Atomic-scale design of energy materials

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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

\[ 2 \ h\nu + \ H_2\text{O}_{(\text{liq})} \rightarrow \frac{1}{2} \ \text{O}_2\text{(gas)} + \ H_2\text{(gas)} \]

\( e^- \rightarrow \text{h chemical potential} \geq 1.23 \ \text{eV} \)

- 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)

Possible semi-conductors

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

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 +

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.

\[ MAE = \frac{1}{n} \sum |y_i - x_i| = 0.29 \text{ eV} \]
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 $A_xB_yO_z(s)$
  - Composition and structure available experimentally
  - Energy calculated from DFT
- Dissolution of metal atoms and reactions with water

Formation energy (in practice more references included):

$$
\Delta E = ABO_3(s) - \min \left( \sum_{i} c_i A(s) + c_2 B(s) + c_3 A_xO_y(s) + c_4 B_xO_y(s) + c_5 O \right)
$$

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

→ Solved by linear programming.
The GLLB xc-functional (Gritsenko, van Leeuwen, van Lenthe and Baerends):

\[ E_{g}^{OP} = E_{g}^{KS} + \Delta_{xc} \]

Derivative discontinuity

\[ v_{x}(r) = v_{S}(r) + v_{\text{resp}}(r) \]

\[ v_{S}(r) = \frac{2\epsilon_{x}^{\text{GGA}}(r; n)}{n(r)} \]

\[ v_{\text{resp}}(r) = \sum_{\text{occ}} K[n]\sqrt{\epsilon_{r} - \epsilon_{i}} \frac{|\psi_{i}(r)|^{2}}{n(r)} \]

\[ \Delta_{x,\text{resp}}(r) = \sum_{i}^{N} K(\sqrt{\epsilon_{N+1} - \epsilon_{i}} - \sqrt{\epsilon_{N} - \epsilon_{i}}) \frac{|\psi_{i}(r)|^{2}}{n(r)} \]

GLLBSC: Screening exchange-correlation from PBEsol


Optical absorption spectra with GLLBSC-BSE

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

The GLLB-SC xc-functional:

\[ E_{g}^{QP} = E_{g}^{KS} + \Delta_{xc} \]

- Bandgaps within \(~0.5\) eV of exp.
- Minimal computational cost
- Neglect of electron-hole interaction
Band edge positions

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

\( \chi = (A + I)/2 \)
(Absolute electronegativity)

\( A \): Electron affinity

\( I \): Ionization potential

\( E_{gap} \): Band gap

\( E_0 = -4.5 \text{ eV} \)
(NHE relative to vacuum)


Y Xu and MAA Schoonen, American Mineralogist (2000)
Cubic perovskites: $\text{ABO}_3$

**Stability:**
Formation energy $< 0.2$ eV

**Light absorption:**
$1.5$ eV $< $ band gap $< 3$ eV

- 13 oxides
- 10 oxides
- (Level alignment)
One-photon water splitting – oxide candidates

Empirical formula for the conduction band relative to NHE:

Butler and Ginley (1978)

\[ E_C = \left( \chi_A \chi_B \chi_O^3 \right)^{1/5} - \frac{1}{2} E_{\text{gap}} + E_0 \]

AgNbO₃ and BaSnO₃ known.
AgNbO₃ works!
BaSnO₃ defect-induced recombination

SrSnO₃ and CaSnO₃:
known in orthorhombic perovskite
→ too large gaps
Oxides, oxynitrides, oxysulfides, oxyfluorides, oxyfluornitrides

Materials candidates:

- ABO$_3$ : 10
- ABO$_2$N : 5
- ABON$_2$ : 2
- ABN$_3$ : 0
- ABO$_2$S : 0
- ABO$_2$F : 3
- ABOFN : 0

~19000 materials

One-photon water splitting

20 candidate materials
Tandem cell water splitting: Screening for anode materials

Selection criteria for anode material:
- Stability: $E_{\text{form}} < 0.2$
- Band gap: $1.3 < E_{\text{gap}} < 3$ eV

12 candidates

Next: Layered perovskites + ICSD

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:

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

Density response function from TDDFT:

\[
\chi^\lambda (\omega) = \chi^0 (\omega) + \chi^0 (\omega) \left[ \lambda \nu + f_{xc}^\lambda (\omega) \right] \chi^\lambda (\omega)
\]

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

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

\[\rightarrow\] Implemented in GPAW with plane wave basis.
Graphene on metals:
A prototypical metal/organic interface

- 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)

Varykhalov et al. PRL 101, 157601 (2008)
Graphene on metals: A challenge for DFT

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<tr>
<th></th>
<th>Co</th>
<th>Ni</th>
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<td>$E_b$ (meV)</td>
<td>30</td>
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<td>33</td>
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<td>-</td>
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<td>weak</td>
<td>weak</td>
<td>weak</td>
<td>weak</td>
<td>-</td>
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</table>

Potential energy surfaces of graphene@Cu(111)

vdW-DF accounts well for dispersive interactions, but misses covalent binding

RPA seems to capture both effects

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

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

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

Correlation energy of 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:
\[
r \rightarrow |r - r'| \quad , \quad k_F \rightarrow [3\pi^2 \bar{n}(r, r')]^{1/3} \quad , \quad \bar{n}(r, r') = [n(r) + n(r')] / 2
\]

<table>
<thead>
<tr>
<th>Atomization energies (kcal/mol):</th>
<th>Absolute correlation energies (kcal/mol):</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>PBE</td>
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<td>H₂O</td>
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T. Olsen and KST, RRB 86, 081103(R) (2012)

→ 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.
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Stanford University:
Tom Jaramillo
Tandem cell efficiency

\[ \text{(J. R. Bolton et al., Nature 1985.)} \]
\[ \text{(M. G. Walter et al., Chem Rev 110, 6446, 2010)} \]
Design rules for two-photon water splitting

### One-photon WS

- **Chemical/structural stability ($\Delta E$)**: $\Delta E \leq 0.2$ eV
- **Bandgap ($E_{\text{gap}}$)**: $1.5 \leq E_{\text{gap}} \leq 3$ eV
- **Band edges**
  - $V_{\text{edge}} > 1.23$ eV
  - $C_{\text{edge}} < 0$ eV

### Two-photon WS

- **Chemical/structural stability ($\Delta E$)**: $\Delta E \leq 0.2$ eV
- **Bandgap ($E_{\text{gap}}$)**: $1.3 \leq E_{\text{gap}} \leq 3$ eV
- **Band edges**
  - $V_{\text{edge}} > 1.23$ eV
  - $C_{\text{edge}} < 0$ eV
  - $V_{\text{cathode}} > C_{\text{anode}}$

### Photocatalysts

- **H$_2$ photocatalyst**: Si
- **O$_2$ photocatalyst**: screening
Tandem cell water splitting:
Screening results

12 candidates
+ 20 from overall WS


LaTiO$_2$N now under experimental investigation at CINF/CASE/DTU.
Analyzing gap formation

**ZnSiO₃**
- Formation energy = -1 eV;
- Band gap = 2.4 eV.
- Valence band: **O – p orbitals** (too deep for water-splitting);
- Conduction band: **Zn – s orbitals**.

**AgNbO₃**
- Formation energy = -0.6 eV;
- Band gap = 3.0 eV.
- Valence band: **Ag – d and O – p orbitals**;
- Conduction band: **Nb – d orbitals**.
BaTaO$_2$N
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

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.

Two semiconductors – two photons

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

H₂ photocatalyst: Si
O₂ photocatalyst: screening
Transparent protecting shield – photoanode

\[ E_{\text{form}} < 0.2 \]

\[ E_{\text{gap}} > 3 \text{ eV} \]