530	-0.996	-0.687
H2/Ni(100)	H Ni (1H, 20Ni)	-0.930	-1.053	-0.737	-1.519	-1.137	-0.439	-0.338	-0.915	-0.602
H2/Rh(111)	H Rh (1H, 20Rh)	-0.810	-1.067	-0.725	-1.431	-0.988	-0.482	-0.423	-0.882	-0.618
H2/Pd(111)	H Pd (1H, 20Pd)	-0.910	-1.117	-0.806	-1.503	-0.972	-0.491	-0.465	-0.941	-0.627
H2/Ir(111)	H Ir (1H, 20Ir)	-0.550	-0.852	-0.535	-1.250	-0.836	-0.283	-0.247	-0.707	-0.426
H2/Co(0001)	Co H (20Co, 1H)	-0.690	-1.131	-0.811	-1.516	-1.128	-0.602	-0.569	-1.006	-0.699
H2/Ru(0001)	H Ru (1H, 20Ru)	-1.040	-1.197	-0.884	-1.555	-1.192	-0.610	-0.591	-1.014	-0.739
N2/Fe(100)	Fe N (20Fe, 2N)	-2.300	-2.885	-2.050	-3.953	-3.386	-2.138	-2.088	-3.190	-1.986
NO/Ni(100)	Ni O (20Ni, 1O)	-3.990	-4.533	-3.889	-5.297	-4.929	-4.045	-3.982	-4.894	-4.060

http://cmr.fysik.dtu.dk

Outlook

- Computational Materials Repository
  - MGI – much more software development needed
  - A GPL standard for software and data?
- Water splitting materials screening
  - Tailoring of bandgaps
  - Additional important factors
    - Carrier mobilities
    - Catalysis
- XC functional development
  - Important for efficient calculations
  - Much larger expt/comp databases needed – coupled cluster/RPA+more – more systematic development
  - More sophisticated machine learning techniques

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Tom Jaramillo

Argonne Nat'l Lab:
Jeff Greeley

Univ. of Chicago:
Svetlozar Nestorov

CAMd Center for Atomic-scale Materials Design

LUNDBECKFONDEN

CASE Catalysis for Sustainable Energy

neec Center on Nanostructuring for Efficient Energy Conversion

DCSC

References

Computational Materials Repository

The database: http://cmr.fysik.dtu.dk

The software: http://wiki.fysik.dtu.dk/cmr - pubilcation to appear in Computing in Science and Engineering

Optimized xc-functionals

J. Wellendorff, K. Lundgaard, A. Møgelhøj, V. Petzold, D. D. Landis, J. K. Nørskov, T. Bligaard, and K. W. Jacobsen, Physical Review B (Condensed Matter) **85**, (2012).

V. Petzold, T. Bligaard, and K. W. Jacobsen, Top Catal **55**, 402 (2012).

J. J. Mortensen, K. Kaasbjerg, S. L. Frederiksen, J. K. Nørskov, J. P. Sethna, and K. W. Jacobsen, Phys Rev Lett **95**, 216401 (2005).

Watersplitting

I. E. Castelli, T. Olsen, S. Datta, D. D. Landis, S. Dahl, K. S. Thygesen, and K. W. Jacobsen, *Energy & Environmental Science,* **5**, 5814 (2012)

I.E. Castelli, D.D. Landis, K.S. Thygesen, S. Dahl, I. Chorkendorff, T.F. Jaramillo, and K.W. Jacobsen, *Energy & Environmental Science*, **5**, 9034 (2012).

Bandgap calculations with GLLB

The GLLB xc-functional (Gritsenko, van Leeuwen, van Lenthe and Baerends):

$$E_g^{QP} = E_g^{KS} + \Delta_{xc}$$

Derivative discontinuity

Screening + response

$$v_x(\mathbf{r}) = v_S(\mathbf{r}) + v_{resp}(\mathbf{r})$$

$$v_S(\mathbf{r}) = \frac{2\epsilon_x^{GGA}(\mathbf{r}; n)}{n(\mathbf{r})}$$

$$v_{resp}(\mathbf{r}) = \sum_{i}^{occ} K[n]\sqrt{\varepsilon_r - \varepsilon_i}\frac{|\psi_i(\mathbf{r})|^2}{n(\mathbf{r})}$$

$$\Delta_{x,resp}(\mathbf{r}) = \sum_{i}^{N} K\left(\sqrt{\varepsilon_{N+1} - \varepsilon_i} - \sqrt{\varepsilon_N - \varepsilon_i}\right)\frac{|\psi_i(\mathbf{r})|^2}{n(\mathbf{r})}$$

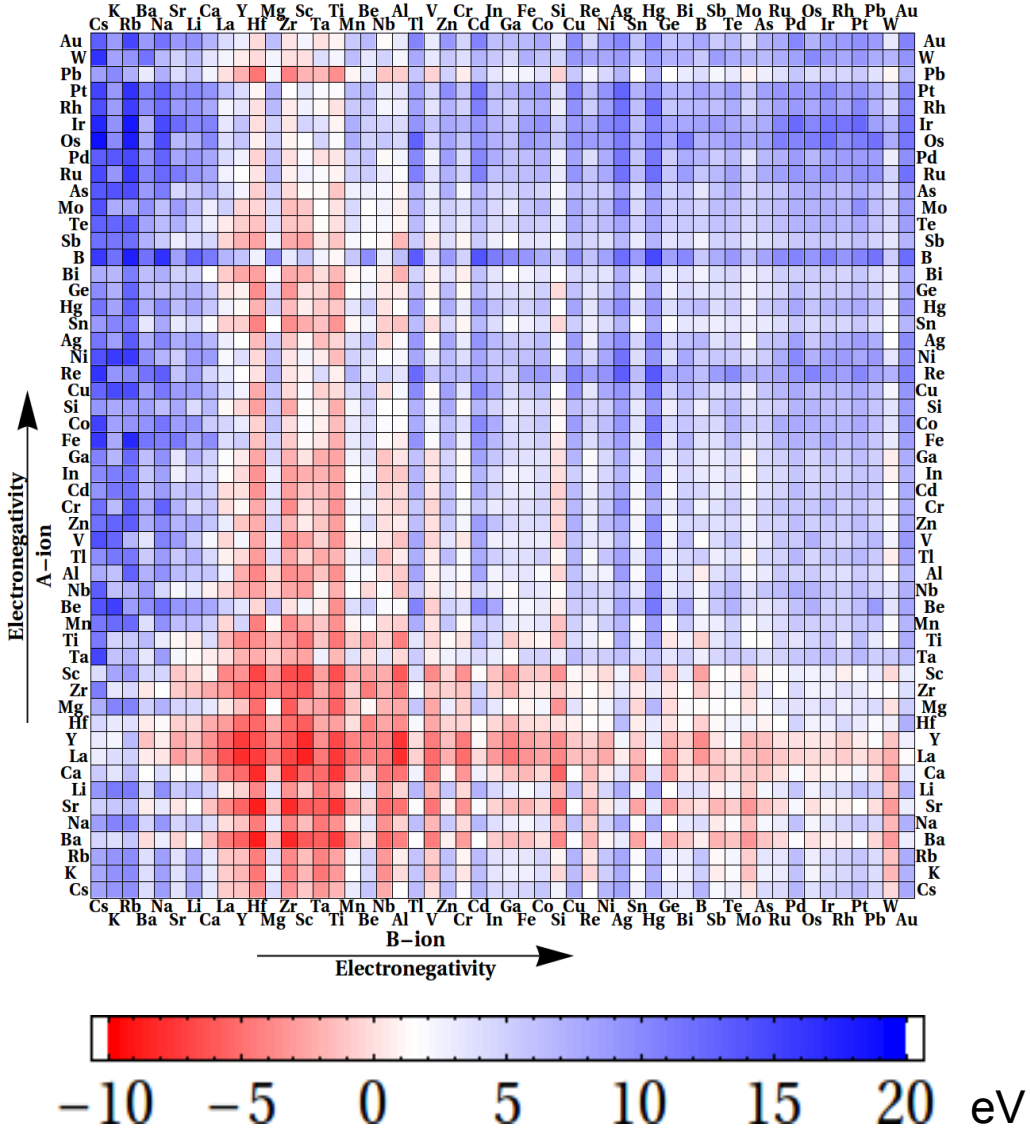
Material	E_g^{KS} (LDA)	E_g^{KS}	Δ_{xc}	E_g^{QP}	Exp.
C	4.09	4.14	1.27	5.41	5.48
Si	0.443	0.68	0.32	1.00	1.17
GaAs	0.36	0.79	0.25	1.04	1.63
AlAs	1.34	1.67	0.82	2.49	2.32
LiF	8.775	10.87	4.09	14.96	14.2
Ar	8.18	10.28	4.69	14.97	14.2

GLLB-SC: Screening exchange-correlation from PBEsol

First description: Gritsenko *et al.*, *Phys. Rev. A* **51**, 1944 (1995).

Implemented in GPAW: Kuisma *et al.*, *Phys. Rev. B* **82**, 115106 (2010).

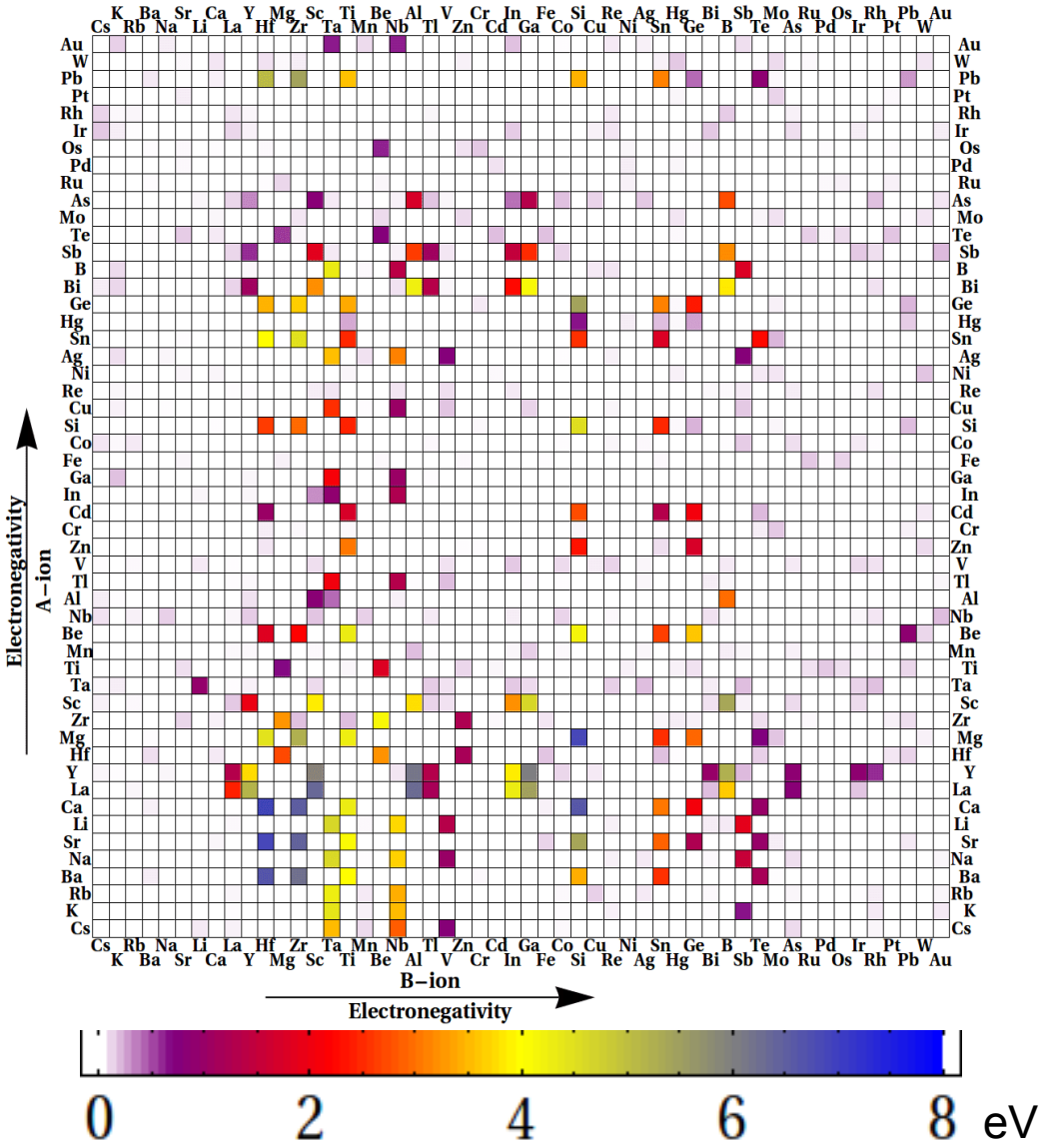
Perovskites: Heat of formation



Stable materials:

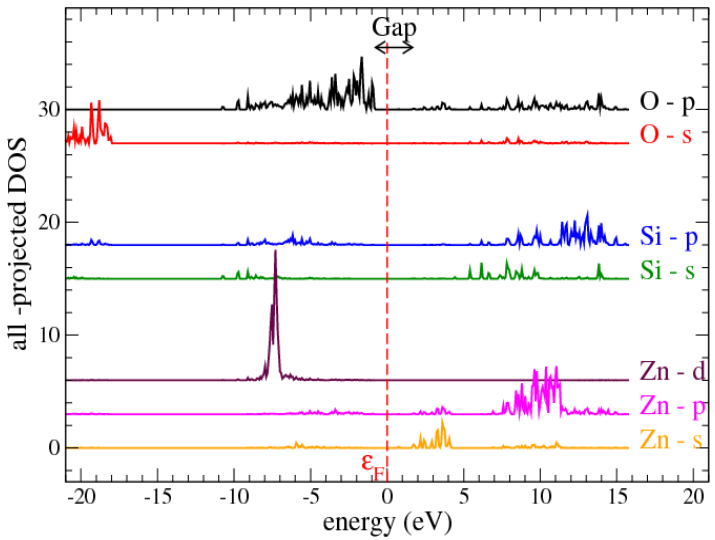
- Low electronegativity
- Sum of oxidation numbers = 6
- Geometric tolerance factor ~1

Perovskites: Band gaps



Most perovskites are metallic or low-gap semiconductors

Analyzing gap formation



$ZnSiO_3$

Formation energy = -1 eV;

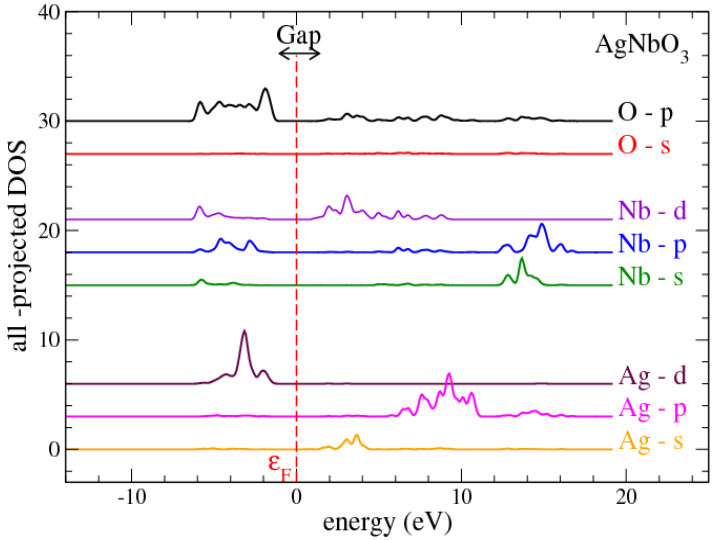
Band gap = 2.4 eV.

Valence band:

O – p orbitals (too deep for water-splitting);

Conduction band:

Zn – s orbitals.



$AgNbO_3$

Formation energy = -0.6 eV;

Band gap = 3.0 eV.

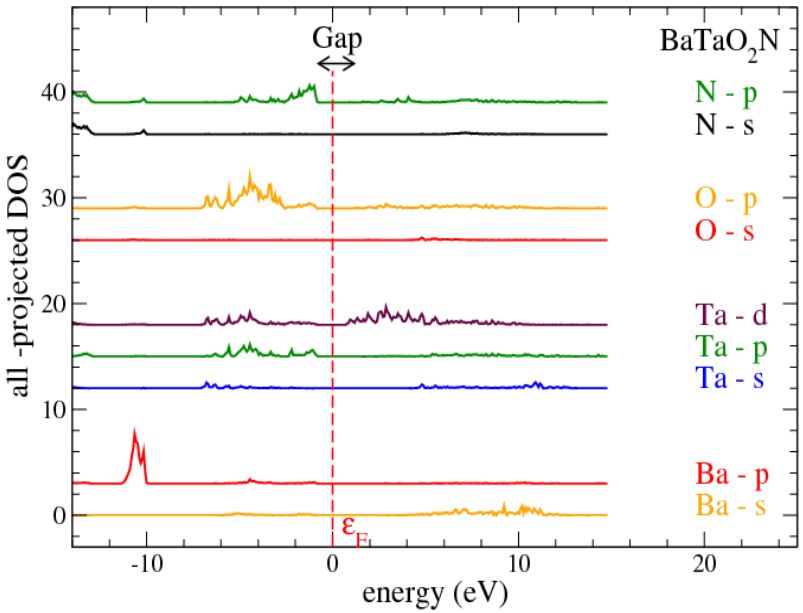
Valence band:

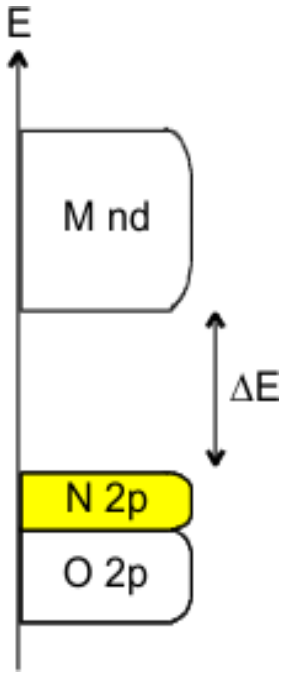
Ag – d and **O – p orbitals**;

Conduction band:

Nb – d orbitals.

Oxynitrides





$BaTaO_2N$

Formation energy = -6.3 eV;

Band gap = 2.0 eV.

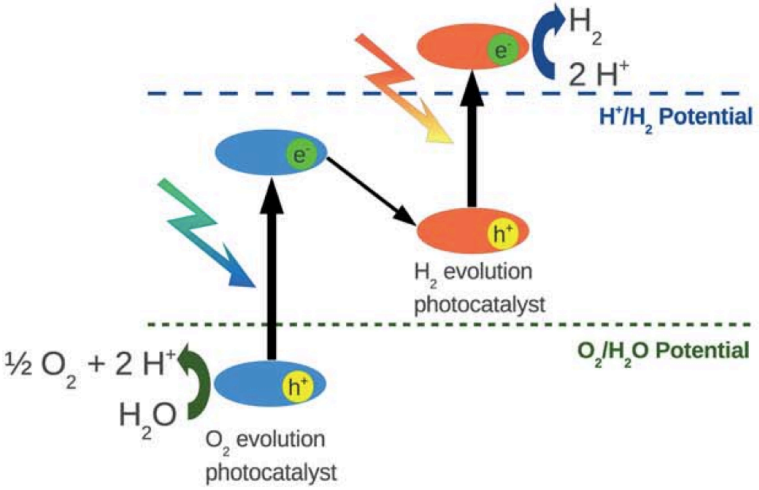
Valence band:

Ta – p and **N – p orbitals**;

Conduction band:

Ta – d orbitals.

Tandem cell principle



Two semiconductors – two photons

- SC 1: Hole for oxygen evolution
- SC 2: Electron fro hydrogen evolution

Requirements:

- structural/chemical stability;

- two visible light harvests (optimal gaps: 1.1 eV and 1.7 eV);

- band edges that match with oxygen and hydrogen potentials;

- Small overlap between the semiconductors band edges for the electron transfer reaction.

H_2 photocatalyst: Si

O_2 photocatalyst: screening

Extended stability analysis

Pool of reference systems:

- Single metal bulk: A(s) and B(s)
- Single metal oxides: A_xO_y(s) (and nitrides, sulfides, …)
- Bimetallic oxides $A_xB_yO_z$(s)

  Obtained from ICSD

  - Composition and structure available experimentally
  - Energy calculated
- Oxygen is taken from water (and hydrogen molecule)

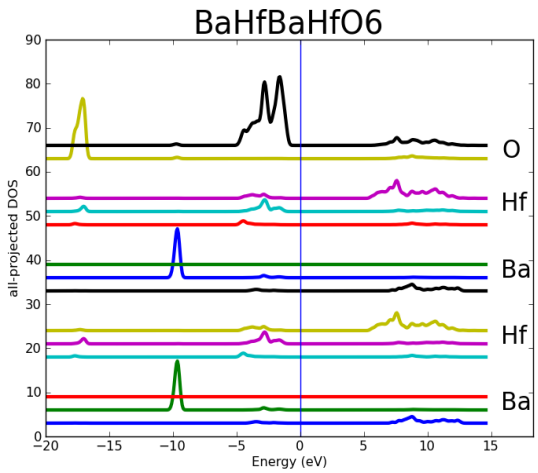
Formation energy:

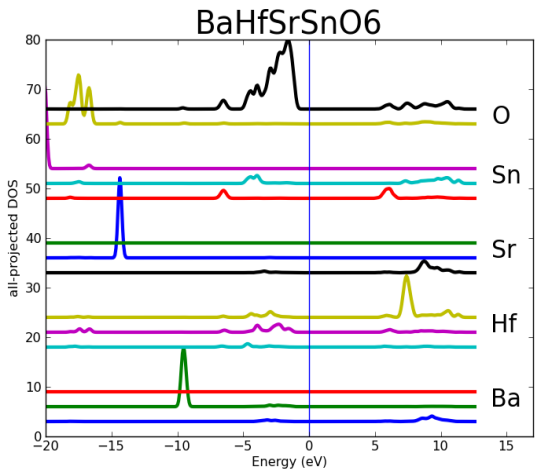
$$\Delta E = \mathrm{ABO_3(s)} - \min_{c_i} \left(c_1 \mathrm{A\,(s)} + c_2 \mathrm{B\,(s)} + c_3 \mathrm{A_xO_y\,(s)} + c_4 \mathrm{B_xO_y\,(s)} + c_5 \mathrm{O} \right)$$

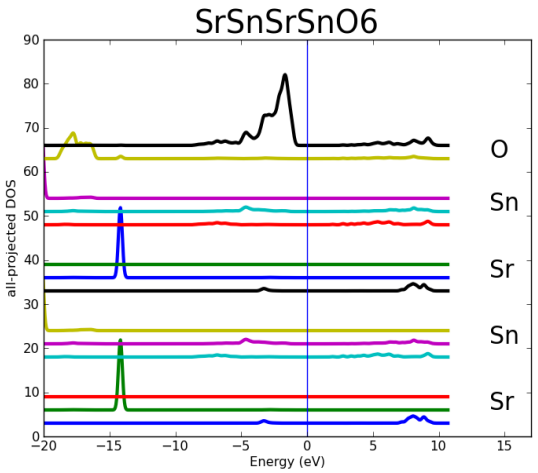
$$c_1 + c_3 = 1\,, \qquad c_2 + c_4 = 1\,, \qquad c_3 + c_4 + c_5 = 3$$

→ Solved by linear programming.

Double perovskite example: $BaHfO_3$, $SrSnO_3$ -> $BaHfSrSnO_6$

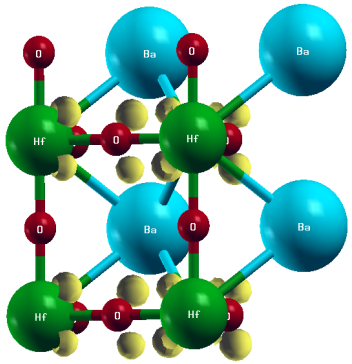


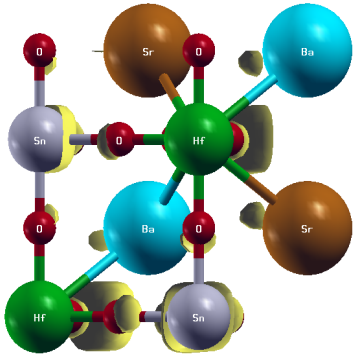


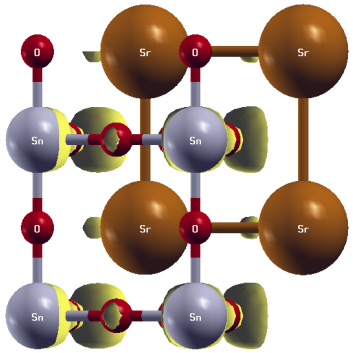


Bandgaps: 6.6 eV 6.3 eV 3.0 eV

<u>Conduction band edge:</u>



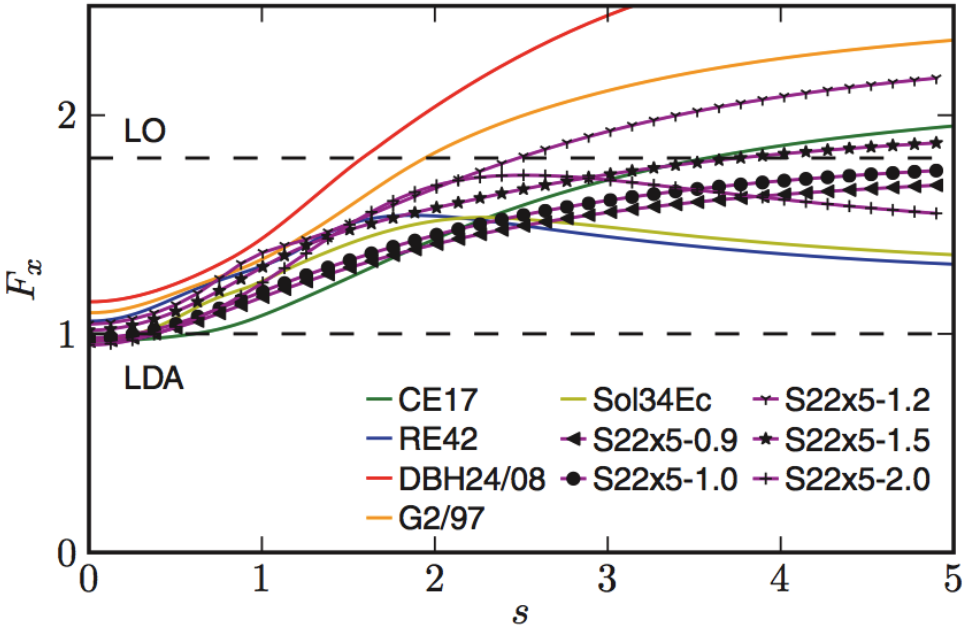


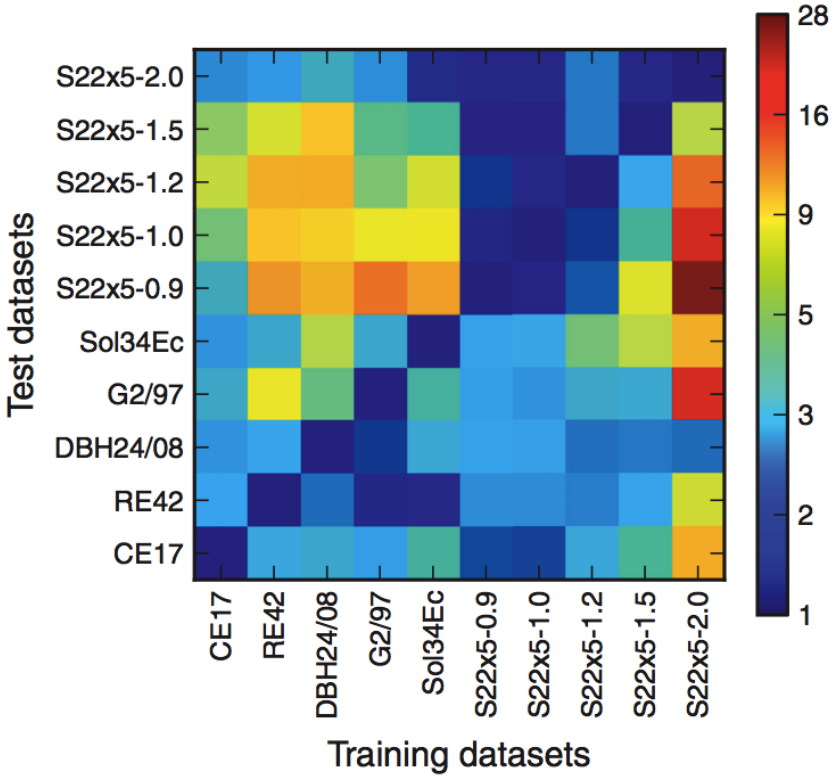


•BaHfO3 •BaHfSrSnO6 •SrSnO3

•Hf(d)-Sn(p) hybridization -> increased bandgap

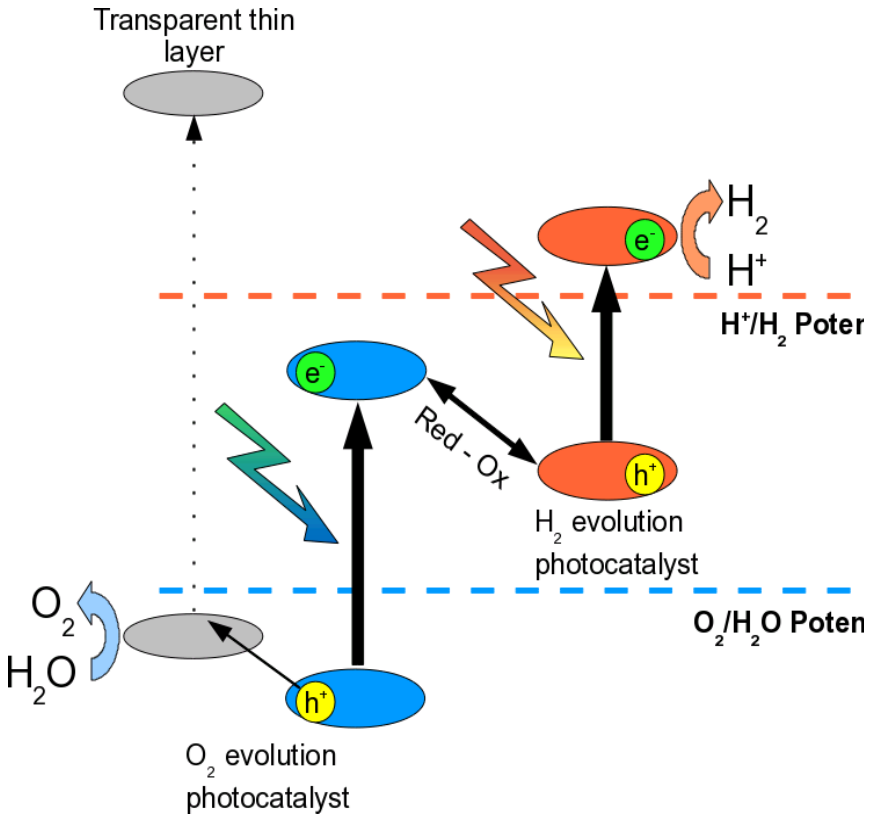
Fitting to individual data sets

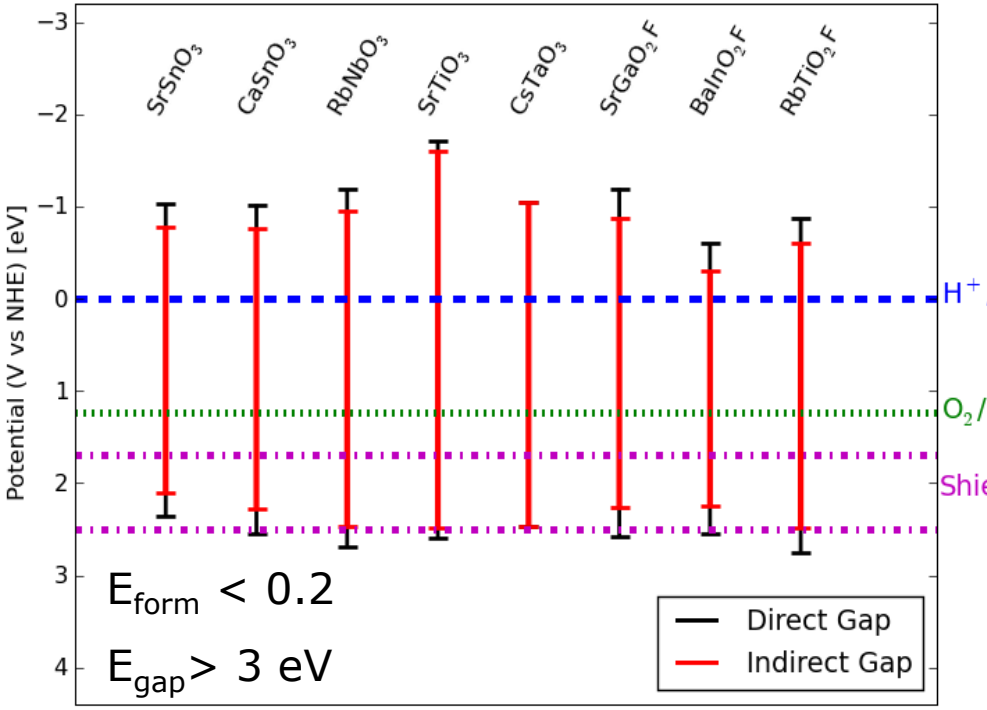




Training conflict between molecules and solids remain.

Transparent protecting shield – photoanode



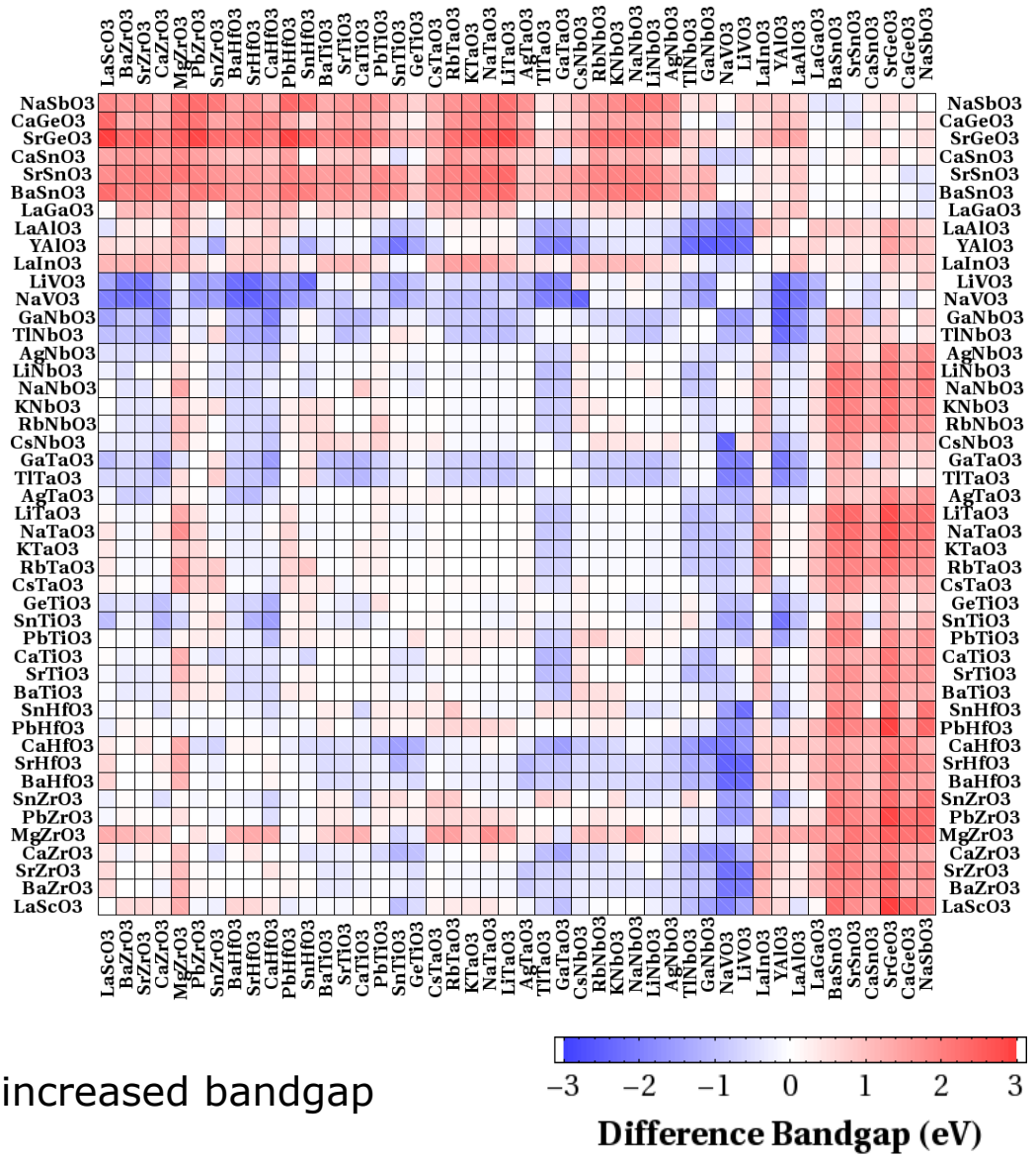


Double perovskites

Difference between the double perovskite bandgap and the average gap coming from the two constituent cubic perovskites

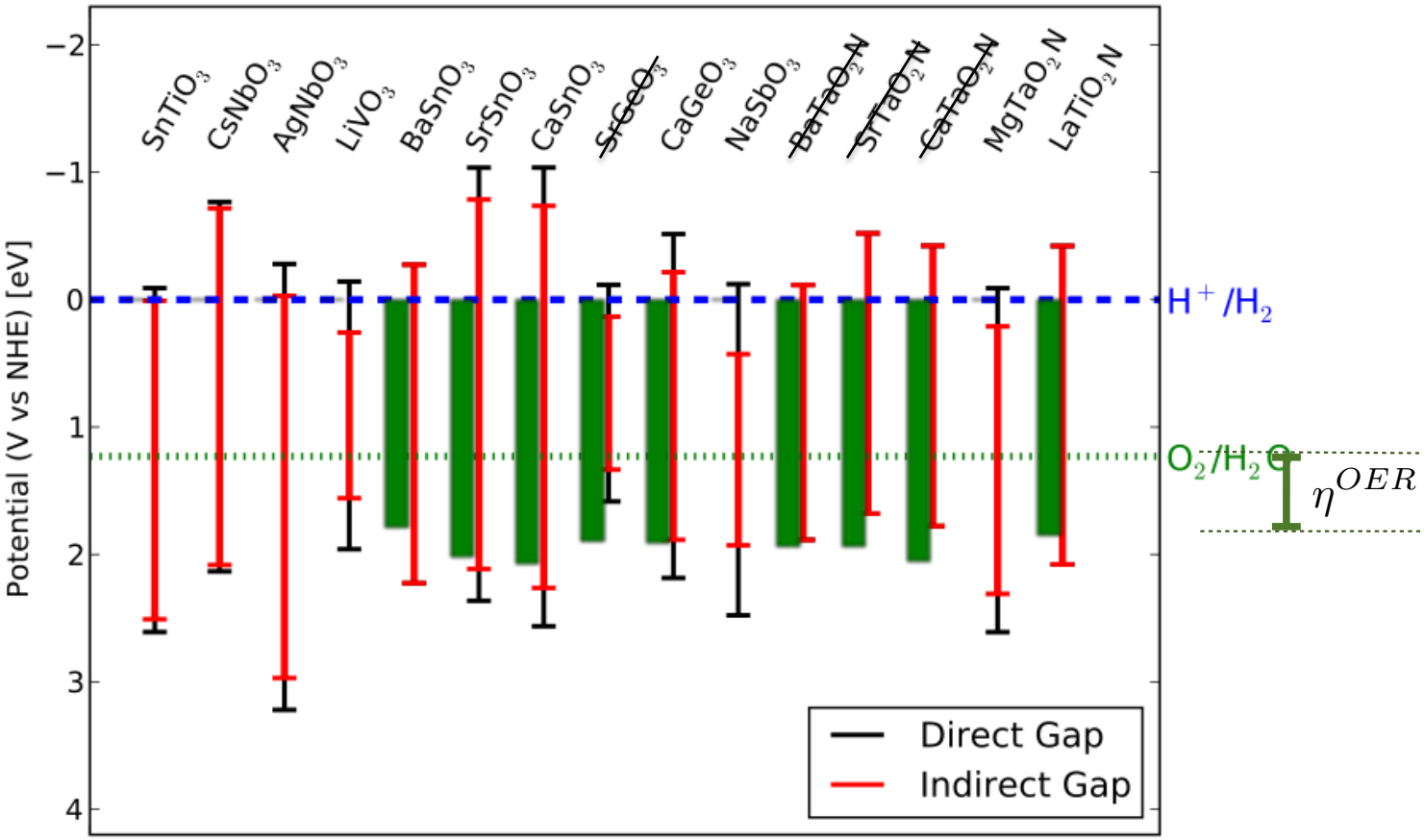
New “design rules”:

- Double perovskite has average of perovskite gaps
- But, for B1 p-metal and B2 d-metal gap is significantly increased (but typically > 4 eV)



•B1-ion(d) - B2-ion(p) hybridization -> increased bandgap

OER overpotentials



$$G^{OER} = Max[\Delta G_1^0, \Delta G_2^0, \Delta G_3^0, \Delta G_4^0]$$

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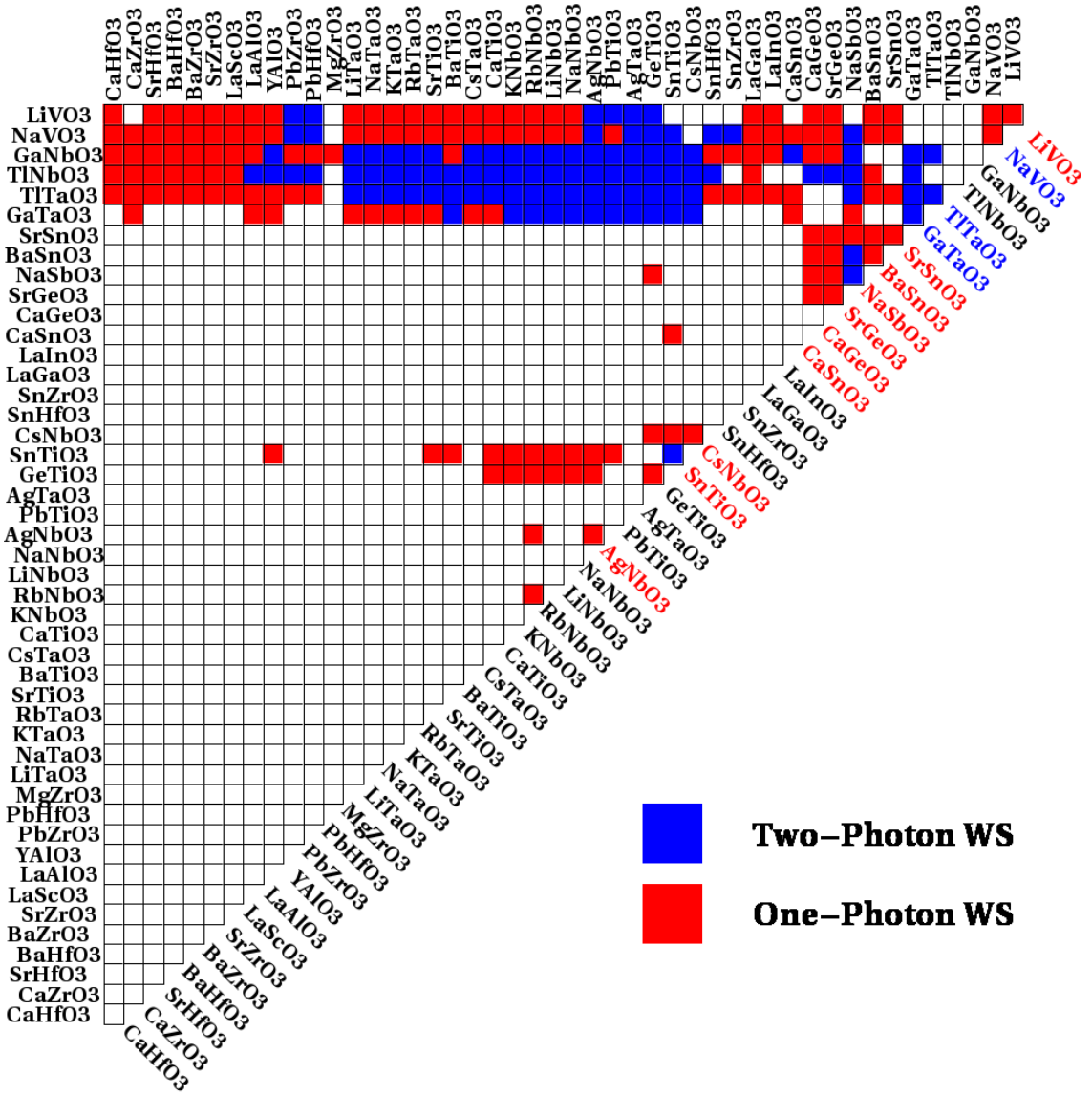
Towards bandgap engineering: double perovskites



152 new materials for one-photon water splitting

100 new materials for two-photon water splitting

Combinations of metals with large-gap semiconductors?

Regularization

Smoothness – Tikhonov reg.

Improves transferability

$$C_{reg} = \omega^2 \int \left(\frac{d^2 F_x(s(t))}{dt^2} \right)^2 dt$$

Bootstrapping

Bootstrapping is used to estimate the dependency of the fit on the database bootstrapping can be used. (Alternative to cross validation).

Consider a database with N points. A bootstrap sample is obtained by selecting N points from the database (with possible repetition)

Averaging over bootstrap samples gives information about both bias and variance

Estimated Prediction Error – 0.632-rule

$$EPE = 0.368\, err + 0.632\, Err_1$$

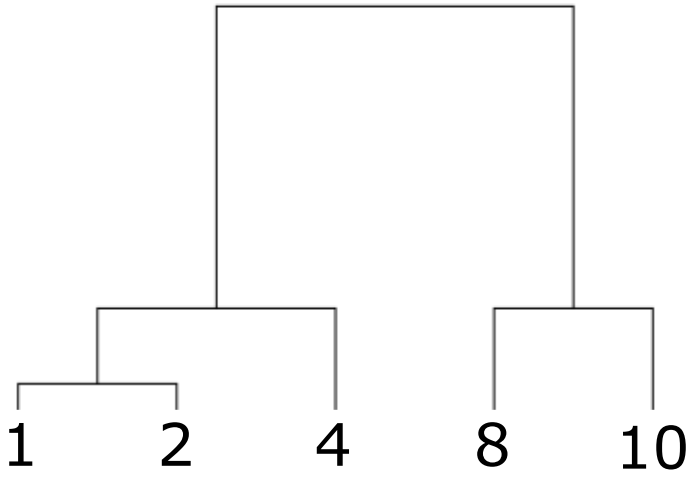
$$err = \frac{1}{N} \Sigma_i (y_i^s - y_i)^2$$

$$Err_1 = \frac{1}{N} \Sigma_i \frac{1}{No\, s : i \notin s} \Sigma_{s : i \notin s} (y_i^s - y_i)^2$$

Cluster analysis: dendrograms

Dendrogram: cluster analysis based on distance

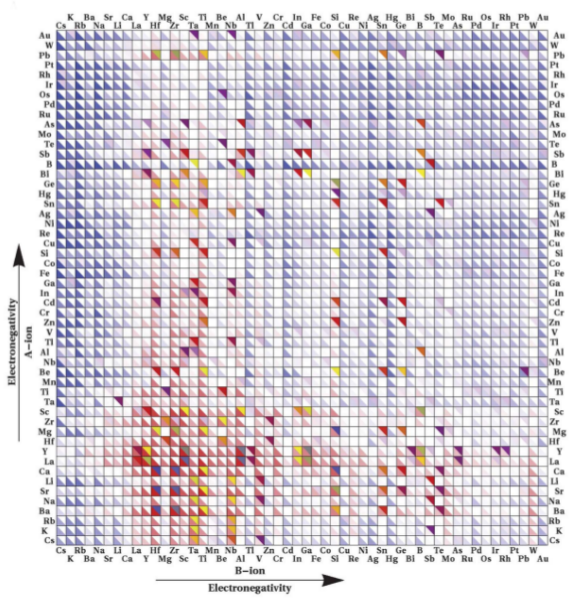
Linkage criterion: cut-off distance *d*; two data points belong to the same cluster if there is a chain of data points with distances less than *d* which connect them.



Distance between two A-ions:

$$d(A_1, A_2) = \frac{1}{N_B} \sum_B \left(E^{gap}_{A_1BO_3} - E^{gap}_{A_2BO_3} \right)^2$$

Measures similarity between rows



Regularization using bootstrap

Smoothness – Tikhonov reg.

Improves transferability

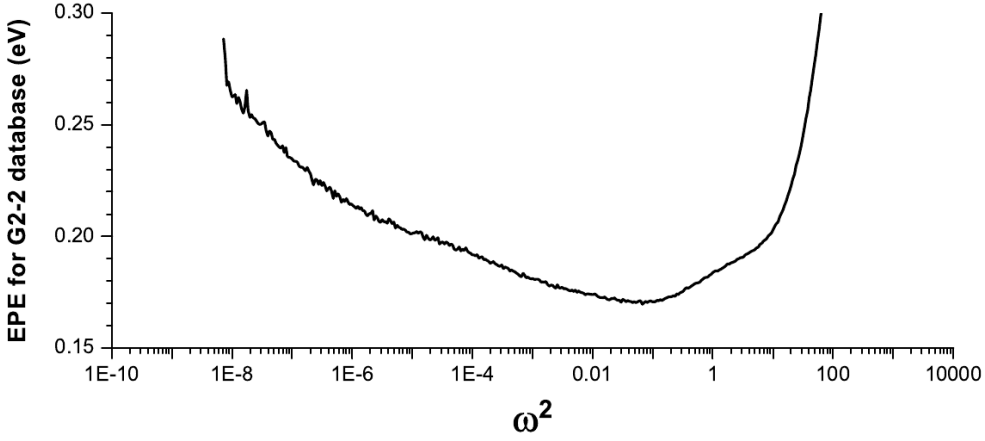
$$C_{reg} = \omega^2 \int \left(\frac{d^2 F_x(s(t))}{dt^2} \right)^2 dt$$

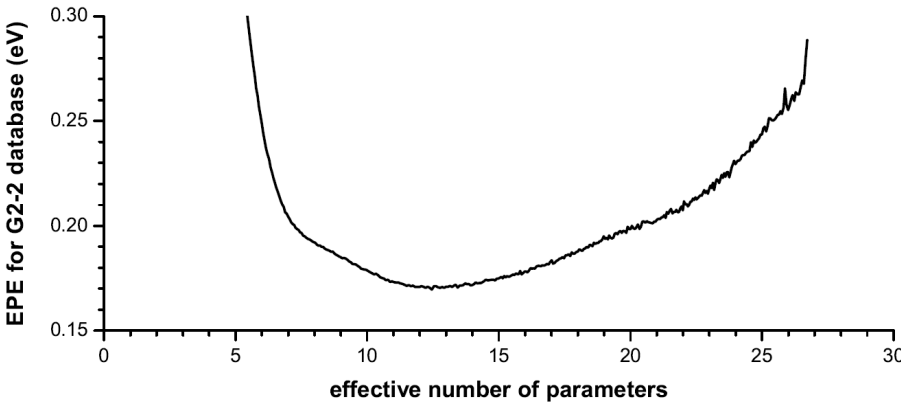
Bootstrapping

Estimates the dependency of the fit on the database: Bias and variance

Estimated Prediction Error – 0.632-rule

Estimated Prediction Error (EPE)

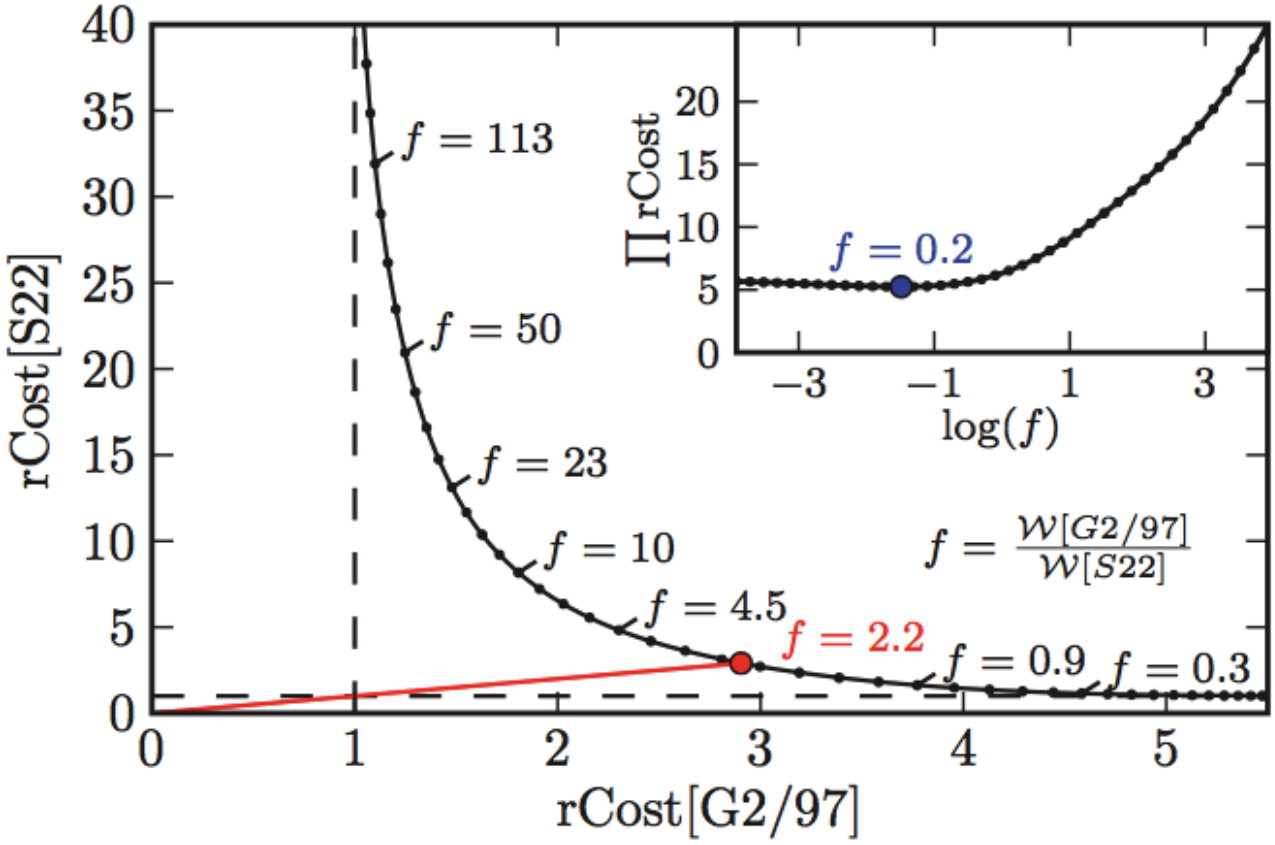




The data sets

- G3/99 Molecular formation energies (223 molecules)
- RE42 Molecular reaction energies (42 reactions)
- DBH24/08 Molecular reaction barriers (12 forward and backward barriers)
- S22x5 Non-covalent interactions (22 molecules at 5 distances)
- Sol34Ec Solid cohesive energies (34 solids)
- Sol27Ec Solid cohesive energies (27 cubic solids)
- Sol27LC Lattice constants (27 cubic solids)
- CE27 Chemisorption energies (27 systems)

Balancing data sets



Avoid the tail regions where one data set is done extremely well and another very poorly.

One solution: Minimize product of relative costs.