Computational screening of light absorbing materials

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CASE
Catalysis for Sustainable Energy

Overview

- Computational Materials Design
- Descriptors
  - Lithium battery cathode materials
  - Superalloys
  - Hydrogen evolution electrocatalysts
  - Ammonia synthesis
- Water splitting
  - One-photon vs tandem
- The toolbox (DFT and friends)
  - Material stabilities vs standard states and beyond
  - Public databases
  - Pourbaix diagrams
  - Bandgaps and light absorption
- Materials
  - Perovskites
    - Oxides, oxynitrides, oxysulfides, oxyfluorides, OFN
    - Double perovskites
    - Layered perovskites (Ruddlesden-Popper)
    - Organic halide perovskites
  - Inorganic crystal structure database (ICSD)
- Outlook

Computational Materials Design

- Many material properties are determined at the electronic/atomic/molecular level
- Improved methods to calculate “ab initio” quantum properties for larger systems
- Increased computational speed (Moore’s law: doubling of CPU performance every 3 years)
- Parallel screening of thousands of materials

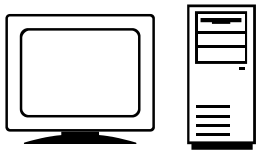
Descriptors

“Real material"

What do we want:

- Battery: High power, rechargeability, long lasting…
- Chemical reactor: High Turn-Over-Frequency
- Structural material: High strength, ductility…
- Solar cell: High solar to electrical energy conversion efficiency
- Photoelectrochemical cell: High solar to fuel conversion efficiency

Identifying key parameters
Multiscale modeling

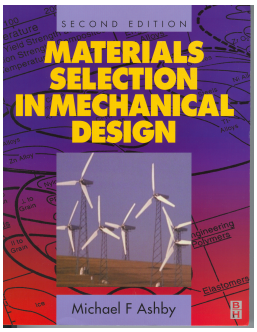


Computing

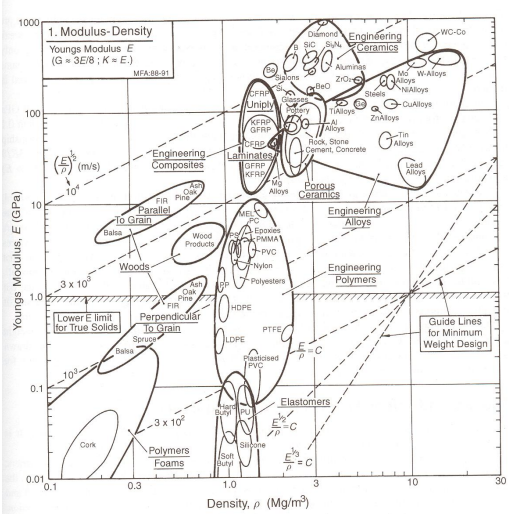
What can we compute at the electronic/atomic level?
“Descriptors”!

Ashby diagrams

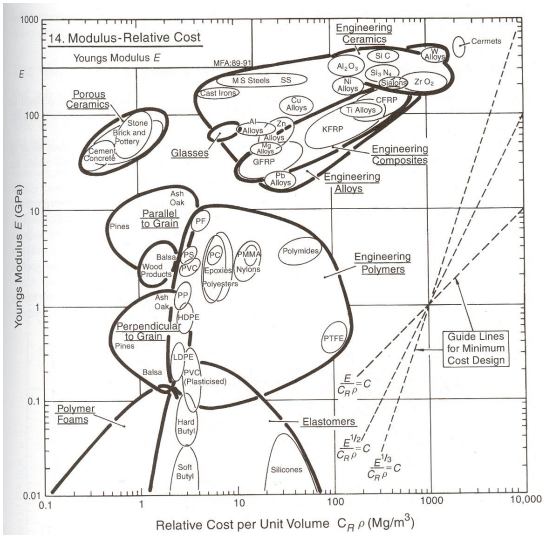
"Materials Selector"



Great variety of materials
Multi-dimensionality
Known materials



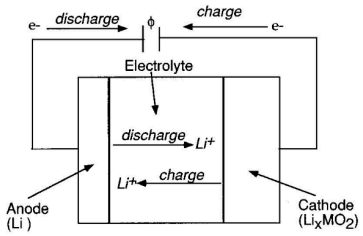
… and how much does it cost?



Lithium cathode material optimization

Cathode:
- $LiCoO_2$ commonly used

Wishlist:
- Reversible intercalation of Li ions
- High cell voltage
- Low weight
- Cheap

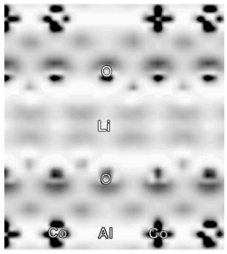


Descriptor!
What is calculated?
Energy change in the reaction:
$Li_xMO_2 + (y-x)Li \rightarrow Li_yMO$

(related to potential of intercalation)

New material suggested: $Li(Co,Al)O_2$

Li-induced charge density in $(Al_{0.33}Co_{0.67})O_2$



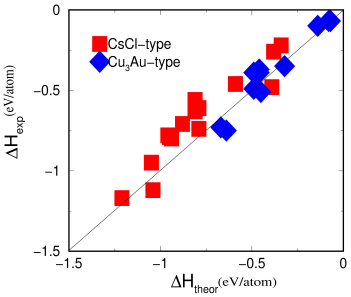
G. Ceder, Y.-M. Chiang, D. R. Sadoway, M. K. Aydinol, Y.-I. Jang, B. Huang, *Nature* **392**, 694 (1998)

Design of superalloys with genetic algorithm

DTU

Superalloys
- Mechanical strength
- Resistance to thermal creep
- Surface stability
- Resistance to corrosion and oxidation

Descriptor?
- Try alloy heat of formation



Calculated heats of formation

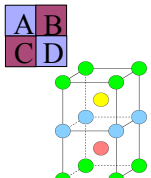
G. Johannesson, Thomas Bligaard, A. Ruban, H. L. Skriver, K. W. Jacobsen, and J. K. Nørskov, Phys. Rev. Lett. **88**, 255506 (2002)
T. Bligaard, G. Johannesson, A. V. Ruban, H. L. Skriver, K. W. Jacobsen, and J. K. Nørskov, Appl. Phys. Lett. (2003)

Genetic algorithm

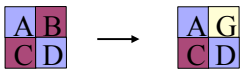
Genes:

Al	Si								
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

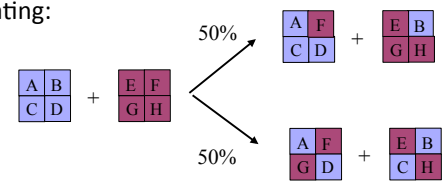
Individuals: 4 atoms



Mutation:



Mating:



Selection fitness: Large negative heat of formation

Genetic algorithm

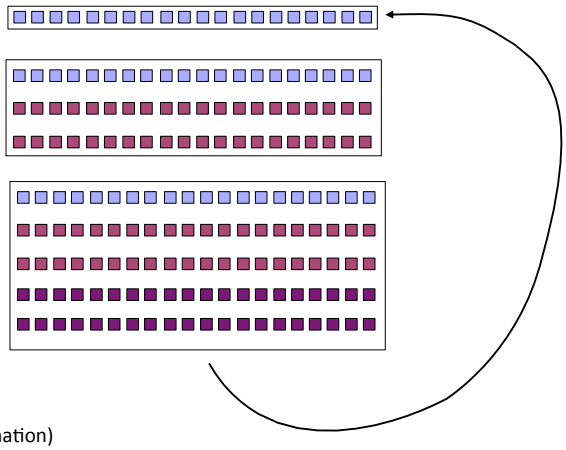
Initial population: 20 alloys

Add 40 offsprings

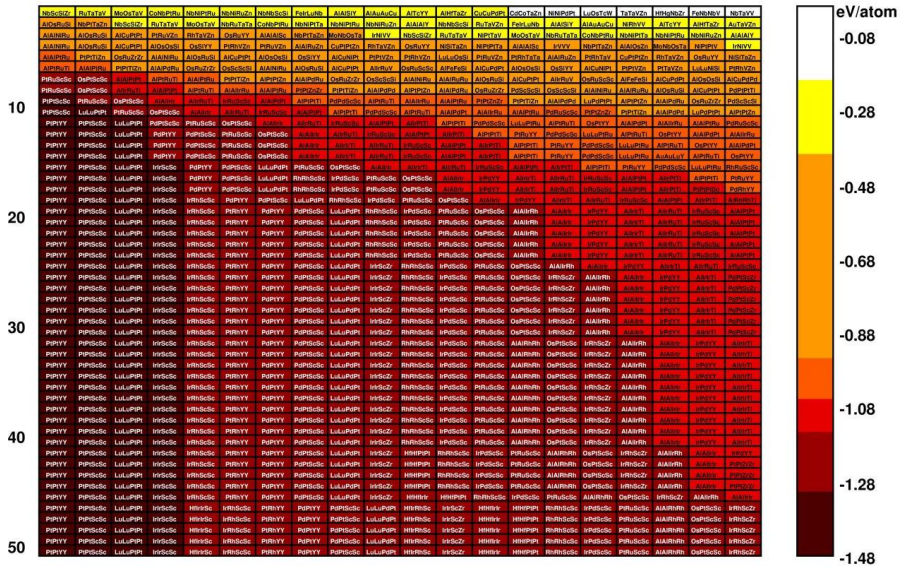
Add 40 mutants

Select the 20 best ones

(largest (negative) heat of formation)



Evolution of population



Learning along the way…

1. run -> All bcc. Known to be brittle -> Focus on stable fcc
2. run -> Early-late TM combinations. Almost always Pd or Pd -> focus on cheaper materials
3. run -> Dominated by Si, environmentally brittle -> Through out Si
4. run

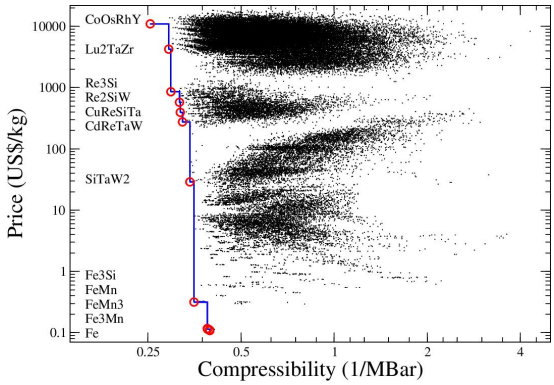
Searching for fcc, cheap and no Si

$AlNi_3$	-0.49
Ni_3Ti	-0.46
$HfNi_3$	-0.44
Al_2Ti_2	-0.43
Al_3Sc	-0.43
Al_2Zr_2	-0.42
Al_2ZnZr	-0.42
Al_2Sc_2	-0.41
Ni_3Sc	-0.41
Al_3Zr	-0.40
Al_2TiZn	-0.39
Al_2ScZn	-0.38
Al_3Ti	-0.38
Co_3Ti	-0.38
Ni_3Zr	-0.36
Al_2NbTi	-0.36
Al_2CuTi	-0.35
Al_2HfZn	-0.34
Al_2CuZr	-0.34
Al_3Lu	-0.34

- Ni_3Al well-known super alloy
- Ni_3Ti is actually hexagonal DO_{24}
  - cannot be used as structural alloy
- Ti based high-temperature super-alloys
- Al_3Sc has $L1_2$-structure. Until now used mostly as precipitate in Al-Sc alloy. Suggested as new possible super-alloy*
- 3-component alloys which crystallize in $L1_2$ structure
  - could be promising as super alloys ?

*Y. Harada and D. C. Dunand, Acta Mater. **48**, 3477 (2000)

Data Mining: Pareto Analysis



64000 alloys

Bligaard, Johannesson, Ruban, Skriver, Jacobsen, Nørskov, Applied Physics Letters **83**, 4527 (2003)

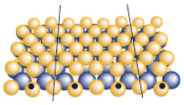
Non-precious catalysts for electrochemical hydrogen production

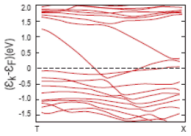
Structure, composition

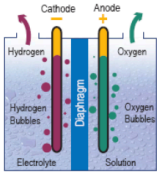
Electronic structure

Functionality (Catalytic activity)

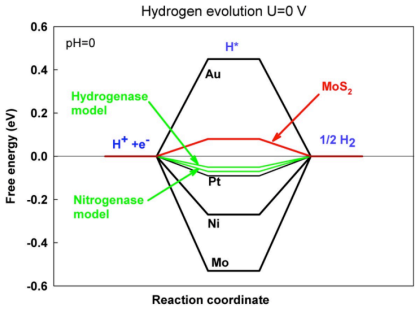
MoS_2 edges







Descriptor: Hydrogen adsorption energy

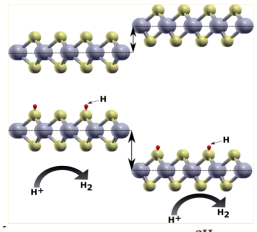


MoS_2 replacing Pt

J. K. Nørskov, T. Bligaard, J. Rossmeisl, and C. H. Christensen, *Nature Chemistry*, vol. 1, no. 1, pp. 37–46, Apr. 2009.

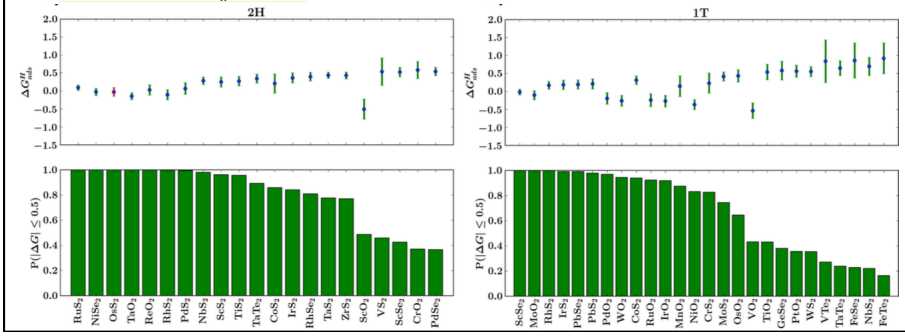
Transition metal dichalcogenides that evolve hydrogen on the basal plane?

2H 1T



Descriptor: Hydrogen adsorption energy

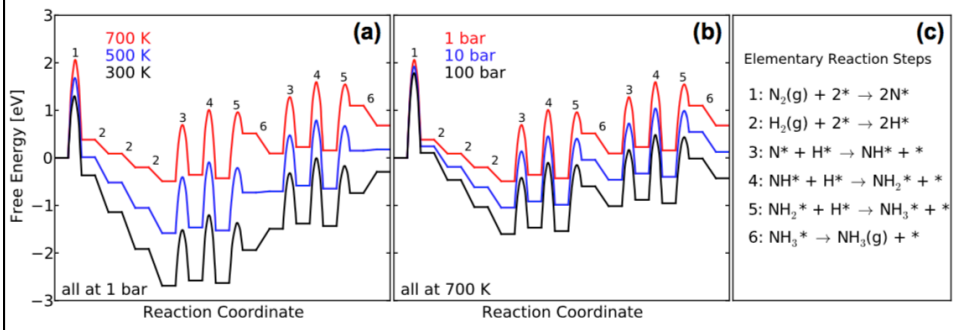
M. Pandey, A. Vojvodic, K. S. Thygesen, and K. W. Jacobsen, *J Phys Chem Lett*, vol. 6, no. 9, pp. 1577–1585, May 2015.



Ammonia synthesis

$$N_2 + 3H_2 \rightarrow 2NH_3$$

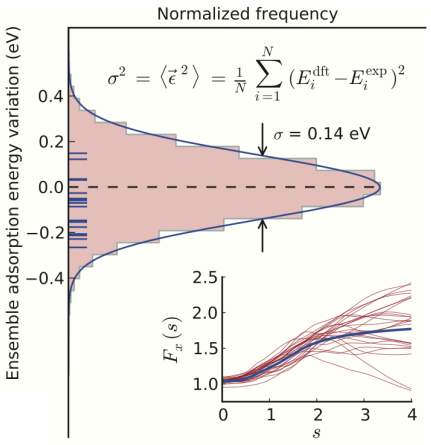
Descriptors: Adsorption energies and reaction barriers
Multiscale modeling: Microkinetics



Number of descriptors can be reduced using scaling relations: the energy barrier scales with the binding energy

Vojvodic, Medford, Studt, Abild-Pedersen, Khan, Bligaard, and Nørskov, *Chemical Physics Letters*, **598**, 108 (2014)

Bayesian error estimation functionals (BEEF): Ensemble of chemisorption energies



Results for 17 chemisorption energies.

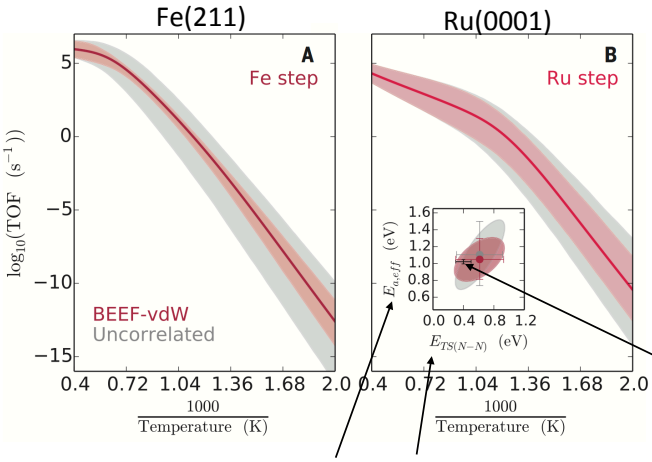
Ensemble generated with BEEF-vdW but rescaled slightly to reproduce chemisortion energies only.

BEEF-vdW ensemble of enhancement factors.

Medford, Wellendorf, Vojvodic, Studt, Abild-Pedersen, Jacobsen, Bligaard, Nørskov, *Science* **345,** 197 (2014)

Turn-over-frequency

Calculations include error bars: Bayesian Error Estimation Functionals (BEEF)



Industrial conditions: 100 bar, 50% approach to equilibrium

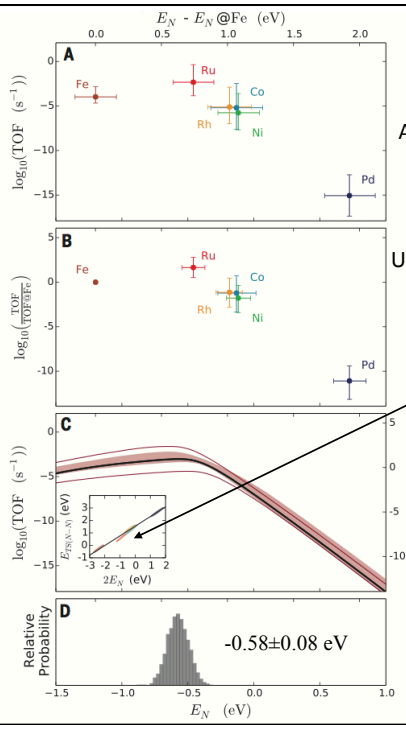
Correlations reduce error bars

Experiment

Effective activation energy

Rate limiting step: N-N dissociation

Investigating other metals



Absolute uncertainties

Uncertainties relative to Fe

Ensembles collapse along scaling relations

Using scaling relations

Red curves: absolute uncertainties

Shaded area: relative to Fe

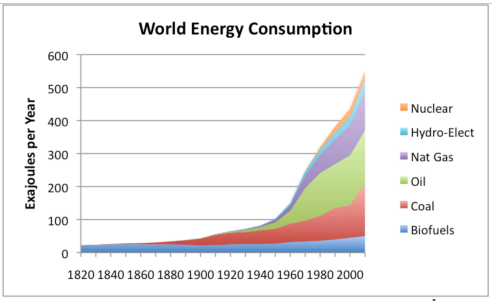
Probability distribution for optimum of volcano

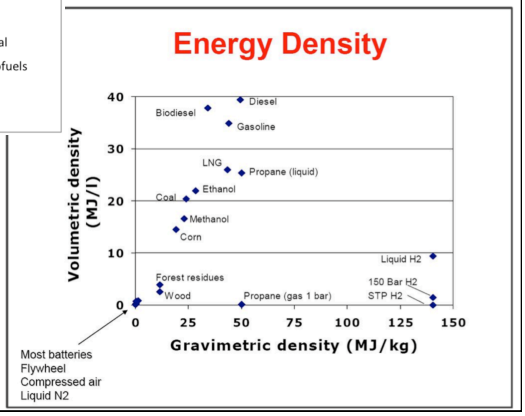
Optimum is well determined!

Reduction to only one descriptor!

Medford, Wellendorf, Vojvodic, Studt, Abild-Pedersen, Jacobsen, Bligaard, Nørskov, *Science* **345,** 197 (2014)

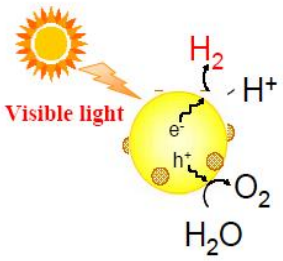
The World needs sustainable energy production – including fuels





Light induced water splitting

Computational search for materials able to collect the visible part of the solar spectrum and to use the energy to split water in oxygen and hydrogen.



Complicated process:

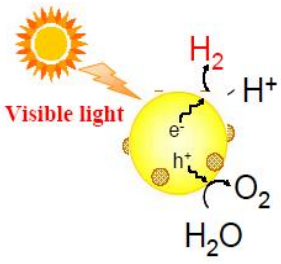
- Light absorption
- Electron-hole transfer
- Induce reactions

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

(Fujishima and Honda, Nature 1972)

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

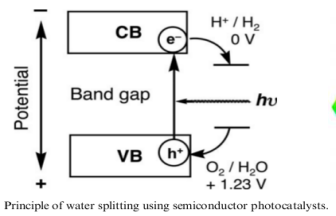
Light induced water splitting



What could be relevant descriptors?

Descriptors for screening

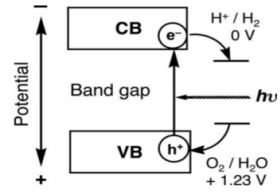
- ❑ **Chemical/structural stability**
- ❑ **Good light absorption**
- ❑ **Photogenerated charges at right potentials**
- ❑ Good electron/hole mobilities
- ❑ Good catalytic properties
- ❑ Low cost, non-toxicity

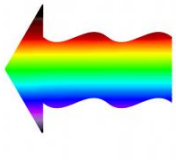


Principle of water splitting using semiconductor photocatalysts.

Descriptors for screening

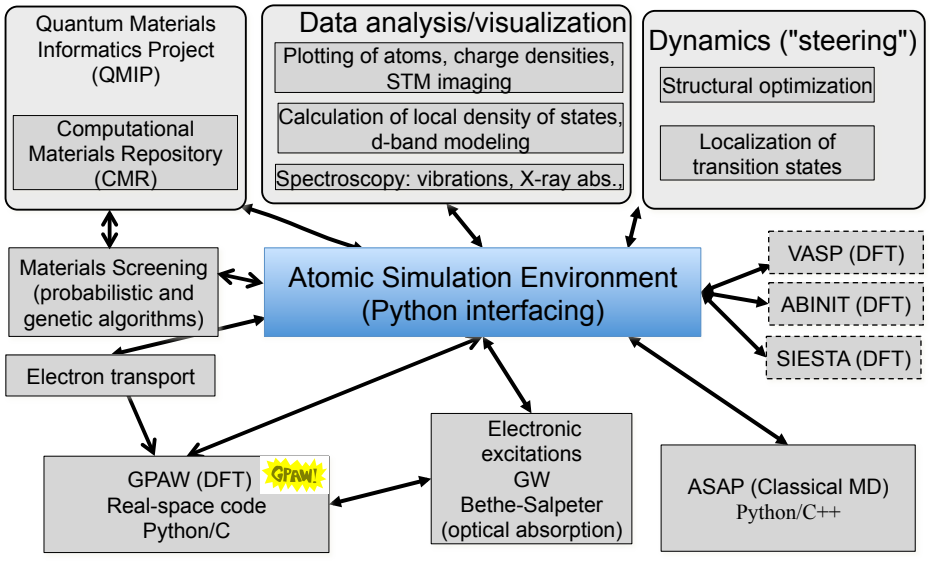
- **Chemical/structural stability**
  - Heats of formation, Pourbaix diagrams
- **Good light absorption**
  - Bandgap in the visible range
- **Photogenerated charges at right potentials**
  - Band edges straddle the water redox potentials
- Good electron/hole mobilities
- Good catalytic properties
- Low cost, non-toxicity





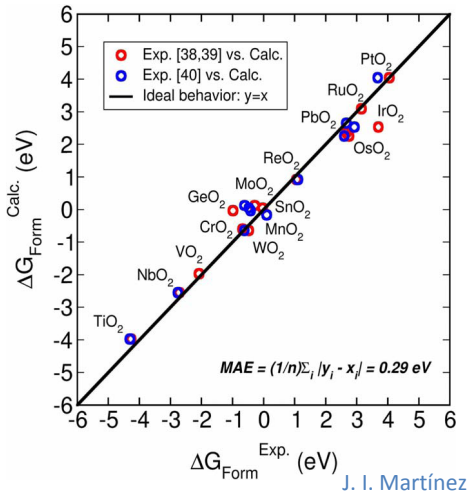
Principle of water splitting using semiconductor photocatalysts.

Toolbox: Atomic Simulation Environment



Toolbox: stability
Example: oxides

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



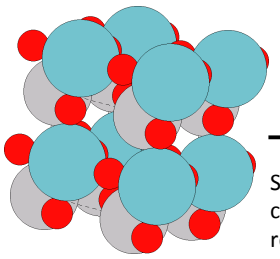
J. I. Martínez *et al.*, Phys. Rev B 2009

DFT and beyond code: GPAW!

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

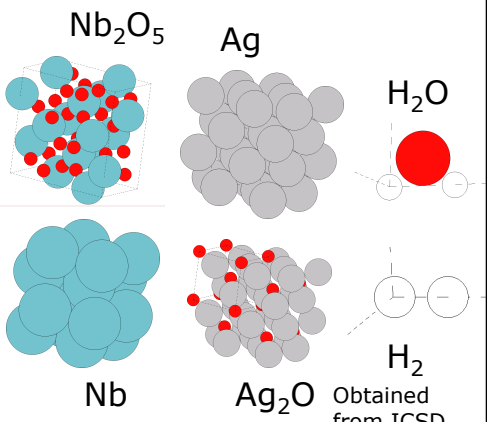
https://wiki.fysik.dtu.dk/gpaw/ ← **Free download, GPL**

Stability vs other solid phases



$AgNbO_3$

Stability of the compound with respect to its possible solid constituents



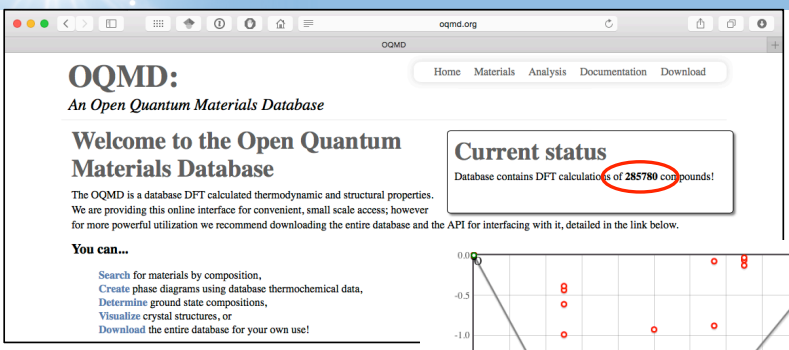
Obtained from ICSD

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

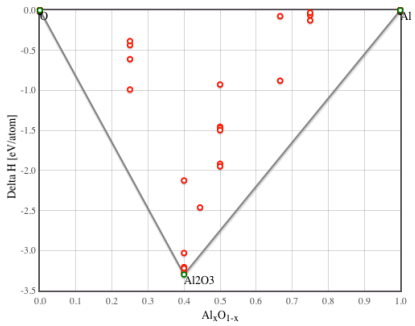
$$c_1 + c_3 = 1\,, \qquad c_2 + c_4 = 1\,, \qquad c_3 + c_4 + c_5 = 3$$

→ Solved by linear programming.

"Standard quantities" now available in public computational databases



Al_xO_{1-x} heats of formation
"Convex hull"
PBE calculations



J. E. Saal, S. Kirklin, M. Aykol, B. Meredig, and C. Wolverton, *JOM*, vol. 65, no. 1, pp. 1501–1509, Nov. 2013.

Computational Databases

- OQMD
- Materials Project
- AFLOWLIB
- NoMaD Repository
- AiiDA
- Computational Materials Repository (CMR) (more about this later)…
- …

- *Several experimental databases*
  - Inorganic Crystal Structure Database (ICSD)
  - …

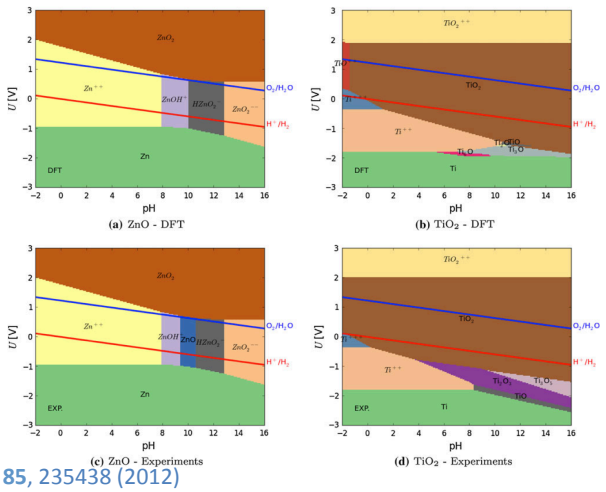
Toolbox: Stability vs dissolution in water – Pourbaix diagrams

$$rR + wH_2O = pP + hH^+ + ne^-$$

- Using the Nernst equation

$$nE = \Delta G + 0.0591 \log \frac{(a_P)^p}{(a_R)^r} - 0.0591 h\ pH$$

- Free energies of dissolved species taken from expt.



(a) ZnO - DFT (b) TiO_2 - DFT (c) ZnO - Experiments (d) TiO_2 - Experiments

K. A. Persson et al. Phys Rev B **85**, 235438 (2012)
I. E. Castelli, K. S. Thygesen, K. W. Jacobsen, Top Catal **57**, 265 (2013)

The bandgap in density functional theory

- DFT is aimed at calculating ground state total energies
- Kohn-Sham states describe the density of a non-interacting electron gas
- But the quasiparticle gap can be determined as a total energy difference for different number of particles
  - Works well with LDA/GGA for molecules
  - Does not work with LDA/GGA for semiconductors

Toolbox: 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

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

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

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

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

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).

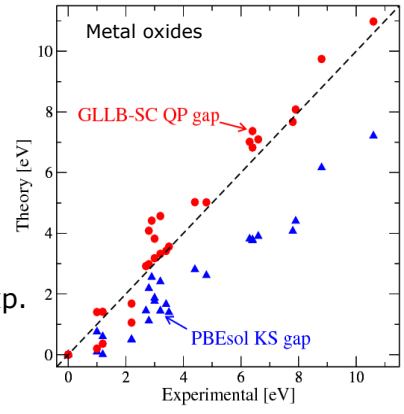
Predicting bandgaps of oxides with GLLB-SC

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

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

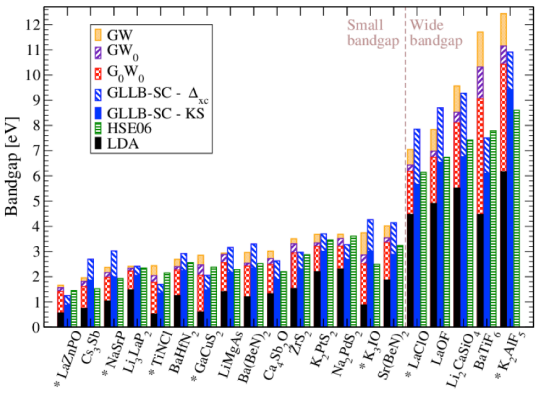
Derivative discontinuity

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



Bandgaps for a selection of systems from Inorganic Crystal Structure Database

20 “randomly” selected systems



MAE (eV) w.r.t. GW

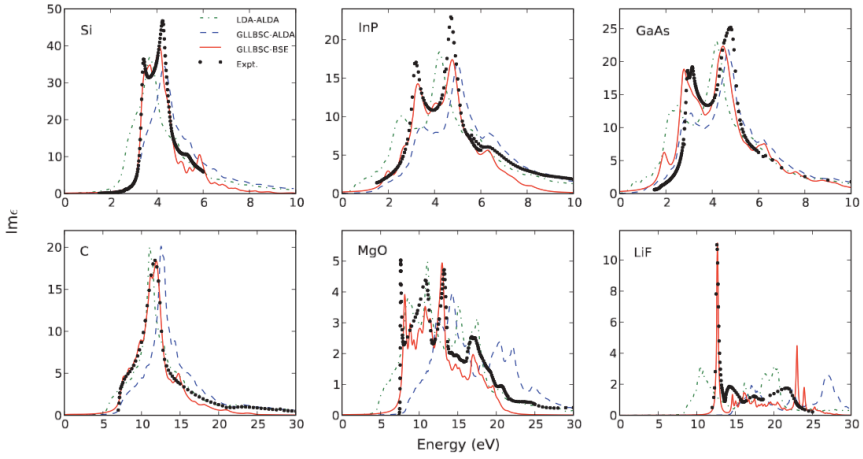
LDA	1.62
GLLB-SC	**0.38**
HSE06	0.47
G_0W_0	0.49
GW_0	0.27

Comutational cost

(Collaboration with Materials Project)

Castelli, Hüser, Pandey, Li, Thygesen, Seger, Jain, Persson, Ceder, Jacobsen, Adv. Energy Mater. **5**, (2014).

Optical absorption spectra with GLLB-SC TDDFT (Adiabatic LDA) or Bethe-Salpeter Eq.

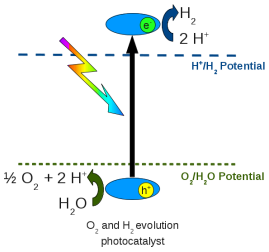


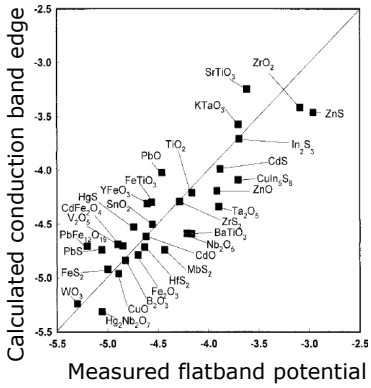
Derivative discontinuity used in spectrum for TDDFT, but not for W in BSE.

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

Toolbox: 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

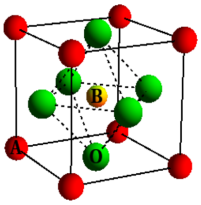
E_0 = Difference between NHE and vacuum ~ -4.5 eV

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

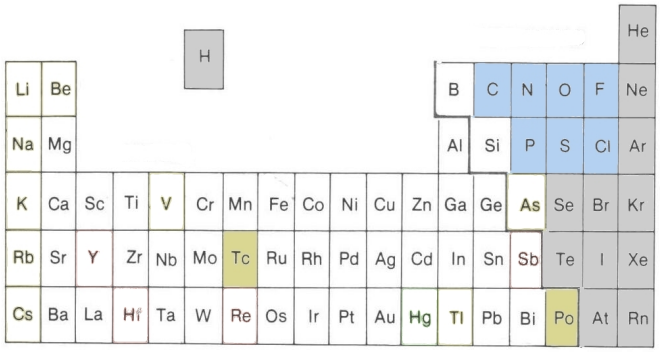
Y Xu and MAA Schoonen, American Mineralogist (2000)

Screening of perovskites in the cubic phase

ABO_3



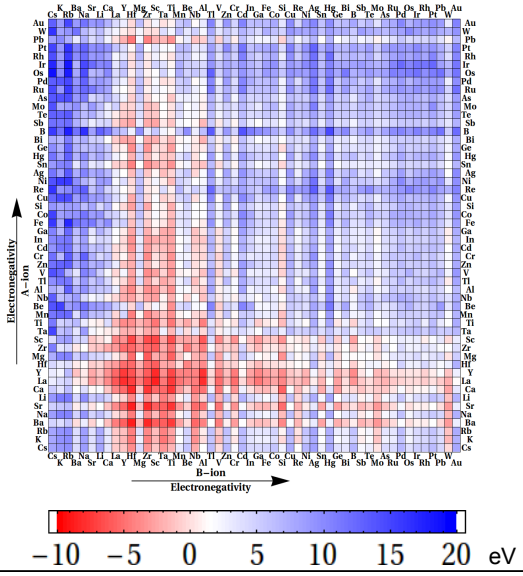
5 atom unit cell



- 52 different metallic elements (no radioactive or toxic)
- Different anions (O, N, S, F, Cl, ...)

(Castelli, Olsen, Datta, Landis, Dahl, Thygesen, Jacobsen, Energy Environ Sci **5**, 5814 (2012))

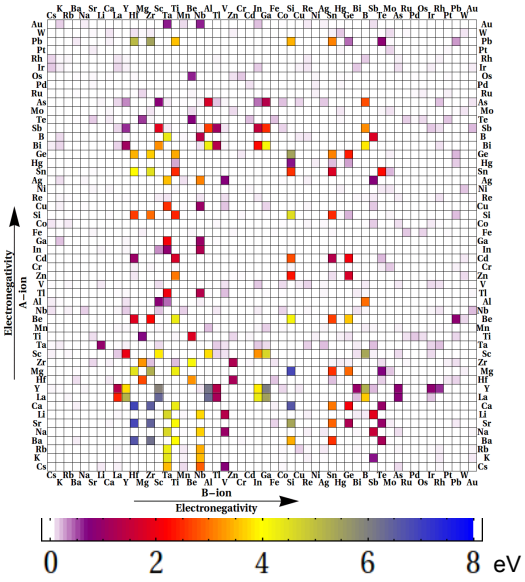
Perovskites: Heat of formation



Stable materials:

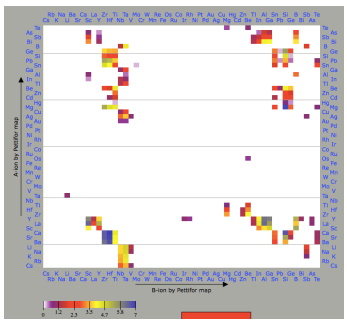
- Low electronegativity
- Sum of oxidation numbers = 6

Perovskites: Band gaps



Most perovskites are metallic or low-gap semiconductors

Using “Pettifor-stringing” of periodic table



Oxides, oxynitrides, oxysulfides, oxyfluorides, oxyfluornitrides

Materials candidates:

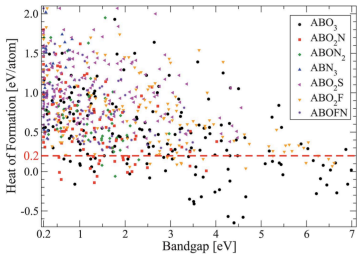
- ABO_3 :10 4 known, 6 unknown
- ABO_2N :5 4 known, 1 unknown
- $ABON_2$:2 $LaTaON_2$ (known) $YTaON_2$ (unknown)
- ABN_3 :0
- ABO_2S :0
- ABO_2F :3
- ABOFN :0

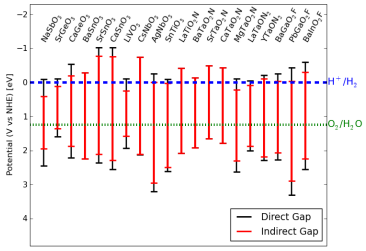
~19000 materials

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

20 candidate materials

About half are known



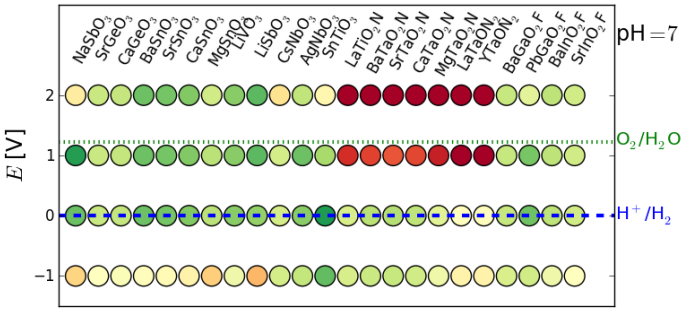


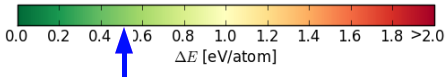
(Castelli, Landis, Thygesen, Dahl, Chorkendorff, Jaramillo, Jacobsen, Energy Environ Sci **5**, 9034 (2012))

Further analysis of candidate materials: stability in water

Oxides and oxyfluorides are reasonably stable (with 0.5 eV threshold).

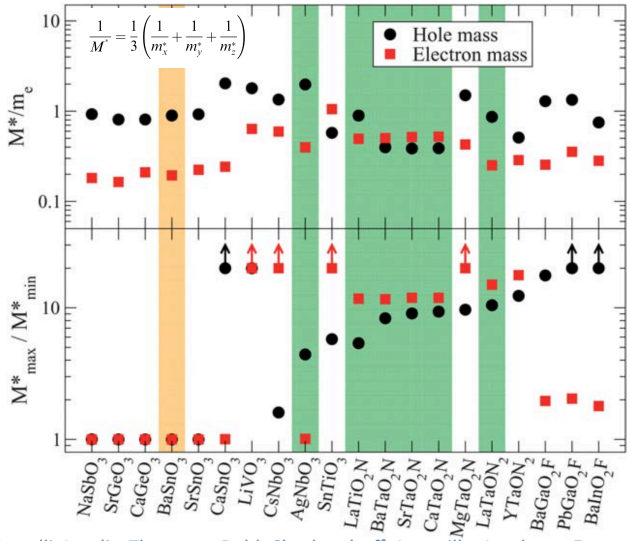
Oxynitrides are less stable, especially at high potential.





New stability threshold to include some metastability/kinetics and perhaps inaccuracies in the calculations.

Further analysis: Effective masses (≈ mobilities)

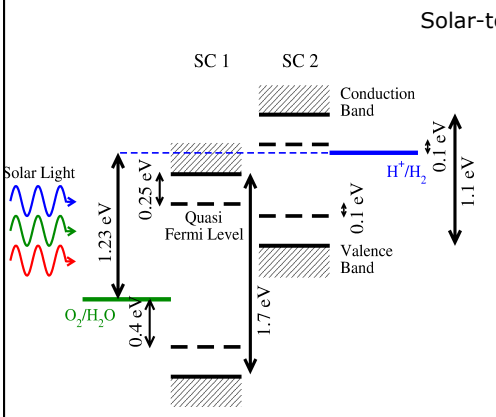


Green systems known to split water (with sacrificial agents).

Working systems do not seem to have large masses.

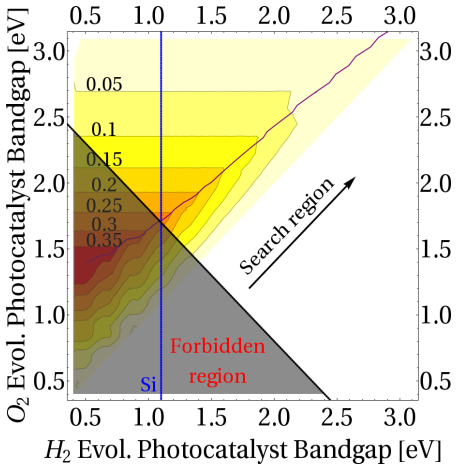
(Castelli, Landis, Thygesen, Dahl, Chorkendorff, Jaramillo, Jacobsen, Energy Environ Sci **5**, 9034 (2012))

Tandem cell water splitting



Max efficiency ~28% (vs ~13% for one-photon)

Solar-to-hydrogen energy conversion efficiency

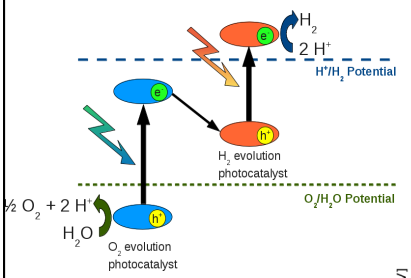


(J. R. Bolton et al., *Nature* 1985.)

(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)

Tandem cell water splitting: Screening results

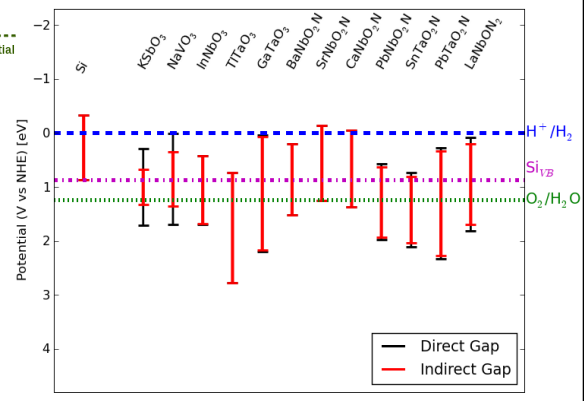


Screening parameters	Two-photon WS
Chemical/structural stability (ΔE)	$\Delta E \leq 0.2$ eV
Bandgap (E_{gap})	$1.3 \leq E_{gap} \leq 3$ eV
Band edges (VB_{edge}, CB_{edge})	$VB_{edge}^{anode} > 1.23$ eV $CB_{edge}^{cathode} < 0$ eV $VB_{edge}^{cathode} > CB_{edge}^{anode}$

12 candidates

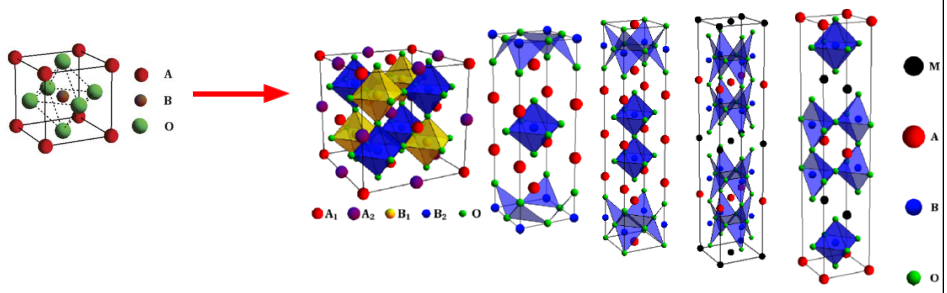
+ 20 from overall WS

$BaNbO_2N$, $SrNbO_2N$, $CaNbO_2N$, and $LaNbON_2$ are known as water splitters.



(Castelli, Olsen, Datta, Landis, Dahl, Thygesen, Jacobsen, Energy Environ Sci **5**, 5814 (2012))

Towards low-symmetry perovskites



Cubic (5 atom/cell) | Double (20) | Ruddlesden-Popper (14-24) | Dion-Jacobson (22-44)

Too expensive to run "brute force" screening for low symmetry structures.

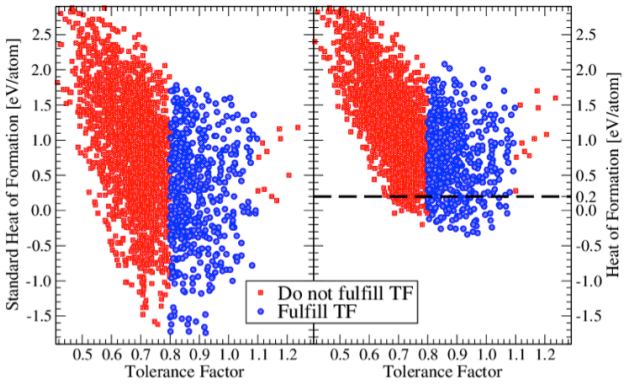
Castelli and Jacobsen, Modelling Simul. Mater. Sci. Eng. **22**, 055007 (2014)

"Traditional" rules not good enough
Example: tolerance factor

Tolerance factor:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

Traditional rule:
$0.8 < t < 1.1$

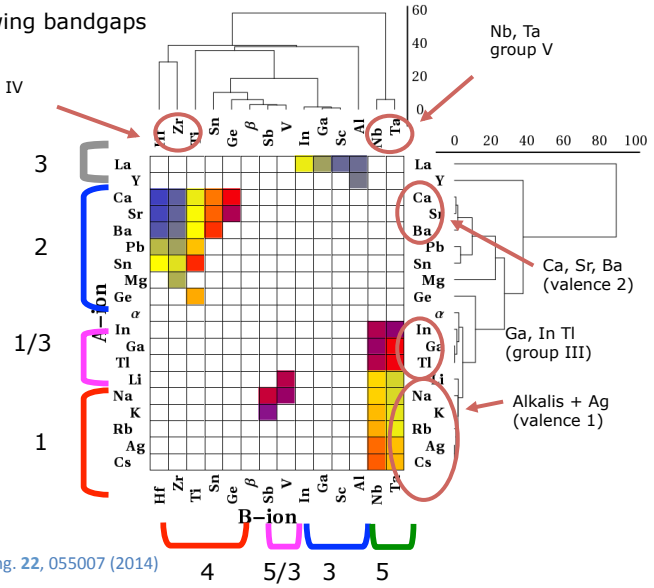


Example: $AgNbO_3$ has t outside [0.8, 1.1]

Castelli and Jacobsen, Modelling Simul. Mater. Sci. Eng. **22**, 055007 (2014)

Cluster analysis based on bandgap for ABO_3: Valence rules!

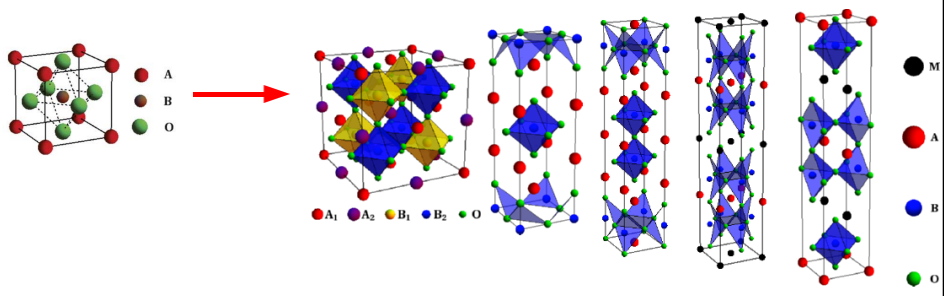
46 stable ABO_3 showing bandgaps



Clusters follow the valences of the elements.

Castelli and Jacobsen,
Modelling Simul. Mater. Sci. Eng. **22**, 055007 (2014)

Towards low-symmetry perovskites



Cubic (5 atom/cell) | Double (20) | Ruddlesden-Popper (14-24) | Dion-Jacobson (22-44)

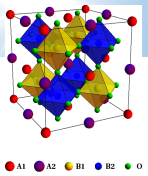
Too expensive to run "brute force" screening for low symmetry structures.

Use three chemical-based rules derived from cubic perovskites:

1) Even-odd rule: Even number of electrons in unit cell to have a bandgap
2) Valence rule: Sum of possible valences should add up to zero.
3) Radius rule: Radius(A) > Radius(B)

Castelli and Jacobsen, Modelling Simul. Mater. Sci. Eng. **22**, 055007 (2014)

Bandgap engineering: Double perovskites



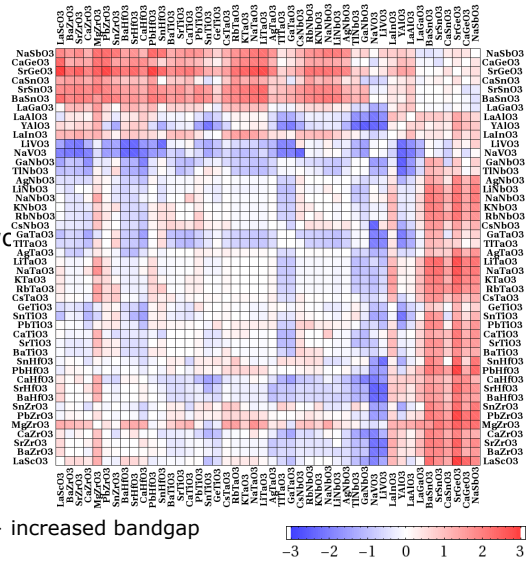
46 stable perovskites with a gap combined

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

New "design rules":

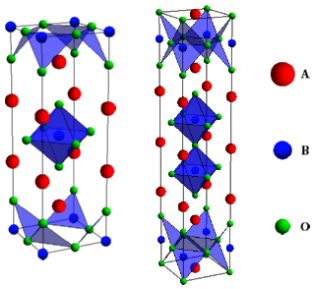
- Double perovskite has average of perovskite gaps
- But, for B1 p-metal and B2 d-metal gap is significantly increased

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



I. E. Castelli, K. S. Thygesen, and K. W. Jacobsen, *MRS Online Proceedings Library* **1523** (2013).

Bandgap engineering: Layered perovskites (Ruddlesden-Popper)

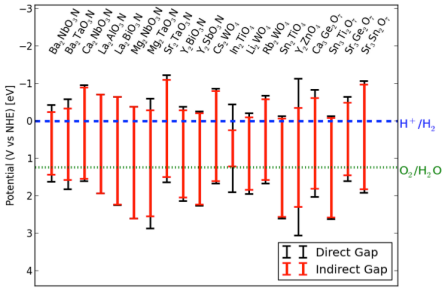


Bandgap decreases with the thickness of the octahedron layer when p-metals are in the B-ion position. Opposite for d-metals.

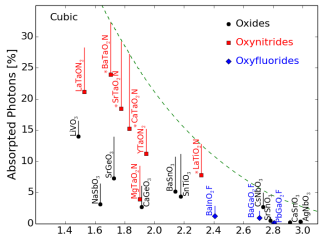
Criterion	One-photon WS	Two-photon WS
Stability (ΔE)	0.2 eV atom^{-1}	0.2 eV atoms^{-1}
Bandgap (E_{gap})	$1.7 \leqslant E_{gap} \leqslant 3$	$1.3 \leqslant E_{gap} \leqslant 3$
Band edges	$VB_{edge} > 1.6$	$VB^{anode}_{edge} > 1.6$
(VB_{edge}, CB_{edge})	$CB_{edge} < -0.1$	$CB^{cathode}_{edge} < -0.1$
		$CB^{anode}_{edge} < VB^{cathode}_{edge}$

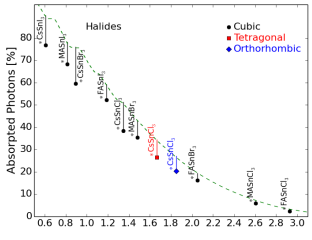
I. E. Castelli, J. M. Garcia-Lastra, F. Huser, K. S. Thygesen, and K. W. Jacobsen, *New J. Phys.* **15**, 105026 (2013).

More candidates for water splitting:

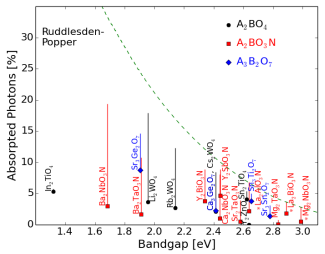


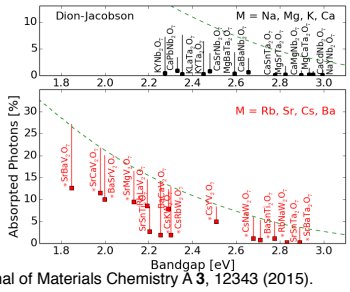
Beyond the bandgap: light absorption TDDFT/ALDA





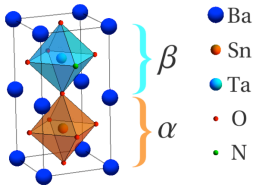
Absorption at 200 nm thickness





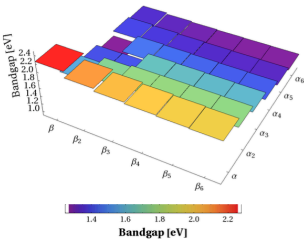
I. E. Castelli, K. S. Thygesen, and K. W. Jacobsen, Journal of Materials Chemistry A **3**, 12343 (2015).

Functionalized stacked perovskites $BaSnO_3$ and $BaTaO_2N$



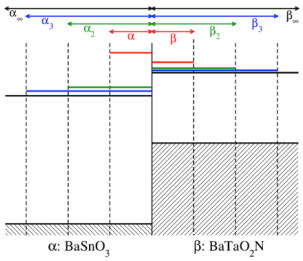
Bandgaps:
$BaSnO_3$: 3.33 eV (indirect)
$BaTaO_2N$: 1.84 eV (direct)

Variation of bandgap for stacked systems ~ 1 eV



Explanation of variation:
Confinement
Tunneling for thin layers

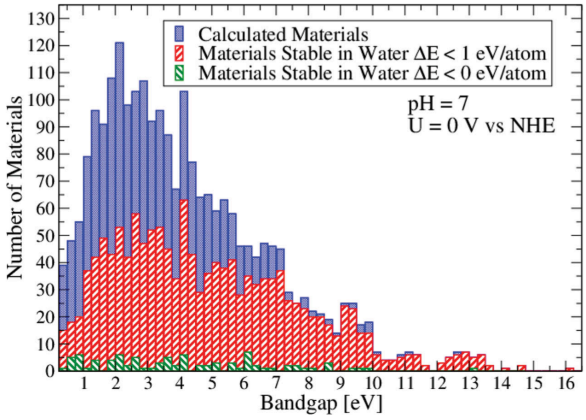
Tuning of bandgaps

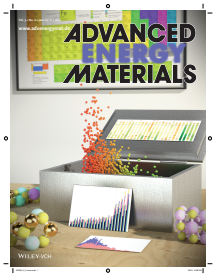


I. E. Castelli, M. Pandey, K. S. Thygesen, and K. W. Jacobsen, Phys. Rev. B **91**, 165309 (2015).

Screening for WS materials based on Inorganic Crystal Structure Database (ICSD)

Bandgaps of 2400 materials from ICSD



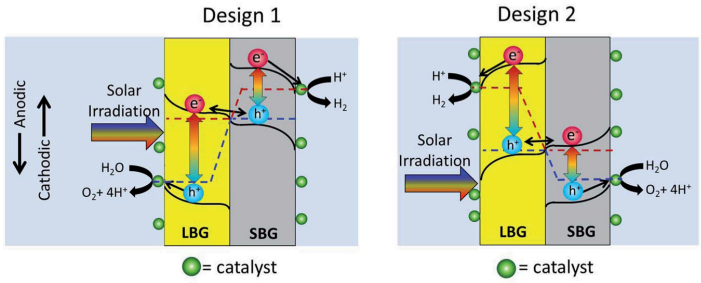


(Collaboration with Materials Project)

Castelli, Hüser, Pandey, Li, Thygesen, Seger, Jain, Persson, Ceder, Jacobsen, *Adv. Energy Mater.* 2014, 1400915

Two-photon water splitting designs

Two basically different designs:



Acidic or basic conditions?
Protection of light absorbers?
p-n junctions to shift levels?

B. Seger, I. E. Castelli, P. C. K. Vesborg, K. W. Jacobsen, O. Hansen, I. Chorkendorff, *Energy Environ. Sci.*, **7**, 2397 (2014)

Screening based on 2400 ICSD entries
No protection layers

Earth abundant compounds shown in bold
Stability in water hard to fulfill!

Design	pH	Screening parameters	Absorber (electrode)	# of candidates	Candidate materials
Design 1	0	$1.5 \leq E_{Gap} \leq 2.1$, VB > 1.6 V *vs.* RHE	LBG, (anode)	6	$AuClO$, $Co(ReO_4)_2$, $Cr_2Ag_2O_7$, $CuRhO_2$, $Mg(BiO_3)_2$, $Zn(RhO_2)_2$
		$0.9 \leq E_{Gap} \leq 1.5$, CB < −0.05 V *vs.* RHE	SBG, (cathode)	11	As_2Os, As_2Ru, $CdTe$, **FeSbS**, $GeAs$, $GeAs_2$, $MoSe_2$, **$NaTiCuS_3$**, $KCuSe$, $SnSe$, Te_2Mo
	14	$1.5 \leq E_{Gap} \leq 2.1$, VB > 1.6 V *vs.* RHE	LBG, (anode)	16	Ag_3VO_4, $AuClO$, Au_2O_3, **Ba_2FeMoO_6**, $Bi^{(III)}{}_3Bi^{(V)}O_7$, $Ca(RhO_2)_2$, $CdHgO_2$, $Cd(RhO_2)_2$, Cd_2SnO_4, $Co(ReO_4)_2$, $Cr_2Ag_2O_7$, $CuRhO_2$, $Mg(BiO_3)_2$, $LaRhO_3$, $LiBiO_3$, $Zn(RhO_2)_2$
		$0.9 \leq E_{Gap} \leq 1.5$, CB < −0.15 V *vs.* RHE	SBG, (cathode)	2	**$Ca_3(CoO_3)_2$**, $LaRhO_3$
Design 2	0	$1.5 \leq E_{Gap} \leq 2.1$, CB < −0.05 V *vs.* RHE	LBG, (cathode)	8	$CdSe$, $Cs_2Ni_2S_4$, $InSe$, $NaHfCuSe_3$, $NaPt_2Se_3$, $NaZrCuSe_3$, $SbIrS$, WSe_2
		$0.9 \leq E_{Gap} \leq 1.5$, VB > 1.6 V *vs.* RHE	SBG, (anode)	2	$Bi_2Pt_2O_7$, $HfNBr$
	14	$1.5 \leq E_{Gap} \leq 2.1$, CB < −0.15 V *vs.* RHE	LBG, (cathode)	1	$NaPt_2Se_3$
		$0.9 \leq E_{Gap} \leq 1.5$, VB > 1.6 V *vs.* RHE	SBG, (anode)	3	$Bi_2Pt_2O_7$, $HfBrN$, PtO_2

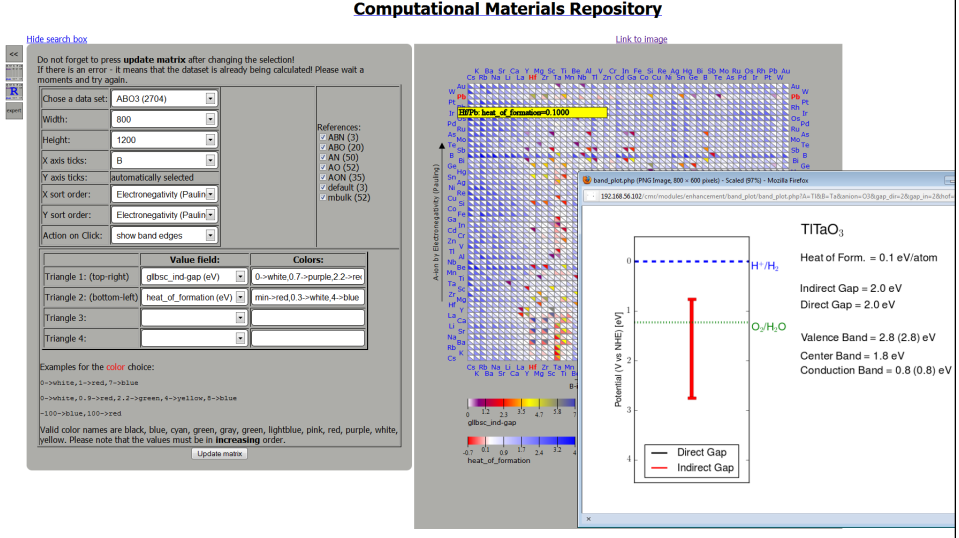
With protection layers and n-p junctions

Only Earth abundant elements shown

Design	Screening parameters	# of candidates	Candidates
SBG	$0.9 \leq E_G \leq 1.5$	51	$BaAs_2$, $BaCaSn$, $Ba_2Cu(PO_4)_2$, Ba_2FeMoO_6, $Ba_3(Si_2P_3)_2$, $BaLaI_4$, Ba_3P_4, $CaBaSi$, $Ca_3(CoO_3)_2$, Ca_2Si, Ca_3SiO, $CoAsS$, $CuCl_2$, CuP_2, FeS_2, $FeSbS$, $K_2Mo_6S_6$, $KNbS_2$, KPb, $KSnAs$, $KZnAs$, $LaAs_2$, $LaZnAsO$, $LaZnPO$, LaS_2, MgP_4, MnP_4, Na_4FeO_3, Na_4FeO_4, $NaNbS_2$, $NaNiO_2$, Na_3Sb, $NaSnP$, $NaTiCuS_3$, $NaTiS_2$, $NaZnP$, $NbFeSb$, NbI_3, Si, SnS, Sr_2As_2, Sr_3As_4, Sr_3SbN, $SrCaSi$, $SrCaSn$, $SrLaI_4$, $Sr(ZnP)_2$, $V(S_2)_2$, $Zn_2Cu(AsO_4)_2$, $ZrBr_3$, $ZrCl_3$
LBG	$1.5 \leq E_G \leq 2.1$	50	B, BP, $BaCu_2SnS_4$, $Ba(MgSb)_2$, BaP_3, Ba_4Sb_2O, Ba_2ZnN_2, Ca_3AlAs_3, $Ca(BC)_2$, $Ca_3(BN_2)N$, $Ca(MgSb)_2$, $Ca\ Na_{10}Sn_{12}$, Ca_3VN_3, $Ca(ZnP)_2$, $CoBr_2$, $CuSbS_2$, Cu_2O, Cu_3VS_4, $FeBr_2$, $FeSO_4$, $Fe(SiP)_4$, I_2, K_3As, $K_2Ni_3S_4$, K_4P_6, $K_3Na_2SnAs_3$, K_2NiAs_2, KSb, $KV(CuS_2)_2$, $KZnP$, $KCuZrS_3$, $MgAs_4$, $NaCuO_2$, $NaNbN_2$, NaP, $NaSbS_2$, Nb_6F_{15}, NbI_5, $SnZrS_3$, SrP, Sr_3P_4, $SrPbO_3$, $TiBrN$, TiI_4, $TiNCl$, Sn_2TiO_4, WBr_6, $ZnSiAs_2$, $ZrCl_2$, Zr_2SN_2

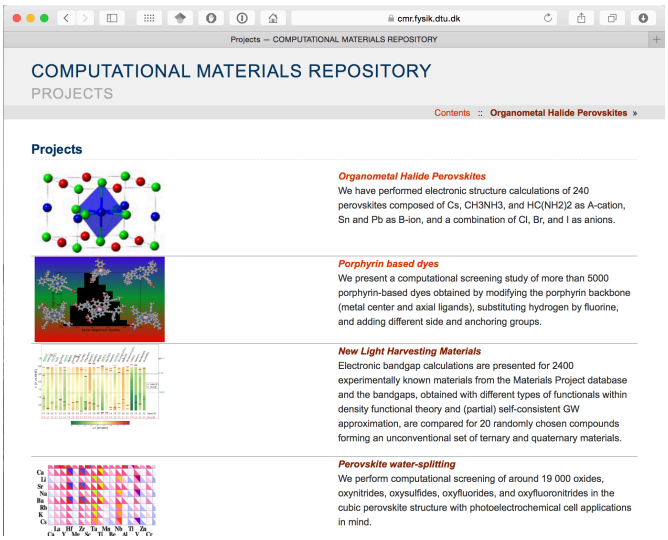
B. Seger, I. E. Castelli, P. C. K. Vesborg, K. W. Jacobsen, O. Hansen, I. Chorkendorff, *Energy Environ. Sci.*, **7**, 2397 (2014)

Computational Materials Repository
"Old" web-interface



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

Computational Materials Repository
New interface



Computational Materials Repository
New ASE database module

In each row we have:

- Taxonomy:
  - Atoms object (positions, atomic numbers, ...)
  - ID, user-name, creation and modified time
  - Constraints
  - Calculator name and parameters
  - Energy, Forces, Stress tensor, dipole moment, magnetic moments
- Folksonomy:
  - Key-value pairs
- Additional stuff:
  - extra data (band structure, ...)

Back-ends: JSON, SQLite3 and PostgreSQL.

Conclusions

Computational Materials Design

- Descriptors and multiscale modeling
- Highly relevant for new energy materials
  - Light absorbers
  - Catalysts
  - Protective layers
  - …

Acknowledgements

CAMD/DTU:
Ivano E. Castelli
Thomas Olsen
David D. Landis
Juan Maria Garcia-Lastra
Falco Hüser
Mohnish Pandey
Hong Li
Kristian S. Thygesen

MIT:
Gebrand Ceder

LBL:
Anbhav Jain
Kristin Persson

CINF/DTU:
Brian Seger
Søren Dahl
Peter Vesborg
Ib Chorkendorff

Stanford:
Tom Jaramillo

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