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Atomic-scale design of energy materials

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Atomic-scale design of materials for water splitting and accurate correlation energies from ACFDT

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Dept. of Physics

Technical University of Denmark

CAMd
Center for Atomic-scale Materials Design

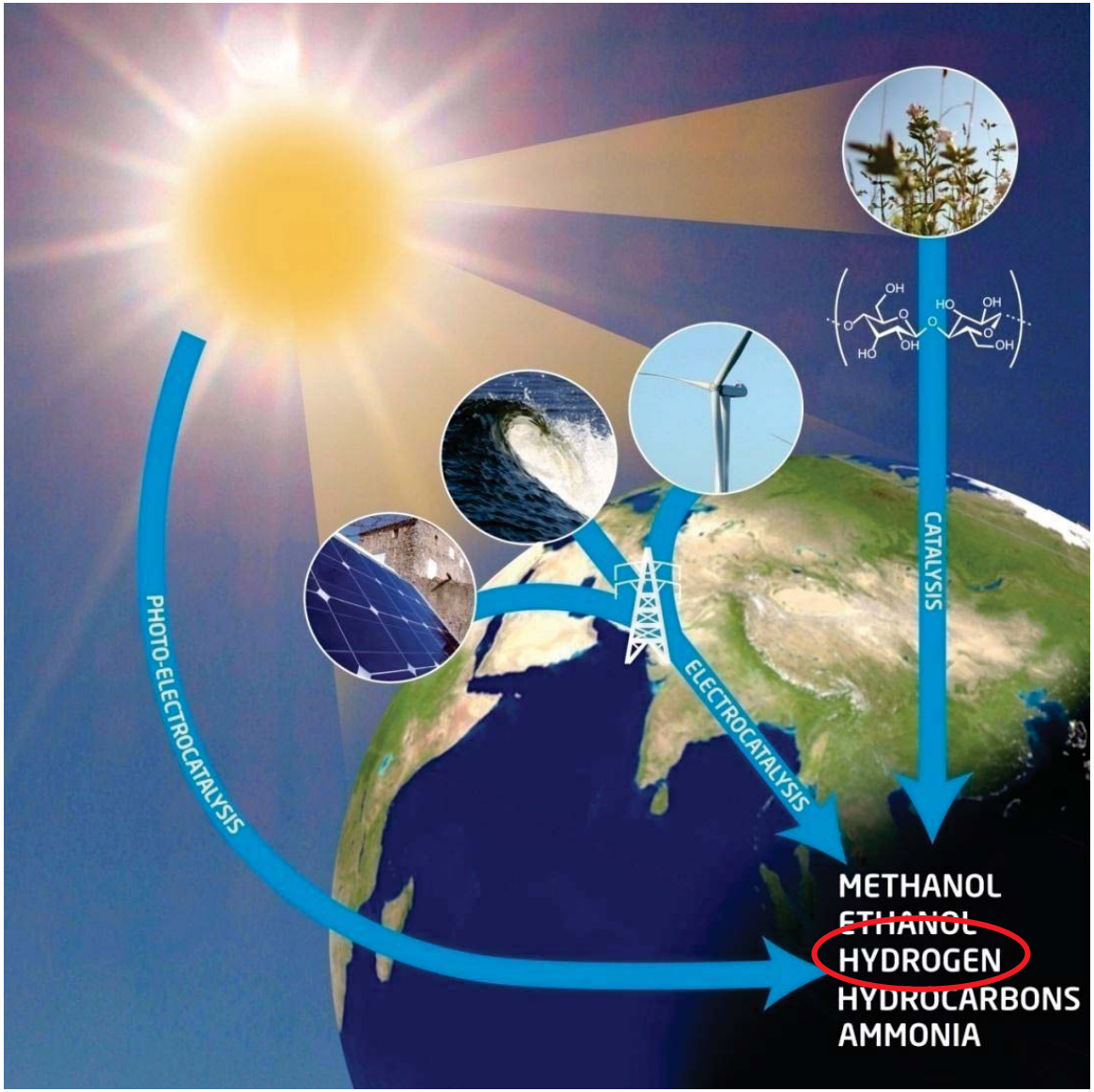
CASE
Catalysis for Sustainable Energy

Outline

- Basic principles of photocatalytic water splitting
- Evaluating stability, band gaps and band edges
- Computational screening of perovskites
- Materials for 1- and 2-photon water splitting

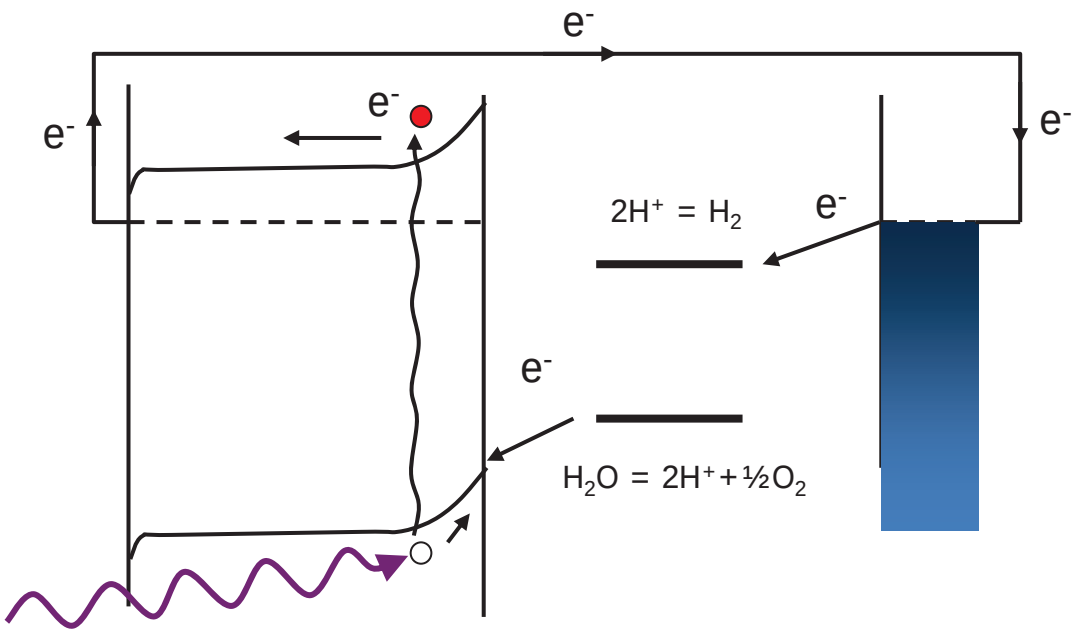
- Correlation energies from the ACDFT
- RPA calculations for graphene@metals
- Beyond RPA: The renormalized ALDA kernel

From sun light to fuels



Photoelectrochemical cell

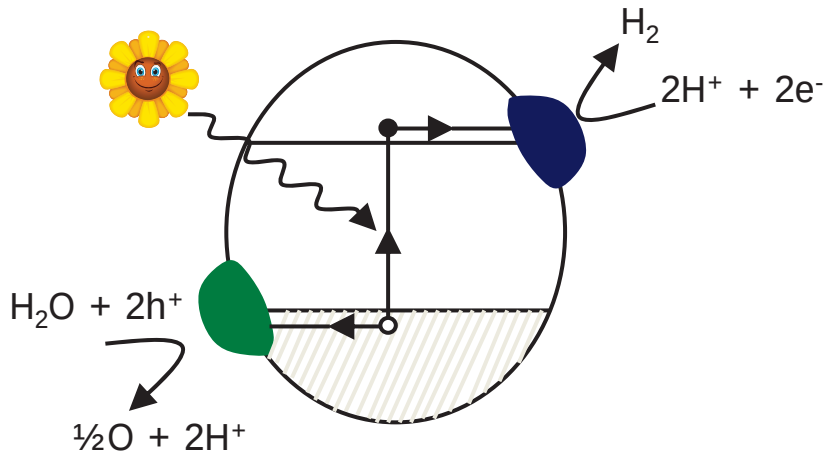
$2\ h\nu + H_2O_{(liq)} \rightarrow ½\ O_{2(gas)} + H_{2(gas)}$
e-h chemical potential ≥ 1.23 eV



Bak et. al., *Int. J. Hydrogen Energy*, vol 27 (2002) 991-1022

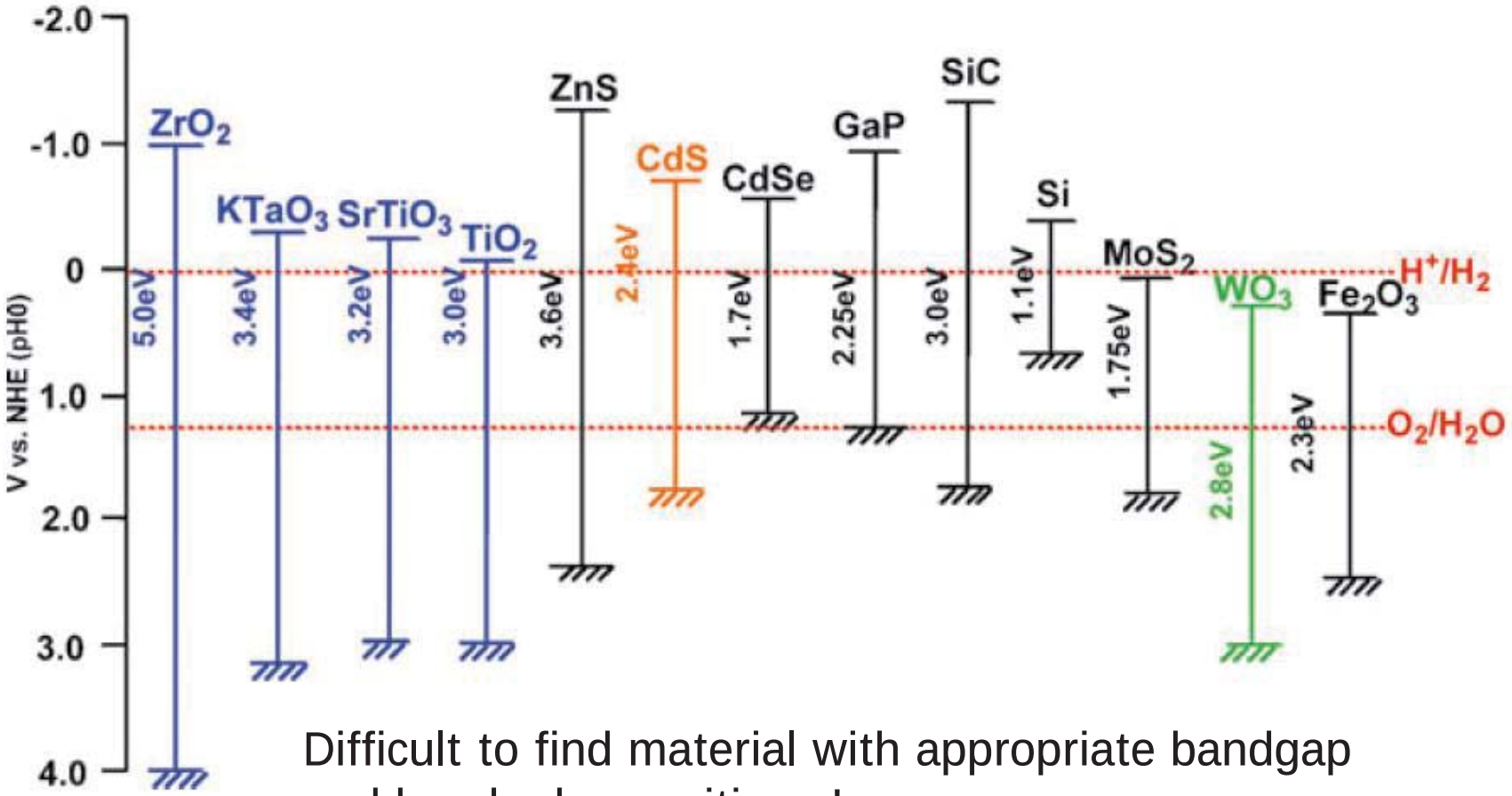
Materials for water splitting

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



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).

Possible semi-conductors

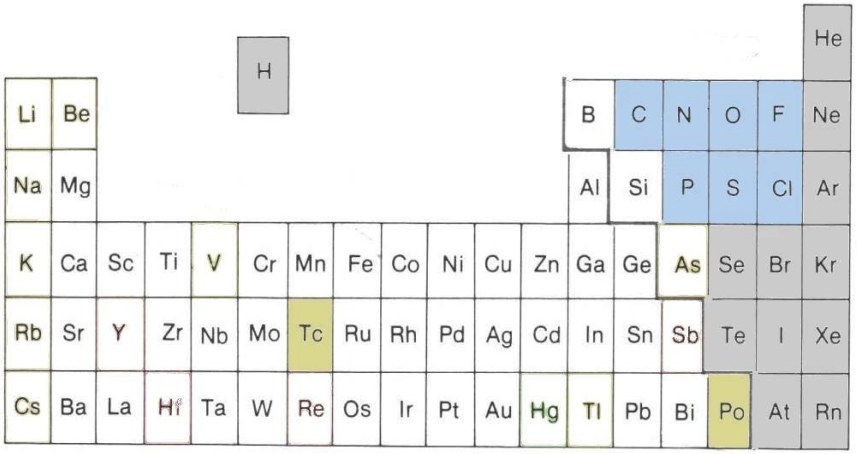


Difficult to find material with appropriate bandgap and band edge positions !

A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, **38**, 253 (2009)

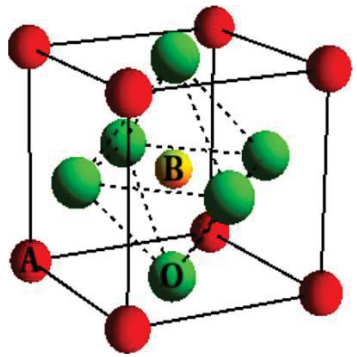
Materials – cubic perovskites

- 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

Density functional theory + friends

GPAW – projector augmented wave method in real space +

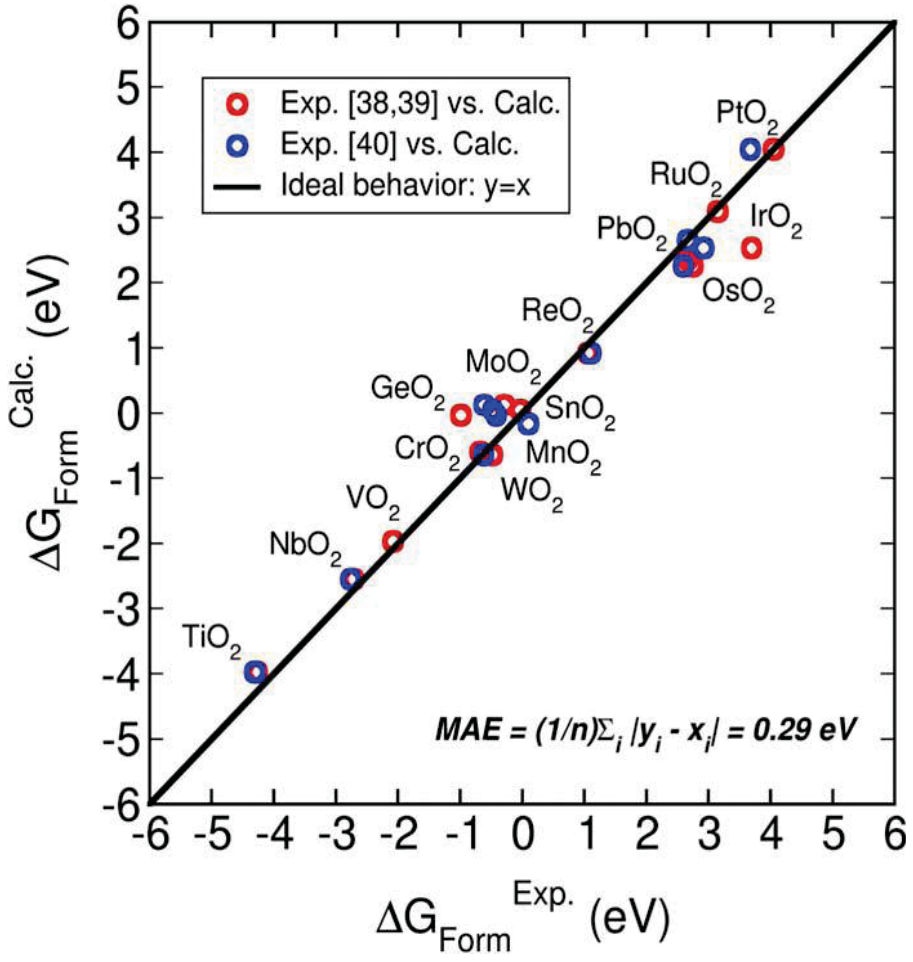
J. Enkovaara *et al.* J. Phys.:Cond. Mat. **22** (2010) ← **Review article**

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 (linear response+time propagation)
- ❑ Many-body perturbation theory (GW and Bethe-Salpeter equation)
- ❑ Phonons and electron-phonon coupling
- ❑ Coherent quantum electron transport
- ❑ QM/MM
- ❑ Atomic Simulation Environment (ASE) python scripting interface

Predicting stability of oxides – Heat of formation

- Oxides are naturally stable 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)

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 from DFT
- Dissolution of metal atoms and reactions with water

Formation energy (in practice more references included):

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

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

→ Solved by linear programming.

Bandgap calculations with GLLB-SC

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

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

Derivative discontinuity

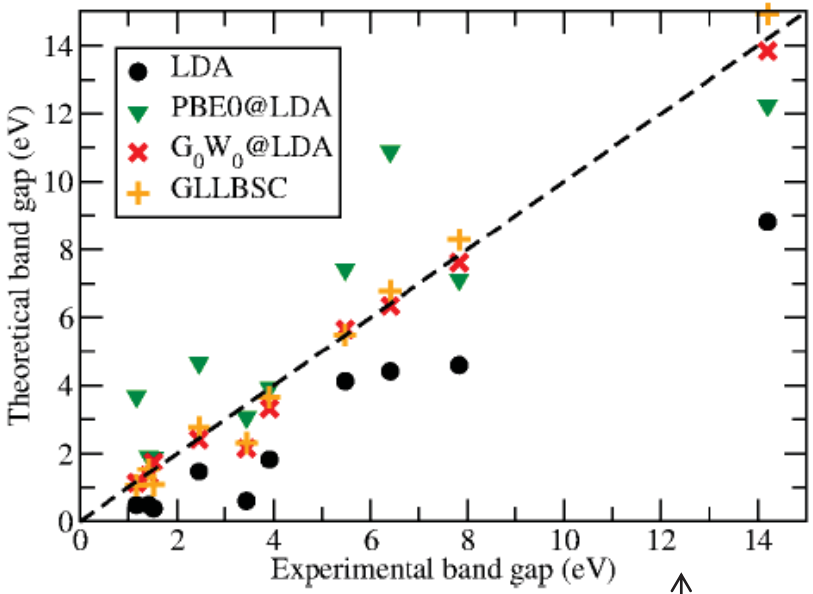
Screening + response

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

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

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

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



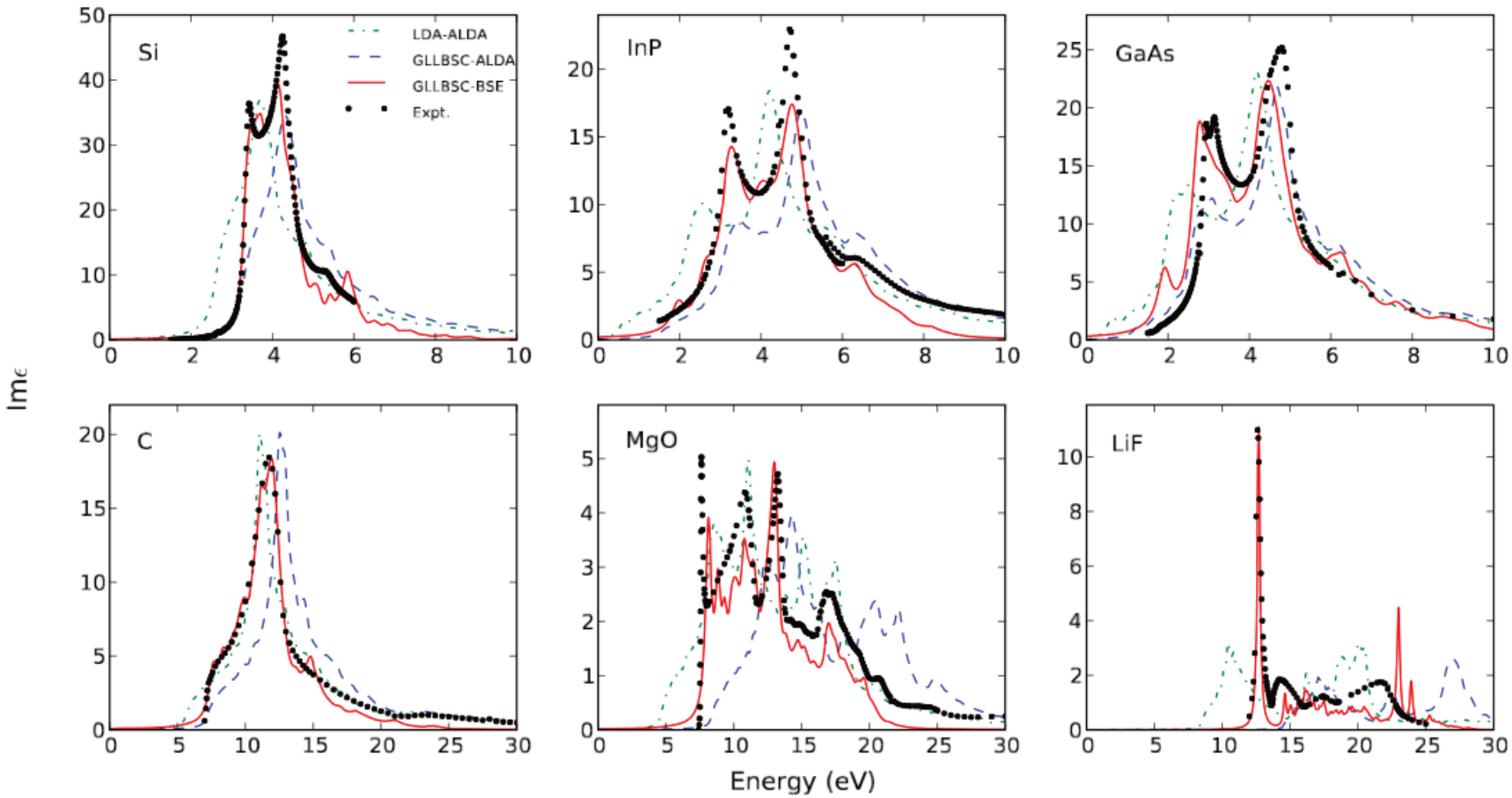
(GPAW calculations by Falco Hüser)

GLLBSC: 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).

Optical absorption spectra with GLLBSC-BSE



Derivative discontinuity used in single-particle energies, but not for W in the BSE.

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

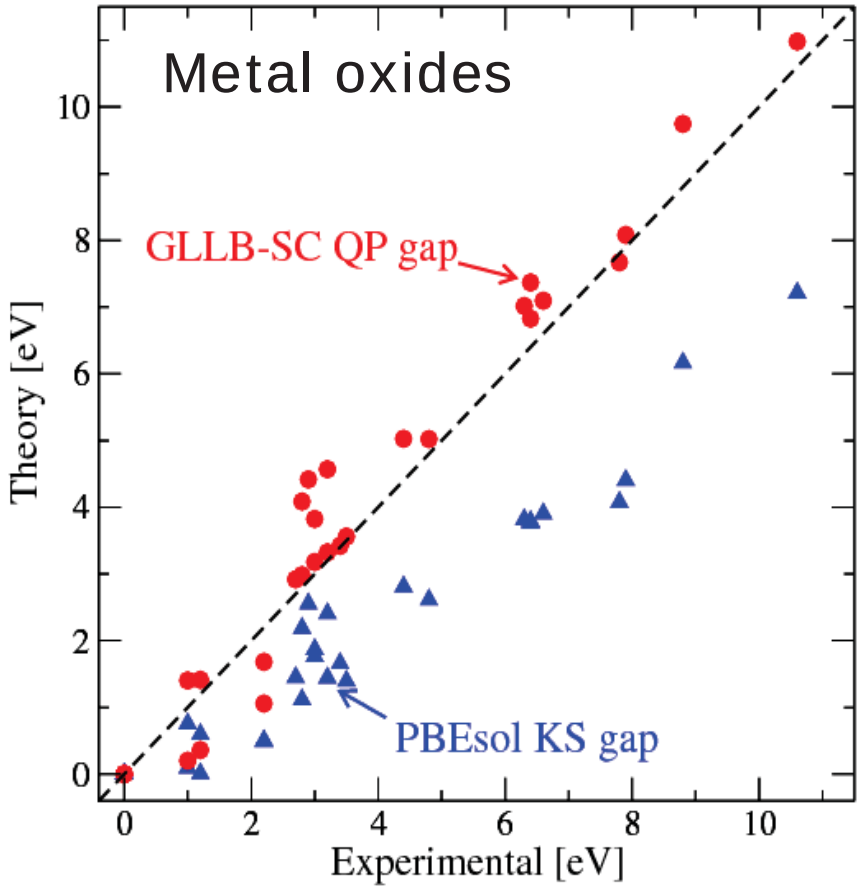
Predicting bandgaps of oxides with GLLBSC

The GLLB-SC xc-functional:

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

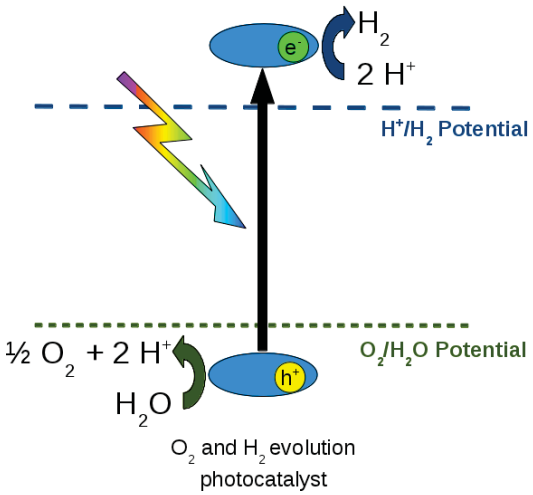
Derivative discontinuity

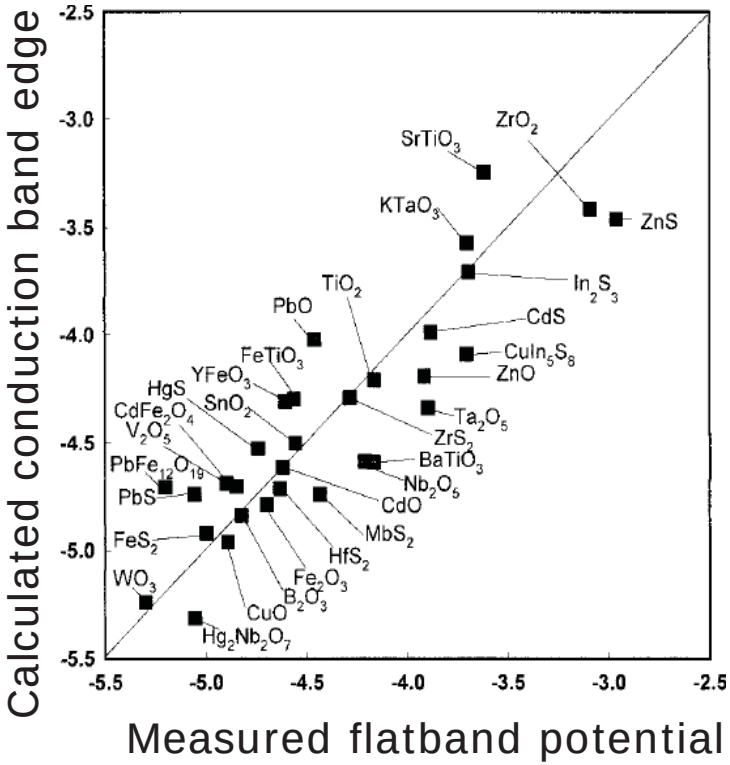
- Bandgaps within ~0.5 eV of exp.
- Minimal computational cost
- Neglect of electron-hole interaction



Band edge positions

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





$\chi = (A + I)/2$

(Absolute electronegativity)

A: Electron affinity

I: Ionization potential

E_{gap}: Band gap

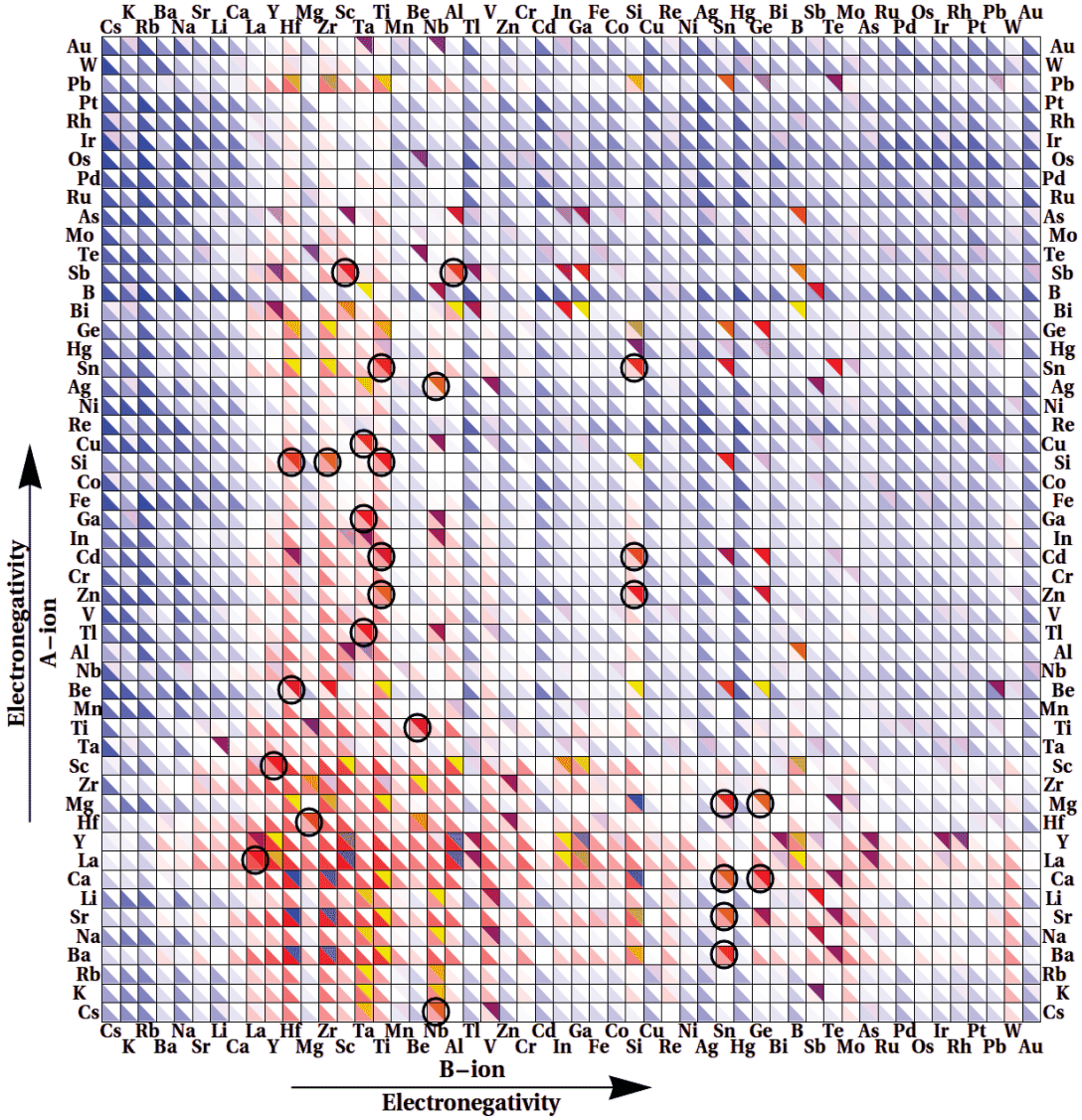
E_0 = -4.5 eV

(NHE relative to vacuum)

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

Y Xu and MAA Schoonen, American Mineralogist (2000)

Cubic perovskites: ABO_3



Stability:

Formation energy < 0.2 eV

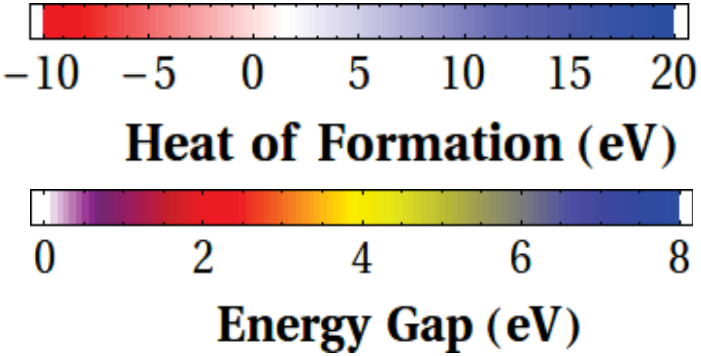
Light absorption:

1.5 eV < band gap < 3 eV

13 oxides

↓ (Level alignment)

10 oxides

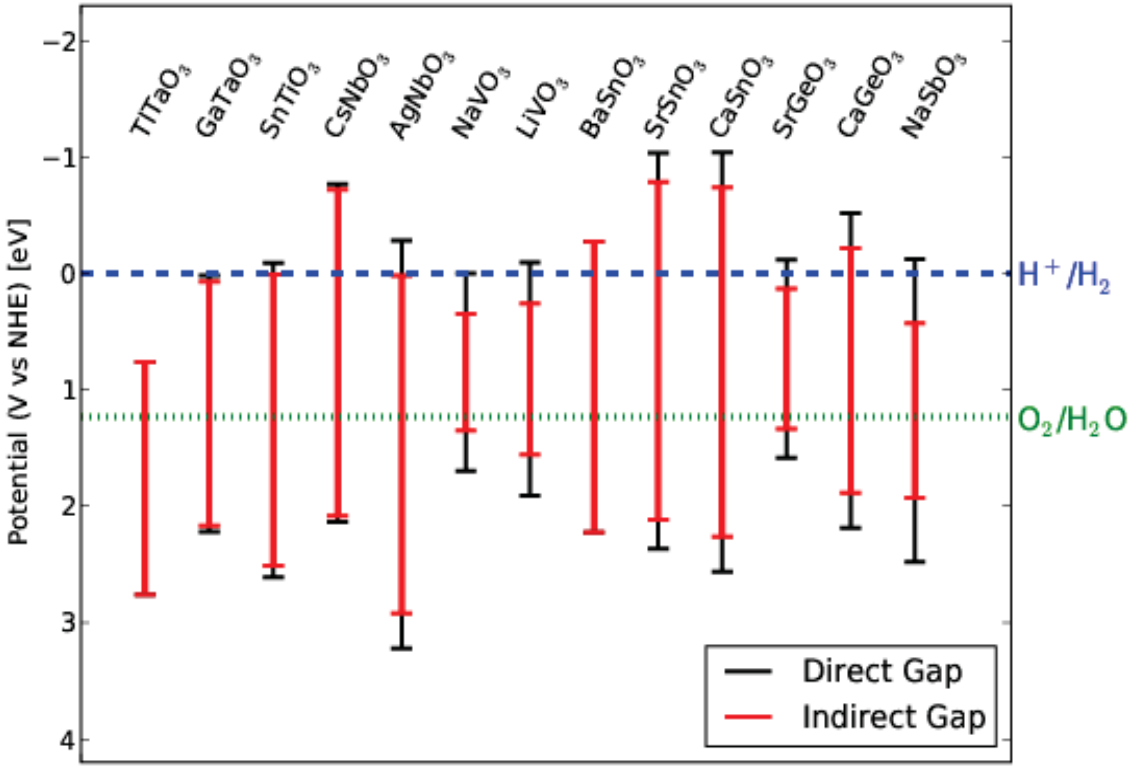


One-photon water splitting – oxide candidates

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

Oxides, oxynitrides, oxysulfides, oxyfluorides, oxyfluornitrides

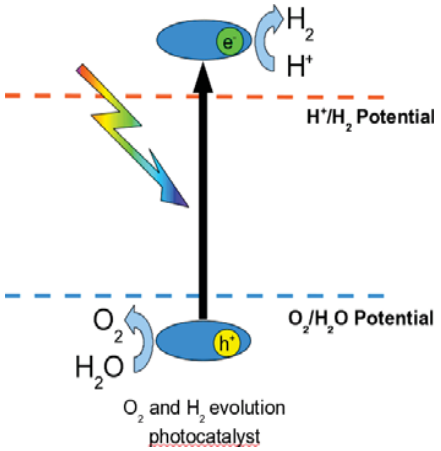
Materials candidates:

- ABO_3 :10
- ABO_2N :5
- $ABON_2$:2
- ABN_3 :0
- ABO_2S :0
- ABO_2F :3
- ABOFN :0

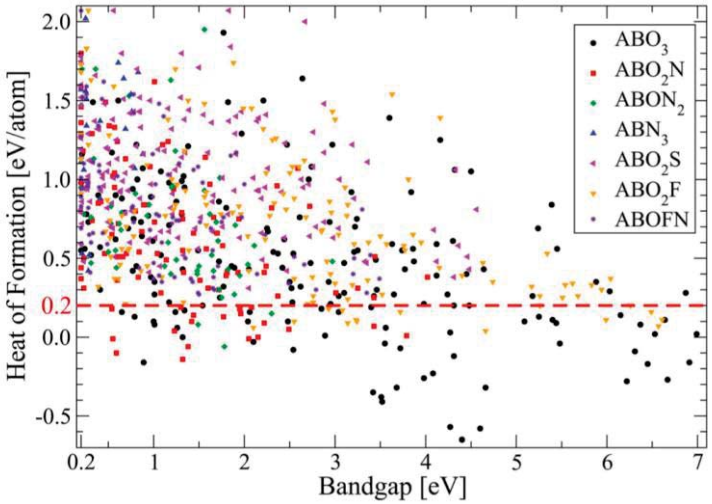
$BaTaO_2N$, $SrTaO_2N$, $CaTaO_2N$, $LaTiO_2N$ (known)
$MgTaO_2N$ (unknown)

$LaTaON_2$ (known)
$YTaON_2$ (unknown)

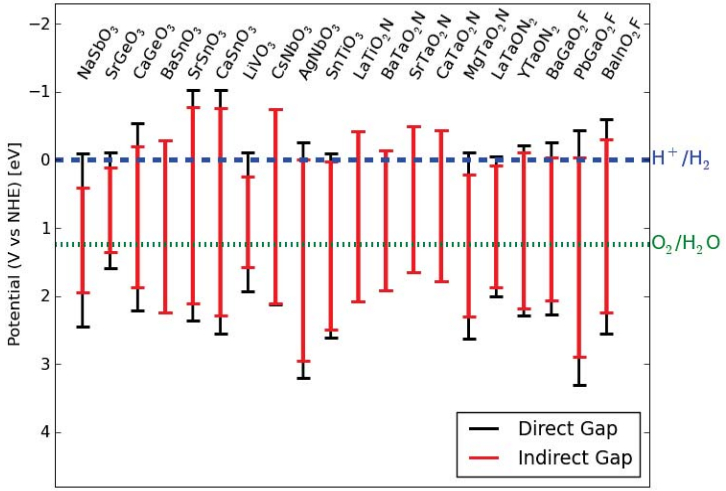
One-photon water splitting



~19000 materials

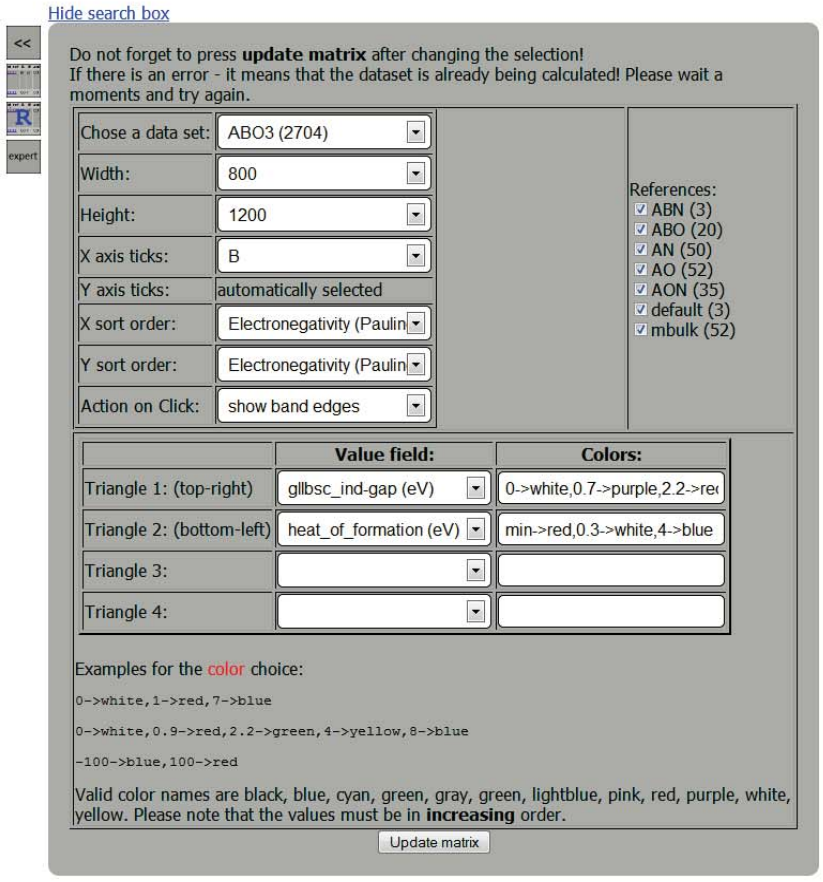


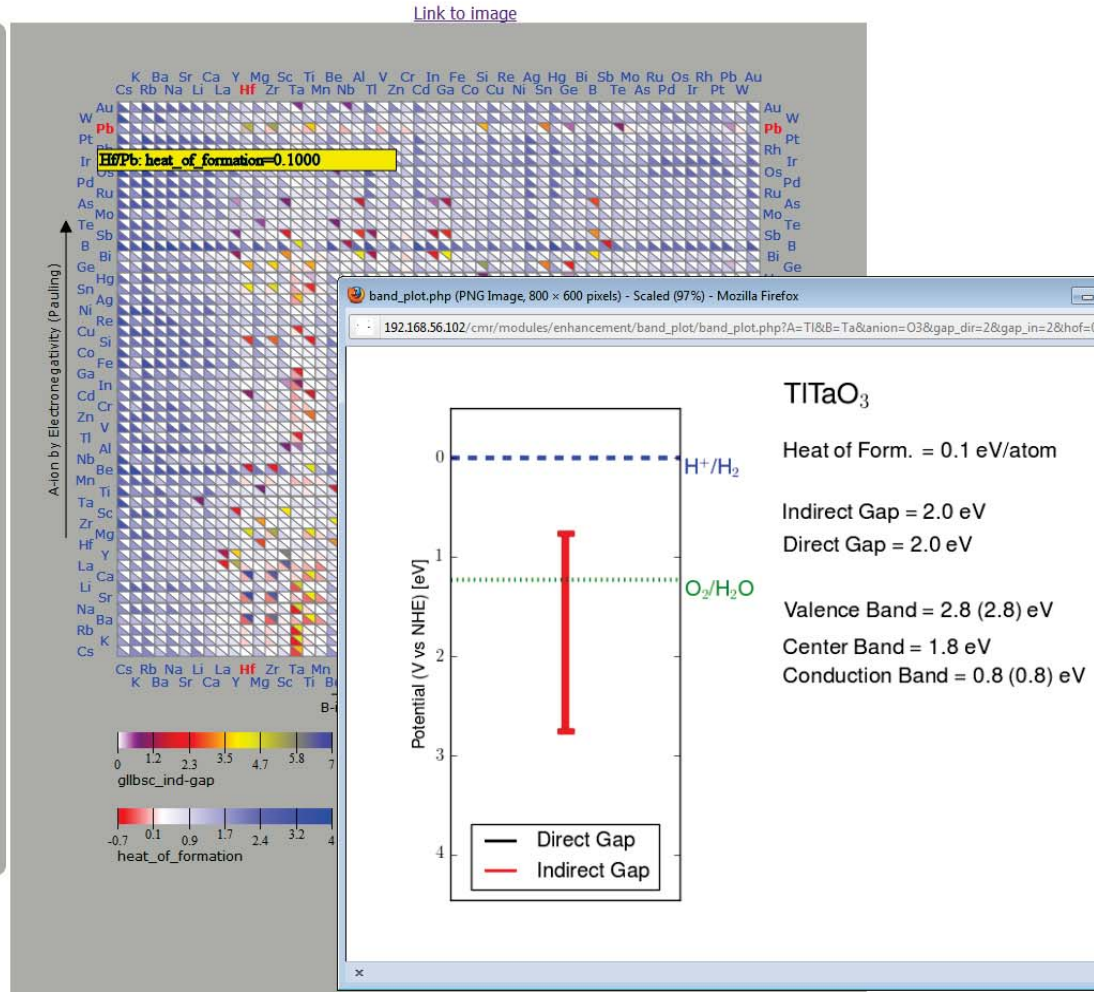
20 candidate materials



Project specific interface:
Light absorbing materials for water splitting

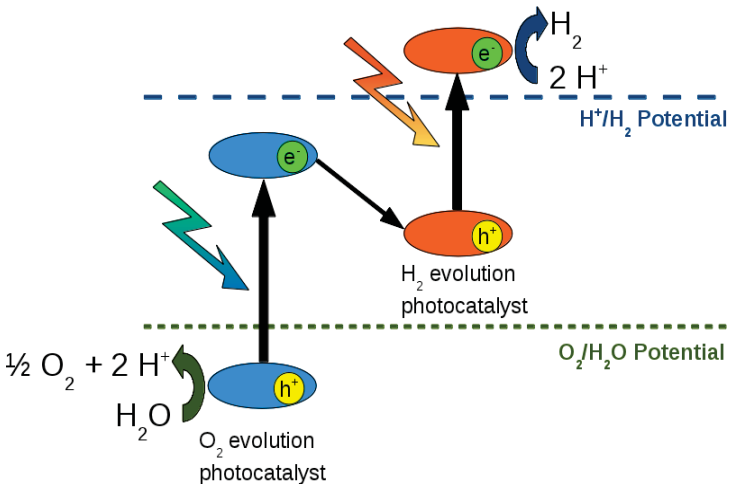
Computational Materials Repository





http://cmr.fysik.dtu.dk

Tandem cell water splitting: Screening for anode materials

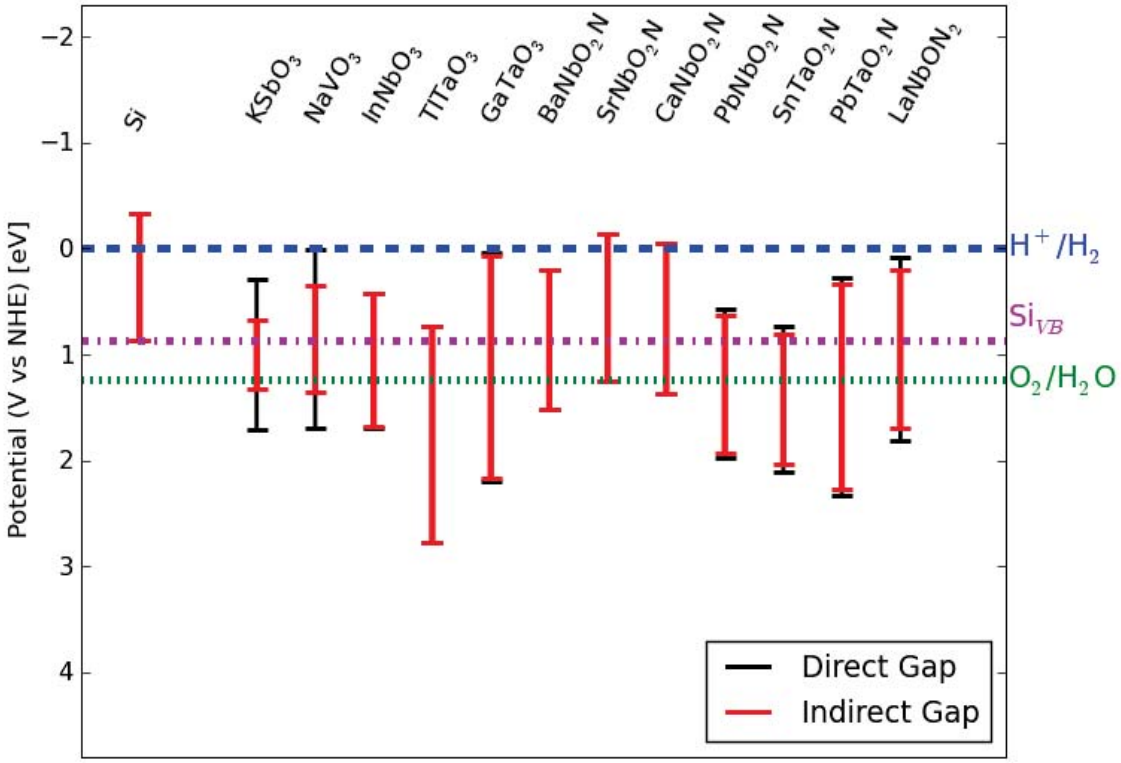


Selection criteria for anode material:

Stability: $E_{form} < 0.2$

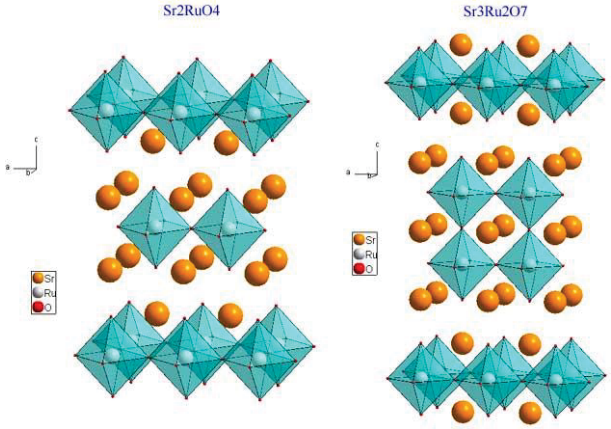
Band gap: $1.3 < E_{gap} < 3$ eV

12 candidates



I.E. Castelli, D.D. Landis, K.S. Thygesen, S. Dahl, I. Chorkendorff, T.F. Jaramillo, K.W. Jacobsen, *EES*, **5**, 9034 (2012).

Next: Layered perovskites + ICSD



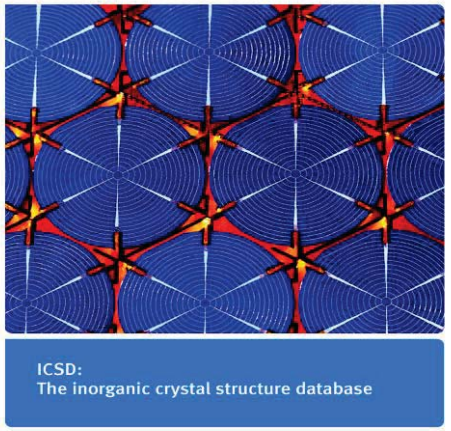
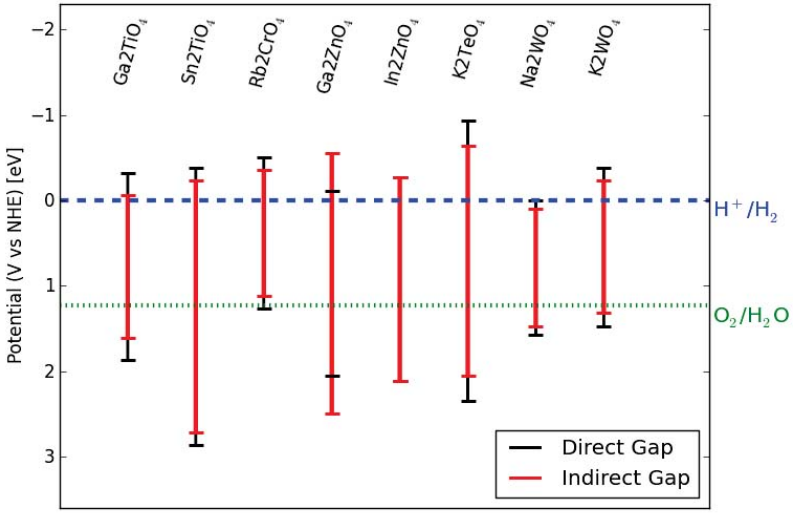
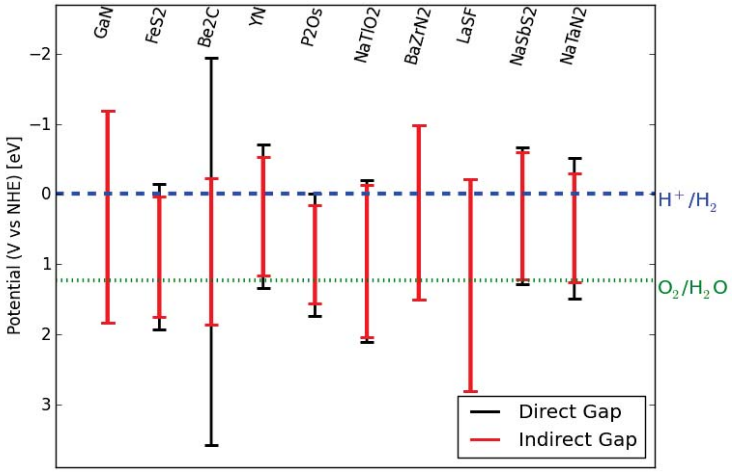


Figure from Cava lab, Princeton

Preliminary screenings:





Collaboration with the **Materials Project**, Anubhav Jain, Kristin Persson, Gerbrand Ceder, *GLLB band gaps for pre-optimized structures*

Total energies from the ACFDT

The **adiabatic connection and fluctuation-dissipation theorem**:

$$E_c = -\frac{1}{2\pi}\int_0^1 d\lambda \int_0^\infty d\omega \mathrm{Tr}\left[v\chi^\lambda(i\omega) - v\chi^0(i\omega)\right]$$

Kohn-Sham response function

Density response function from TDDFT:

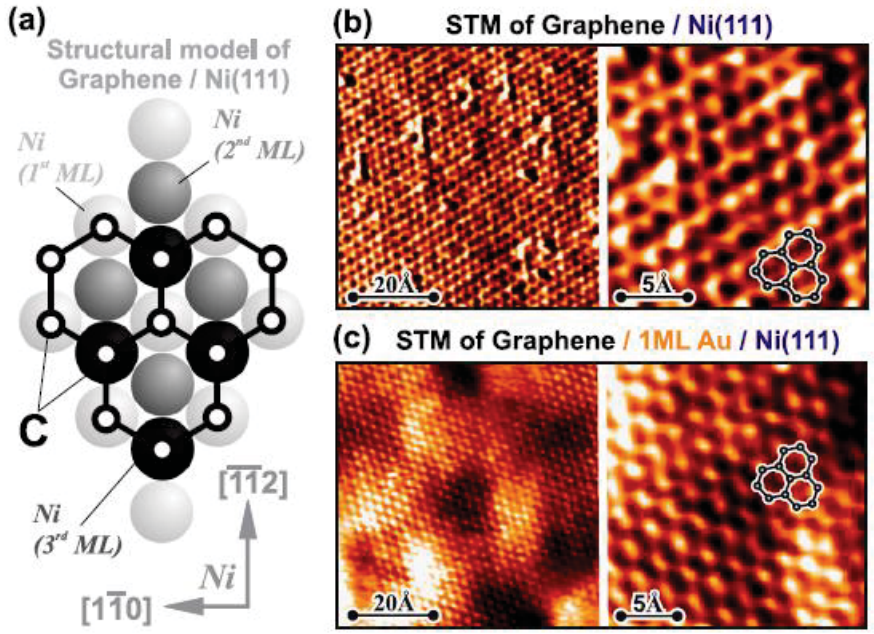
$$\chi^\lambda(\omega) = \chi^0(\omega) + \chi^0(\omega)[\lambda v + f_{xc}^\lambda(\omega)]\chi^\lambda(\omega)$$

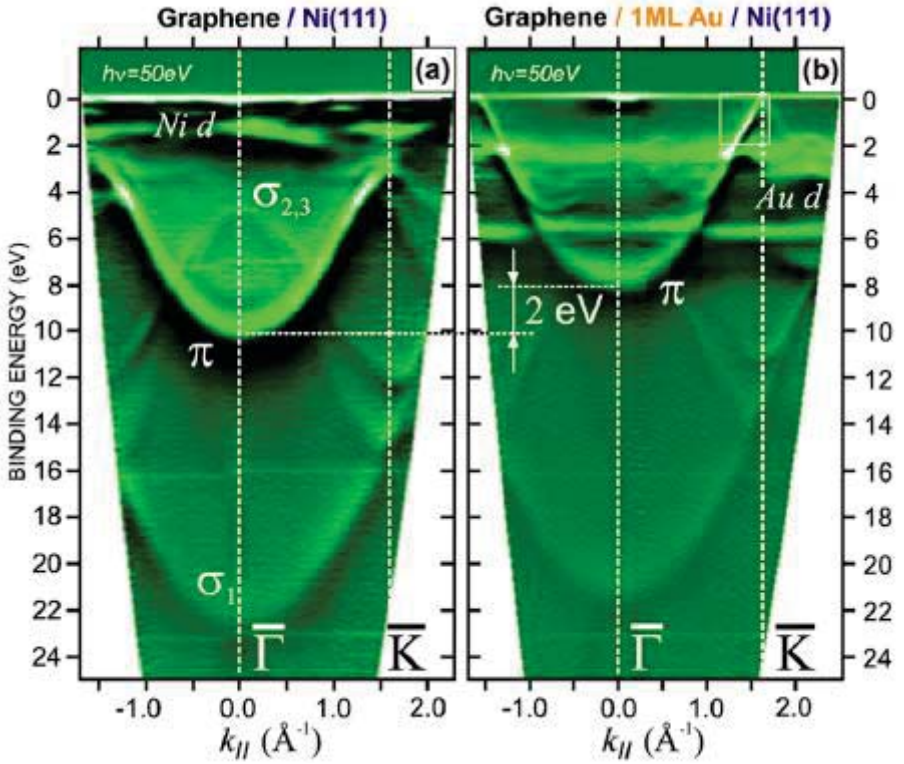
With the RPA one obtains (λ-dependence integrated analytically):

$$E_c^{RPA} = \int_0^\infty \frac{d\omega}{2\pi} \mathrm{Tr}\left[\ln\left(1 - v\chi^0(i\omega)\right) + v\chi^0(i\omega)\right]$$

→ Implemented in GPAW with plane wave basis.

Graphene on metals:
A prototypical metal/organic interface



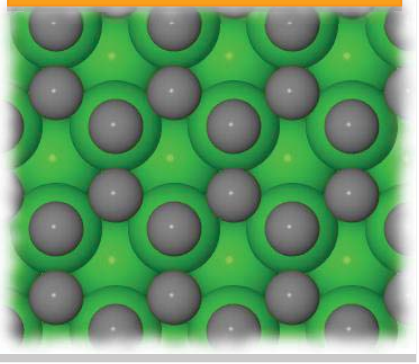


Varykhalov *et al.* PRL **101**, 157601 (2008)

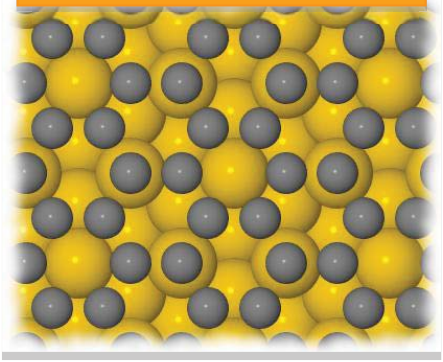
- ❑ Graphene is strongly bound on Ni(111) (hybridization opens band gap)
- ❑ Intercalation of a monolayer Au restores the Dirac cone
- ❑ Weak physisorption found for Pt(111), Ag(111), Cu(111), Au(111)
- ❑ Strong chemisorption found for Ni(111), Co(0001), Pd(111)

Graphene on metals: A challenge for DFT

Structure for Co, Ni and Cu



Structure for Pd, Ag, Au, Pt and Al

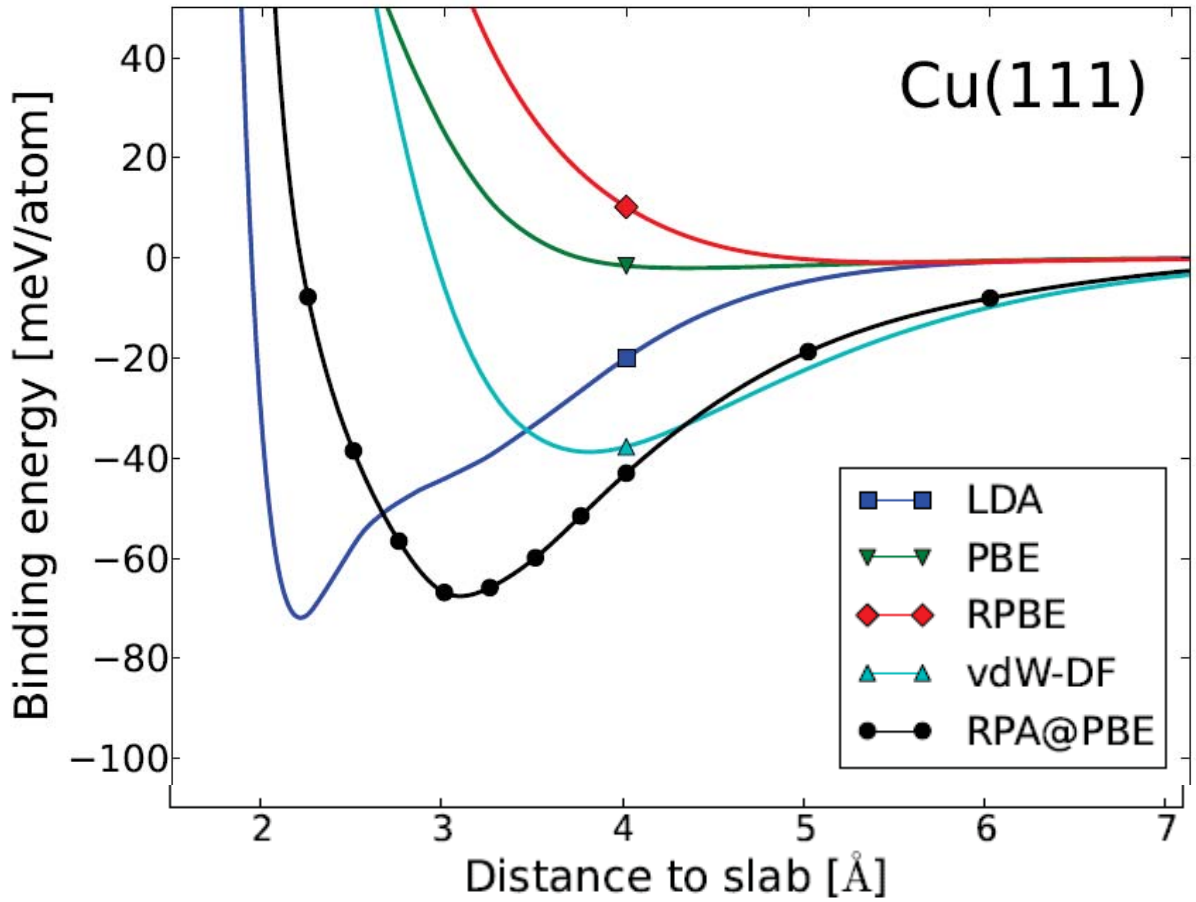


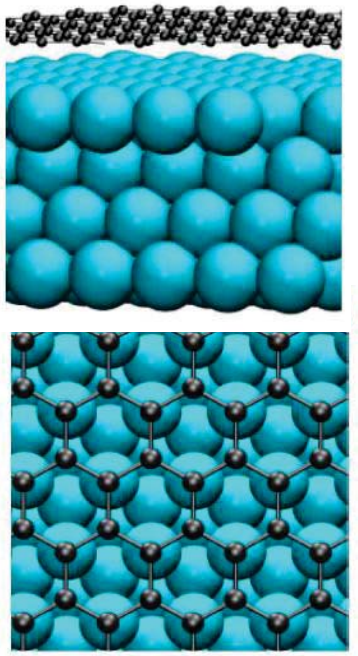
		Co	Ni	Pd	Ag	Au	Cu	Pt	Al
vdW-DF	d (Å)	3.40	3.50	3.50	3.55	3.57	3.58	3.67	3.72
	E_b (meV)	30	37	39	33	38	38	43	35
LDA	d (Å)	2.08	2.08	2.33	3.32	3.35	3.21	3.25	3.46
	E_b (meV)	175	123	79	45	31	35	33	25
Exp.	d (Å)	1.5-2.2	2.1	-	-	5	-	3.3	-
	Hybridization	strong	strong	strong	weak	weak	weak	weak	-

G. Giovannetti, P. A. Khomyakov, G. Brocks, V. M. Karpan, van den Brink, P. J. Kelly, PRL **101**, 026803 (2008)

M. Vanin, J.J. Mortensen, A.K. Kelkkanen, J.M. Garcia-Lastra, K.S. Thygesen, K.W. Jacobsen, PRB **81**, 081408 (2010)

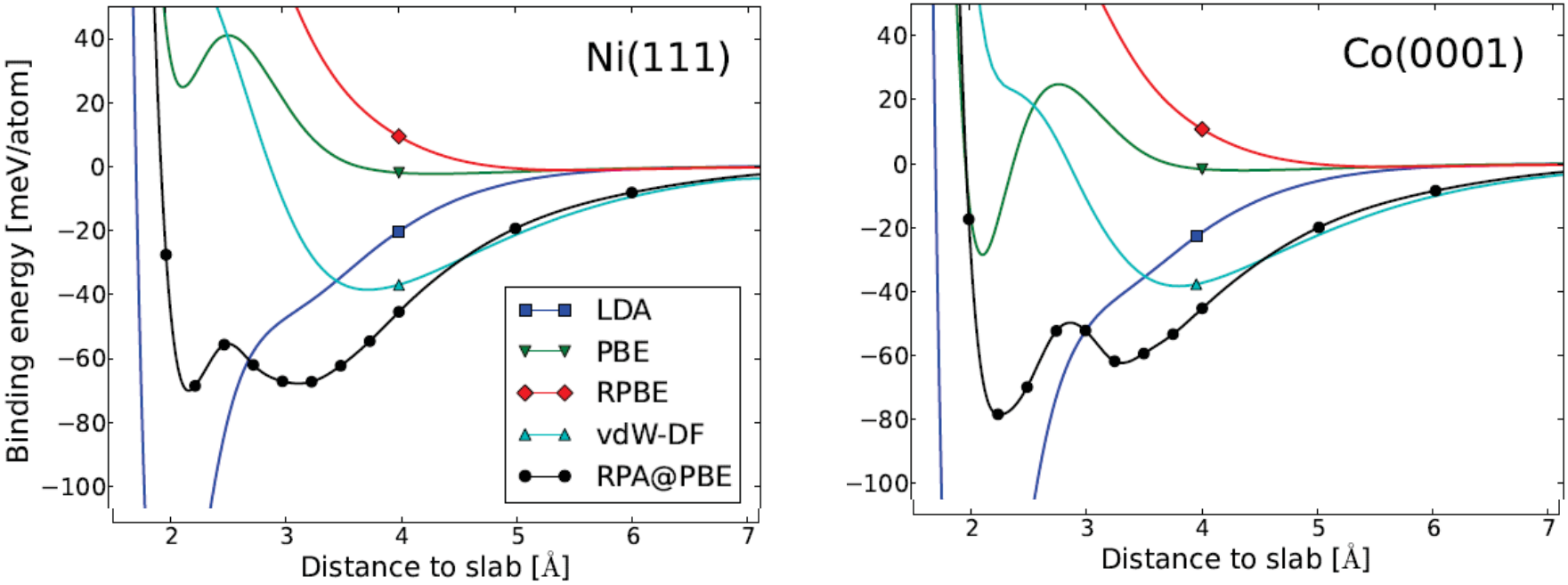
Potential energy surfaces of graphene@Cu(111)





T. Olsen, J. Yan, J. J. Mortensen, and KST, Phys. Rev. Lett. **107**, 156401 (2011)

Covalent vs. dispersion interaction



- vdW-DF accounts well for dispersive interactions, but misses covalent binding
- RPA seems to capture both effects

T. Olsen, J. Yan, J. J. Mortensen, and KST, Phys. Rev. Lett. **107**, 156401 (2011)

Towards chemical accuracy

- RPA gives proper description of long-range correlation, but…
- RPA severely underestimates absolute correlation energies
- RPA underestimates covalent bonds
- This could be improved by inclusion of an xc kernel

For the adiabatic LDA (ALDA) one has

$$f_x^{\lambda} = \lambda f_x$$

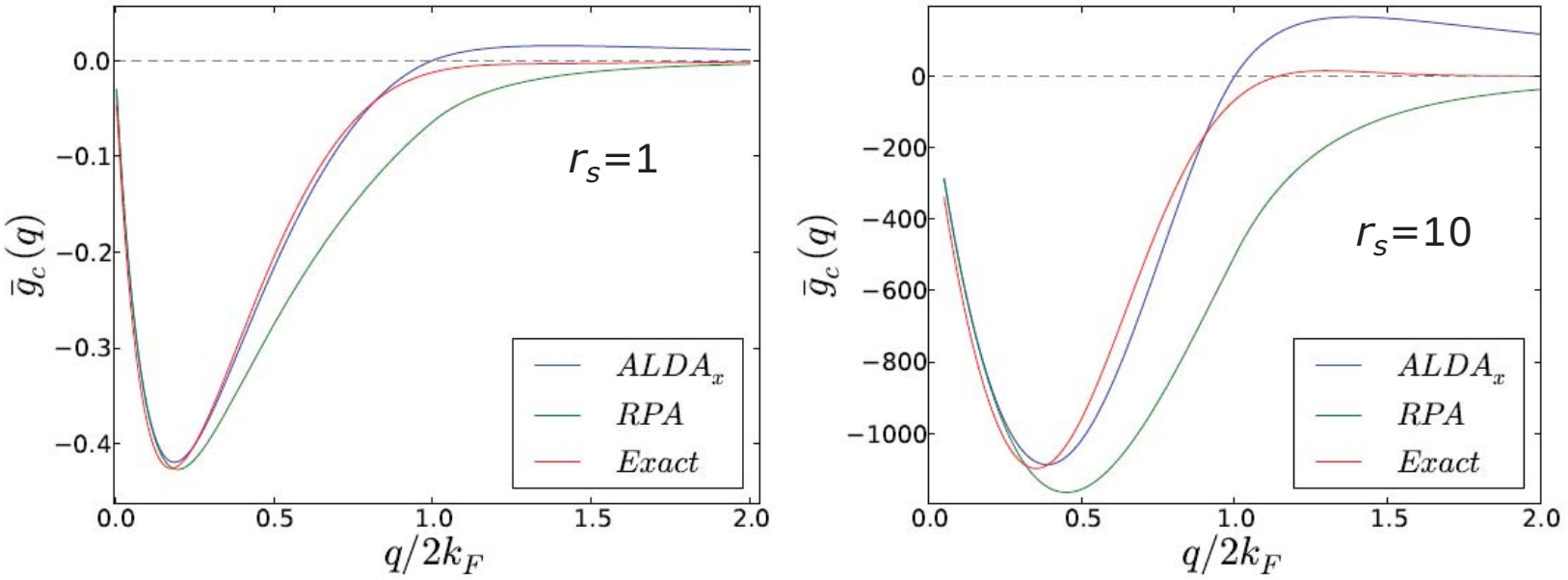
The coupling constant integration can then be performed to yield

$$E_c^{ALDA\_X} = \int_0^{\infty} \frac{d\omega}{2\pi} \mathrm{Tr}\left[\chi^0(i\omega) v \left(\chi^0(i\omega) f_x\right)^{-1} \ln\left(1 - \chi^0(i\omega) f_x\right) + v\chi^0(i\omega)\right]$$

But… ALDA does not improve RPA (overbinds) and suffers from convergence problems [Furche and Voorhis JCP **122**, 164106 (2005)].

The renormalized ALDA kernel (rALDA)

Coupling constant averaged correlation hole of the uniform gas:



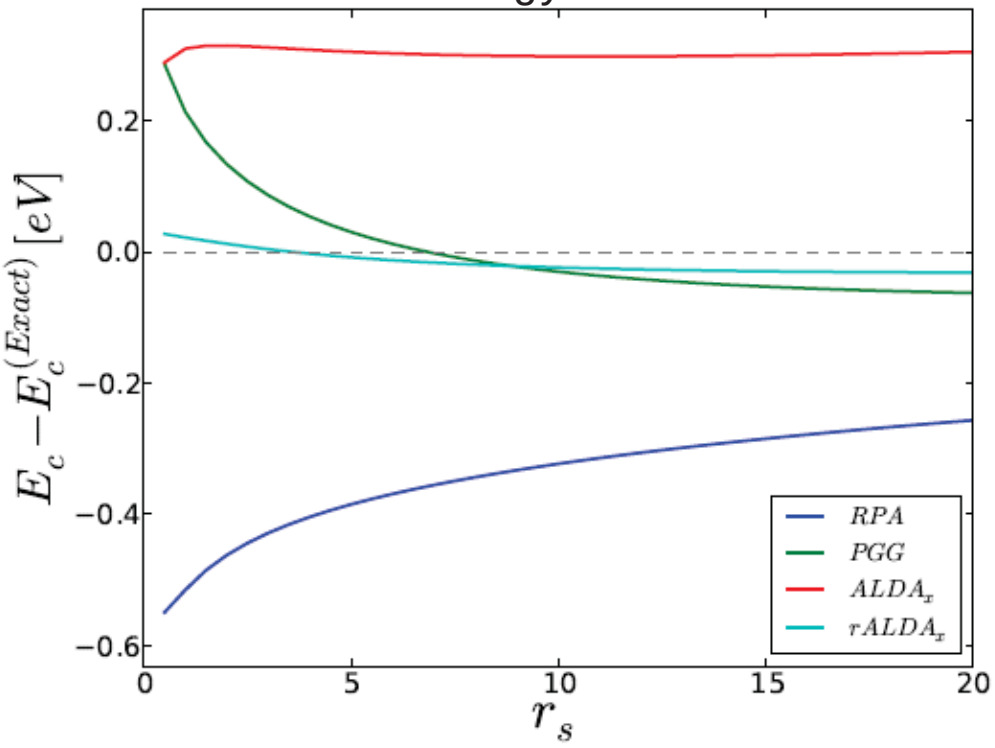
- RPA (ALDA) underestimate (overestimates) correlation energies
- For $q<2k_F$ the ALDA kernel is close to the exact result

Renormalized ALDA kernel: $f_{Hxc}^{rALDA}[n](q) = \theta(2k_F - q)\, f_{Hxc}^{ALDA}[n]$

Correlation energy of HEG

Renormalized ALDA kernel: $f_{Hxc}^{rALDA}[n](q) = \theta(2k_F - q)\, f_{Hxc}^{ALDA}[n]$

Correlation energy of the HEG:



T. Olsen and KST, RRB **86**, 081103(R) (2012)

rALDA for inhomogeneous systems

Renormalized ALDA kernel: $f_{Hxc}^{rALDA}[n](q) = \theta(2k_F - q)\, f_{Hxc}^{ALDA}[n]$

For inhomogeneous systems we replace:

$$r \to |r - r'| \quad , \quad k_F \to [3\pi^2 \tilde{n}(r,r')]^{1/3} \quad , \quad \tilde{n}(r,r') = [n(r) + n(r')]/2$$

Atomization energies (kcal/mol):

	LDA	PBE	RPA@LDA	RPA@PBE	ALDA	rALDA	Exp.
H_2	-113	-105	-109	-109 (109)	-110	-107	-109
N_2	-268	-244	-225	-224 (223)	-229	-226	-228
O_2	-174	-144	-103	-112 (113)	-155	-118	-120
CO	-299	-269	-234	-242 (244)	-287	-253	-259
F_2	-78	-53	-13	-30 (30)	-74	-39	-38
HF	-161	-142	-122	-130 (133)	-157	-136	-141
H_2O	-266	-234	-218	-222 (223)	-249	-225	-233
MAE	33	10.1	14.9	8.4	19	3.7	

T. Olsen and KST, RRB **86**, 081103(R) (2012)

Absolute correlation energies (kcal/mol):

	LDA	PBE	RPA	$ALDA_X$	rALDA	Exact
H	-14	-4	-13	6	-2	0
H_2	-59	-27	-51	-16	-28	-26
He	-70	-26	-41	-19	-27	-26

→ For more about rALDA including results for solids see **Thomas Olsen's** poster.

Conclusions

- High-throughput screening of >19.000 light-harvesting perovskites for water splitting
- Efficient and reliable calculation of band gaps from the GLLB-SC xc-functional + empirical model for band alignment
- Future: Extend to other materials and structures (double/layered perovskites) + include experimental data (ICSD)

- Graphene@metals: A challenge for ab-initio theory. RPA indicates a delicate balance between covalent and dispersive interactions
- RPA underestimates covalent bonding (local correlation problem)
- ALDA does not improve on RPA: xc-hole diverges for $r = 0$!
- The renormalized rALDA cures the problems of ALDA and yields very accurate energies for both molecules and solids.

Acknowledgements

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Ib Chorkendorff

Søren Dahl (now at Topsøe A/S)

Stanford University:

Tom Jaramillo

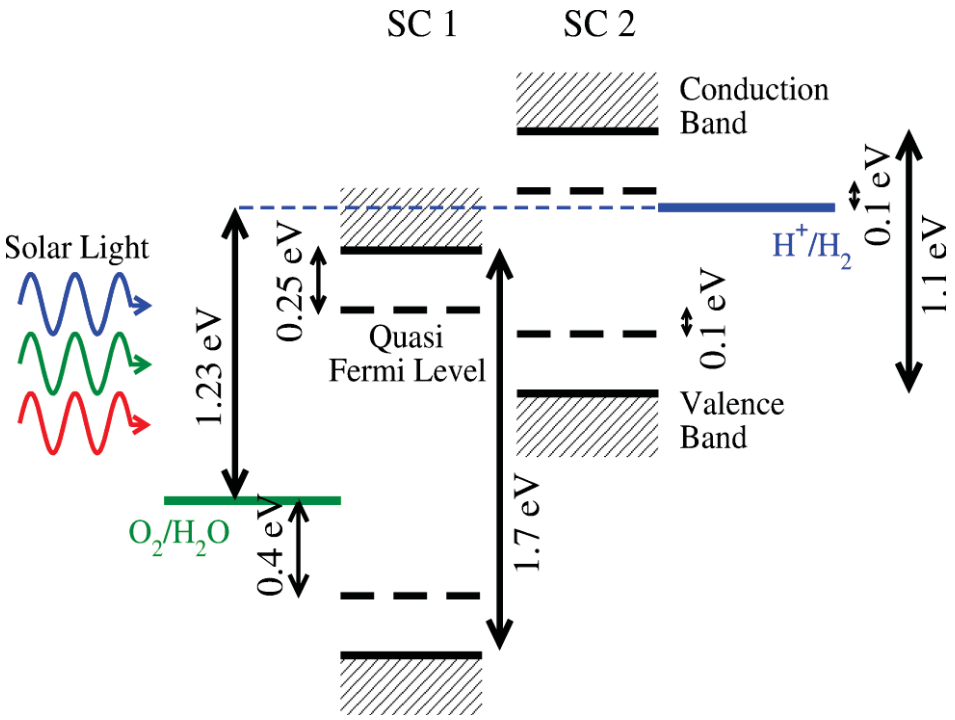
CAMd
Center for Atomic-scale Materials Design

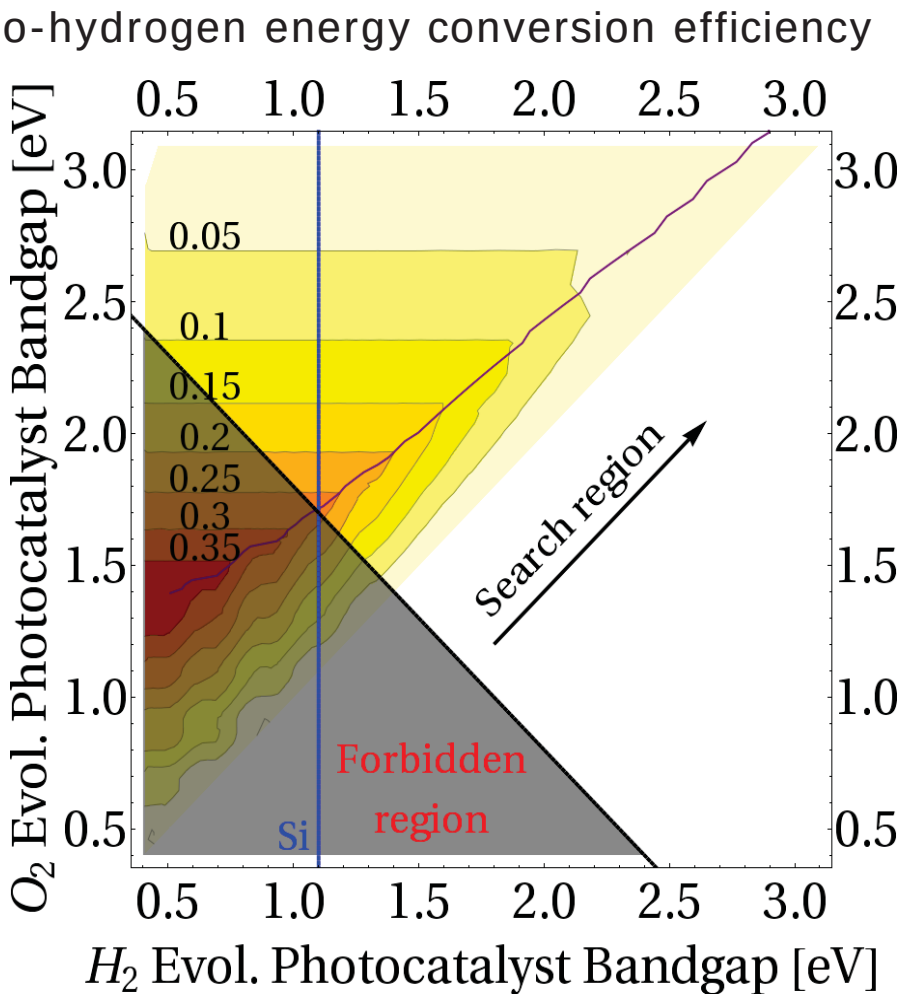
CASE
Catalysis for Sustainable Energy

Cneec
Center on Nanostructuring for Efficient Energy Conversion

Danish Agency for Science Technology and Innovation
Ministry of Science, Innovation and Higher Education

Tandem cell efficiency





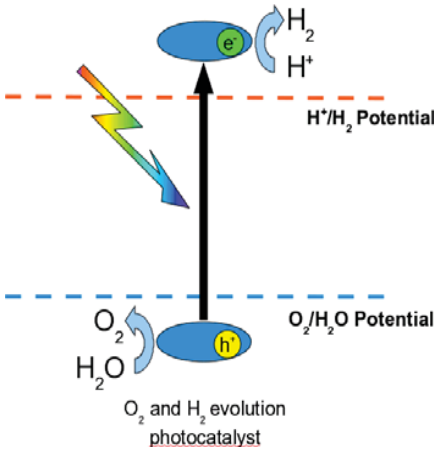
(J. R. Bolton et al., *Nature* 1985.)

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

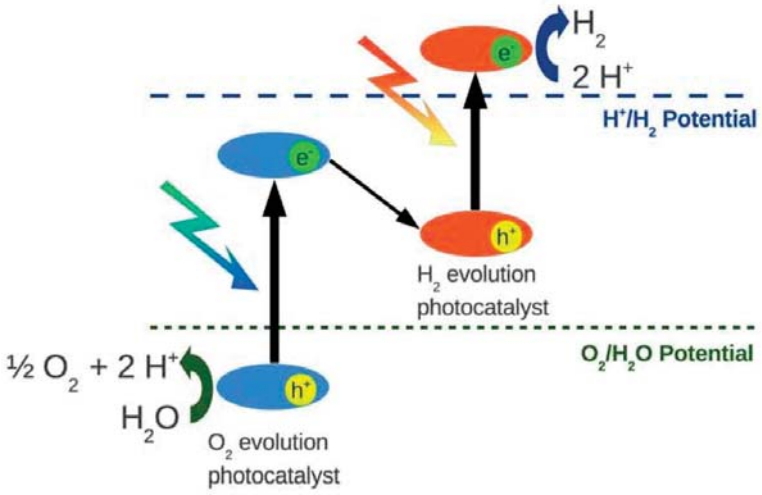
(I.E. Castelli, D.D. Landis, K.S. Thygesen, S. Dahl, I. Chorkendorff, T.F. Jaramillo, and K.W. Jacobsen, *Energy & Environmental Science*, doi: 10.1039/c2ee22341d)

Design rules for two-photon water splitting

One-photon



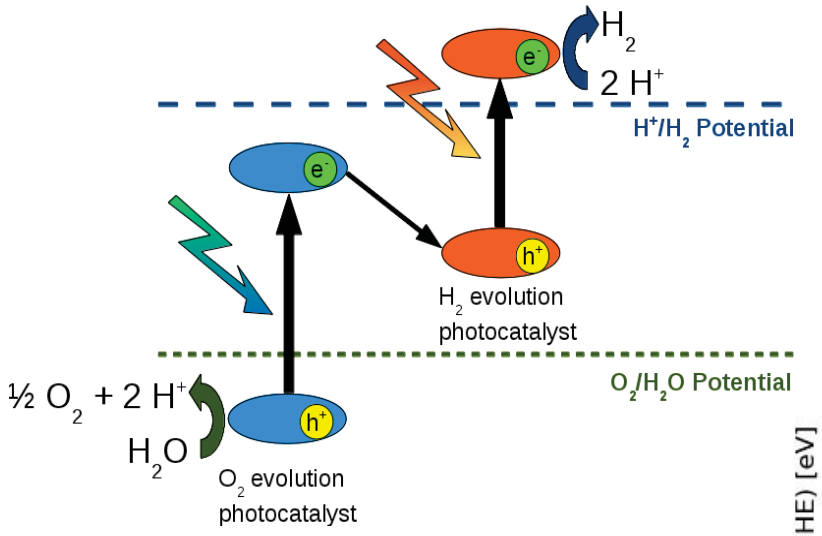
Two-photon



H_2 photocatalyst: Si
O_2 photocatalyst: screening

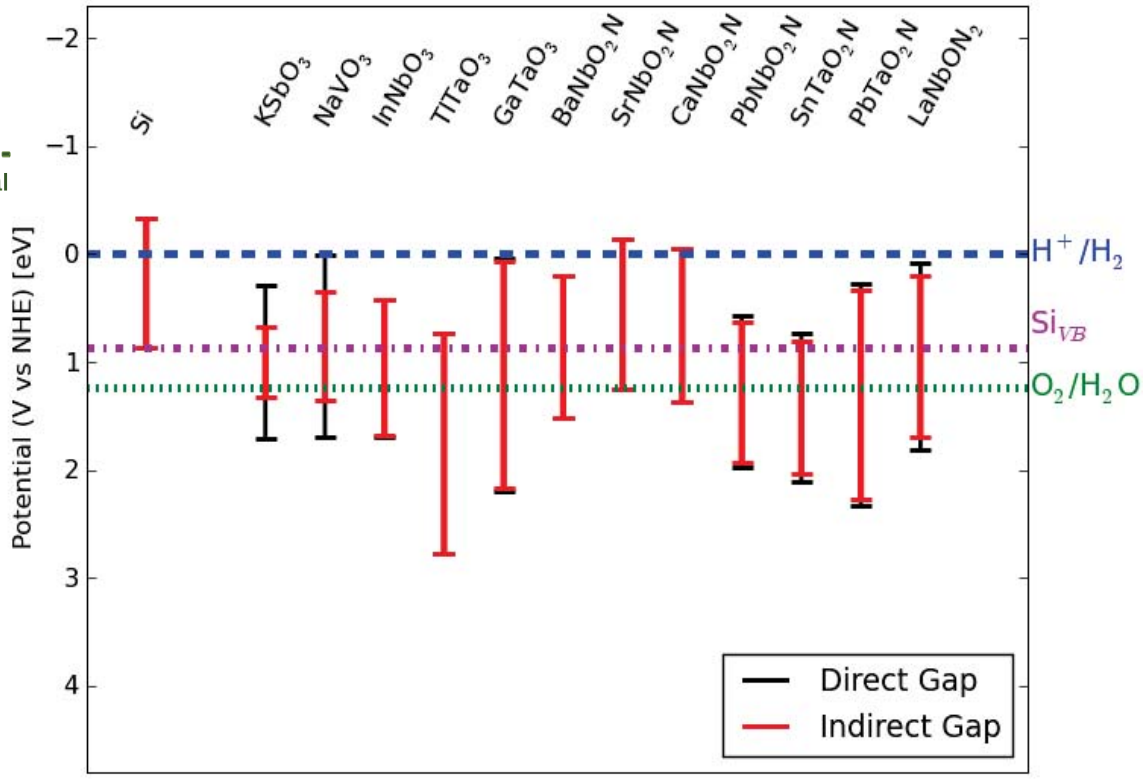
Screening parameters	One-photon WS	Two-photon WS
Chemical/structural stability (ΔE)	$\Delta E \leq 0.2$ eV	$\Delta E \leq 0.2$ eV
Bandgap (E_{gap})	$1.5 \leq E_{gap} \leq 3$ eV	$1.3 \leq E_{gap} \leq 3$ eV
Band edges	$VB_{edge} > 1.23$ eV	$VB_{edge}^{anode} > 1.23$ eV
(VB_{edge}, CB_{edge})	$CB_{edge}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

Tandem cell water splitting: Screening results



$E_{form} < 0.2$

$1.3 < E_{gap} < 3$ eV



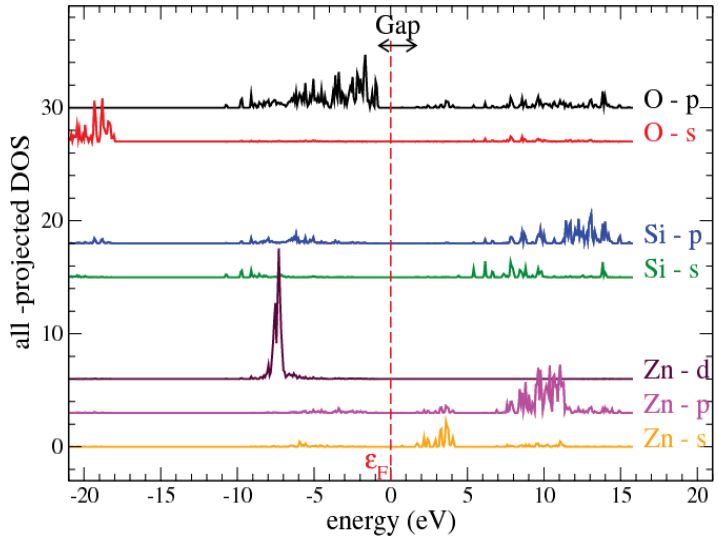
12 candidates

+ 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.

Analyzing gap formation



$ZnSiO_3$

Formation energy = -1 eV;

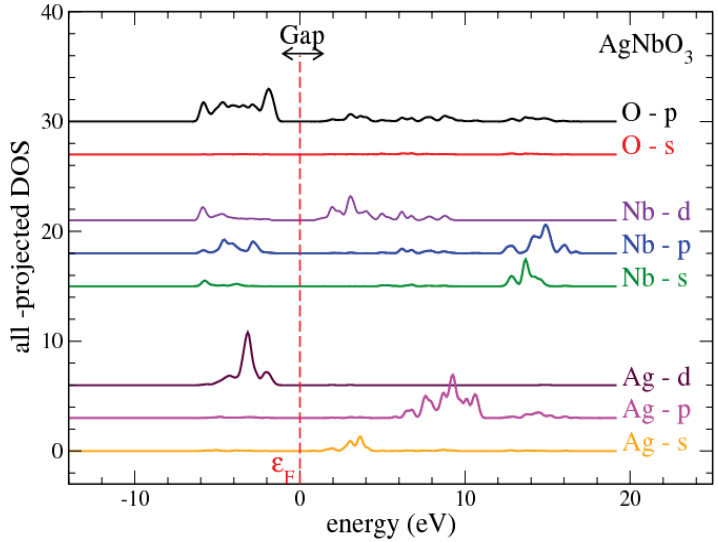
Band gap = 2.4 eV.

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.

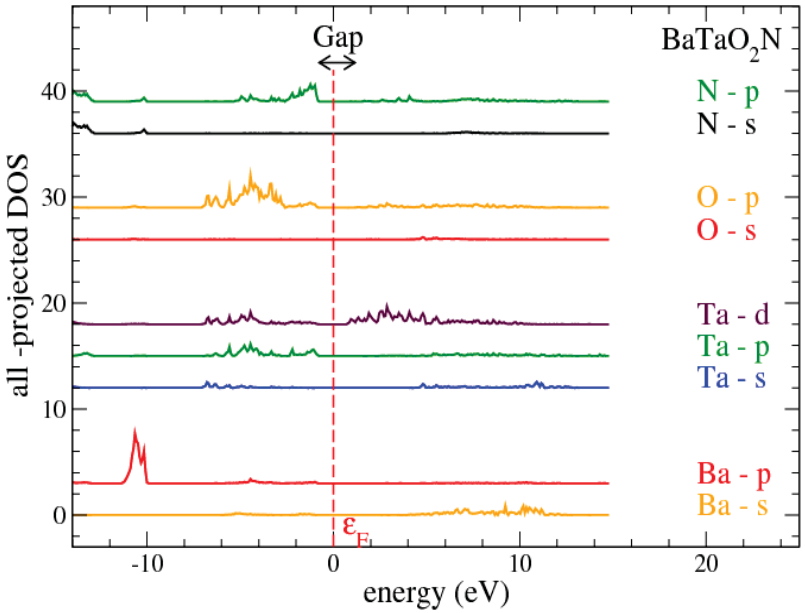
Valence band:

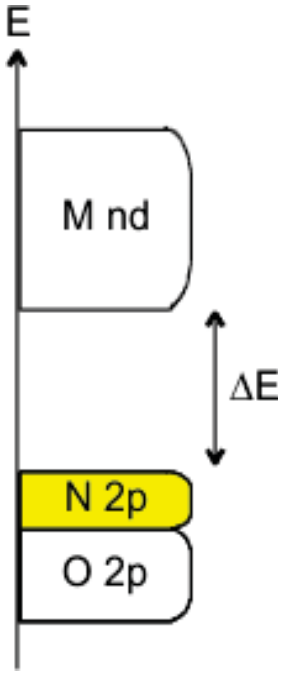
Ag – d and **O – p orbitals**;

Conduction band:

Nb – d orbitals.

Oxynitrides





$BaTaO_2N$

Formation energy = -6.3 eV;

Band gap = 2.0 eV.

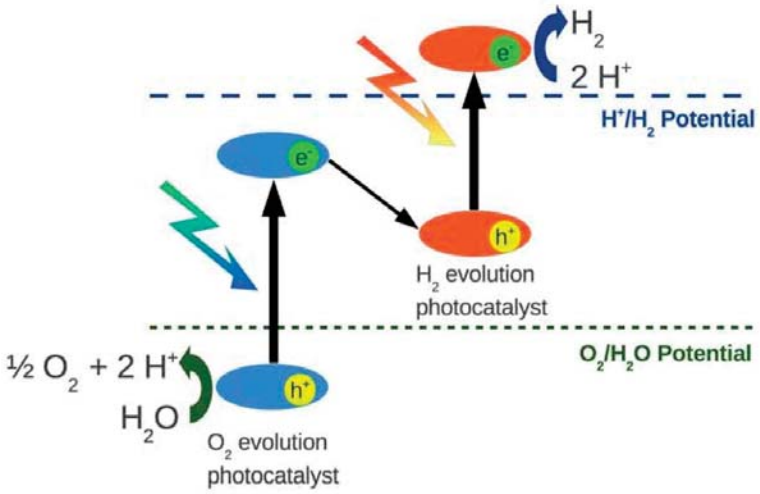
Valence band:

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

Transparent protecting shield – photoanode