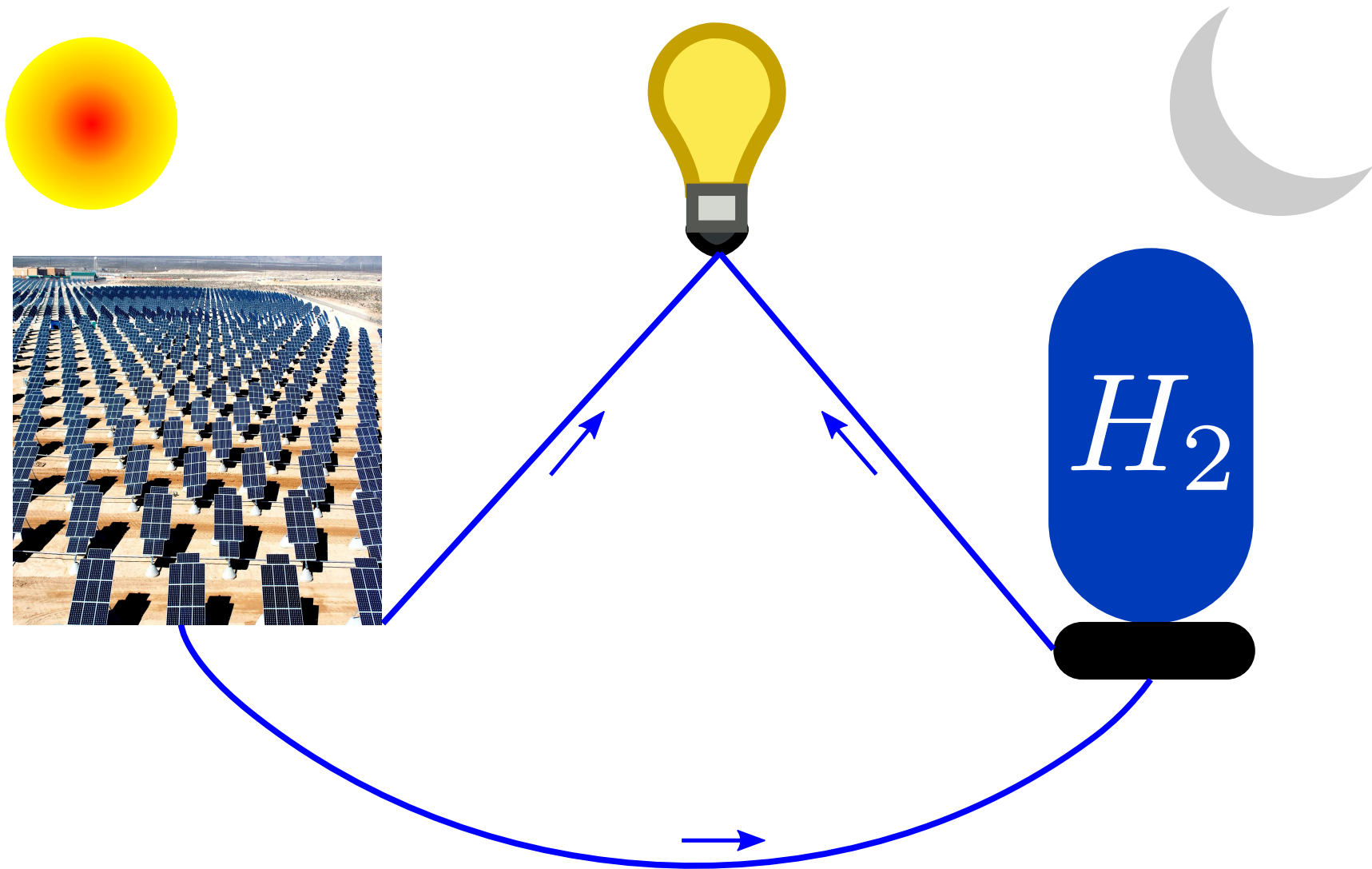# Harvesting solar energy
using computer simulations

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28th June 2012

Solar energy, production and storage
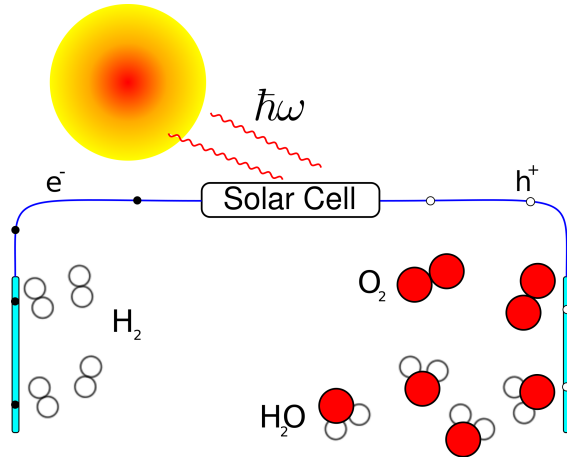
Harald Oberhofer

Harvesting solar energy
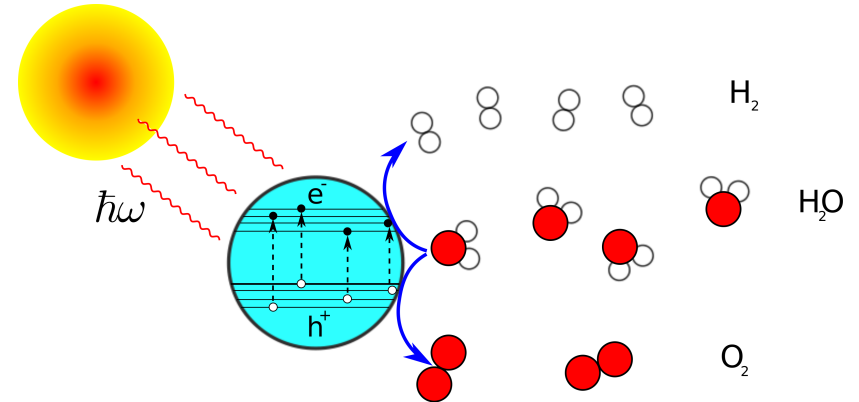
Water electrolysis.

Efficiency (water splitting):
$60\% - 80\%^2$
Efficiency of the solar cell:
$0.5\% - 45\%$

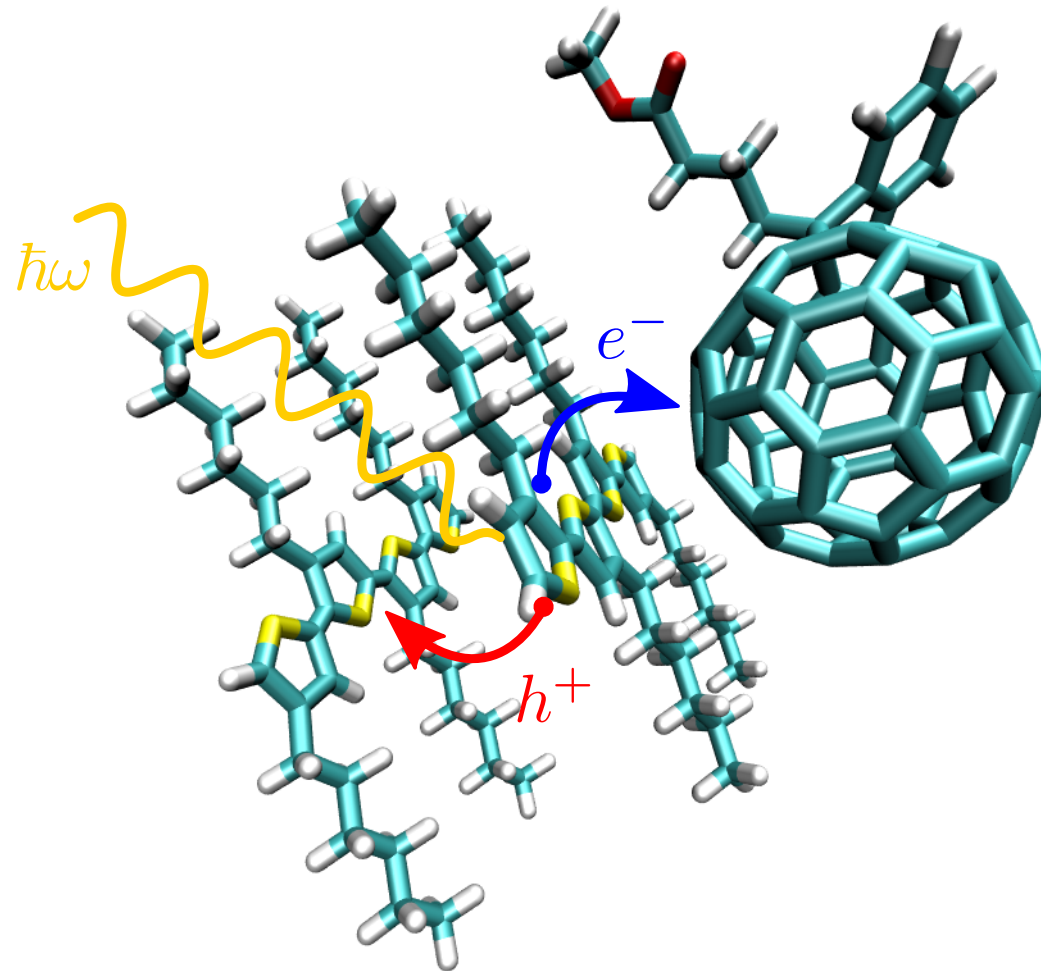## Direct water splitting.

Efficiency: $\approx 5\%^{1\ 2}$

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[1]Centi and Perathoner, ChemSusChem **3**, 195 (2010)
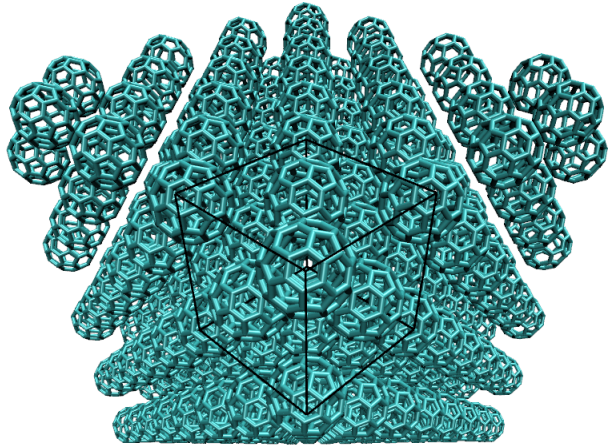[2]Dau *et. al.* , ChemCatChem **2**, 724 (2010)

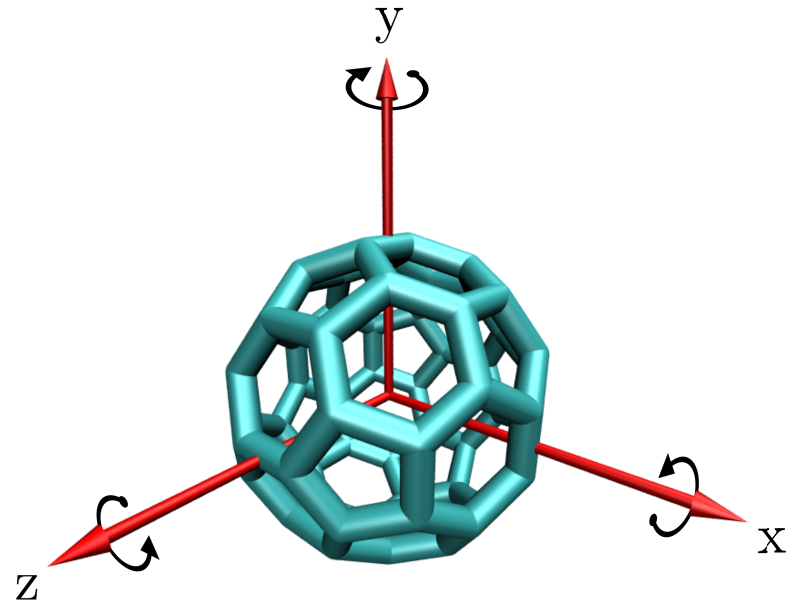# Part I: Solar cells

$\hbar\omega$

e^-

h^+

Predict electron mobility in a macroscopic fullerene crystal.

Below 250K, C_{60} crystals are stable in FCC configuration and exhibit no special features.

Over 250K every C_{60} molecules pseudo-rotates at its site.

Simulations need to consider these different regimes.

The mobility of an electron can be defined as the derivative of the drift velocity $\mathbf{v}$ with respect to the applied external field $\mathbf{E}$:

$$\mu_{ij} = \frac{\partial \langle v_i(\mathbf{E}) \rangle}{\partial E_j}$$

$\rightarrow$ need a way to calculate field dependent electron velocities.
$\rightarrow$ assume electron localisation on single molecules: hopping model
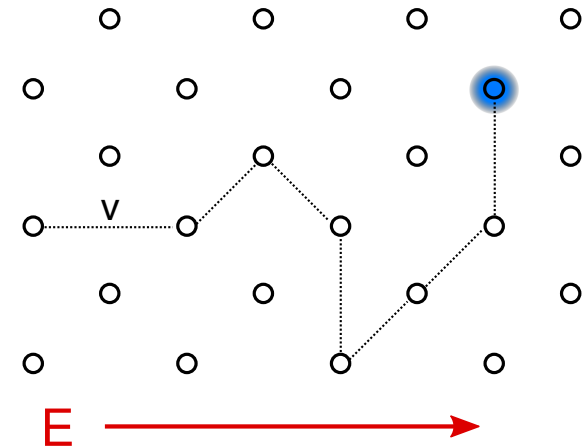$\rightarrow$ within macroscopic hopping model calculate microscopic rates

$\Downarrow$

use DFT to estimate microscopic rate parameters for each possible electron transfer
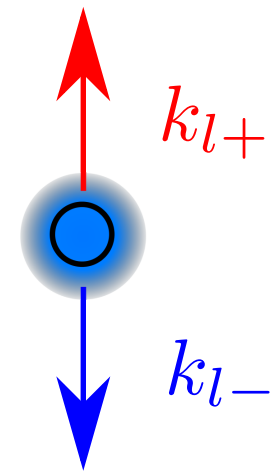
Hopping model:

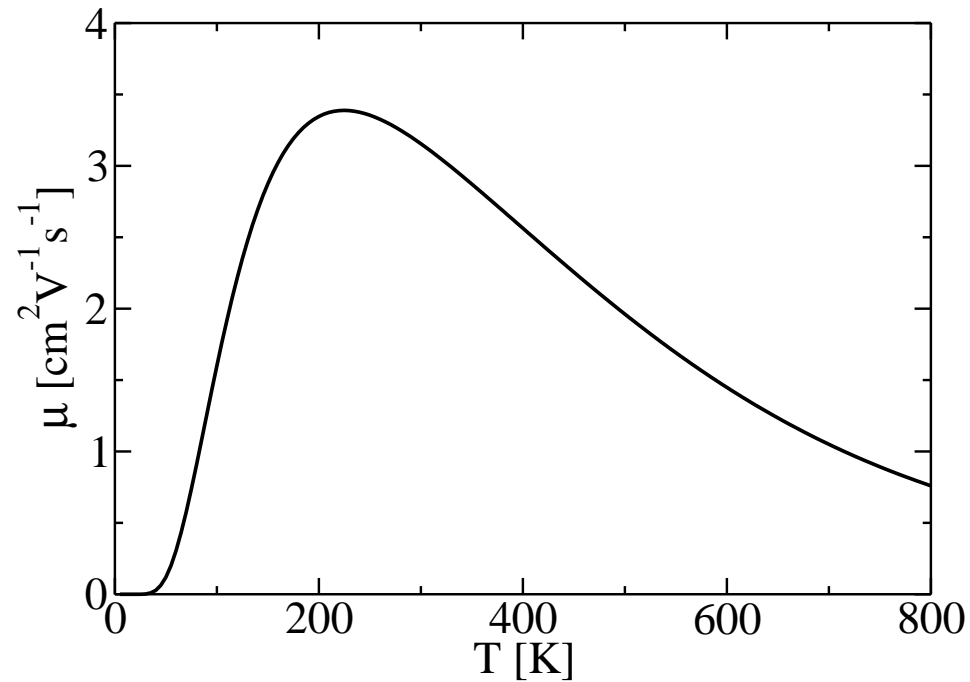Need derivative of average drift velocity $\langle \mathbf{v} \rangle$.

Within hopping model this is given as the sum of all forward and backward hops in each direction. Determined by rate k_l and hopping distance $\mathbf{d}_l$

$$\mu_{ij} = \frac{\partial \langle v_i \rangle}{\partial E_j} = \sum_l \frac{\partial \langle k_l \rangle}{\partial E_j} d_{li}$$

Can be solved analytically for crystals.

k_{l+}

k_{l-}

Temperature dependence of mobility.

Experimental value $\mu(T = 300\text{K}) = 0.5\text{cm}^2/s/V$[1]
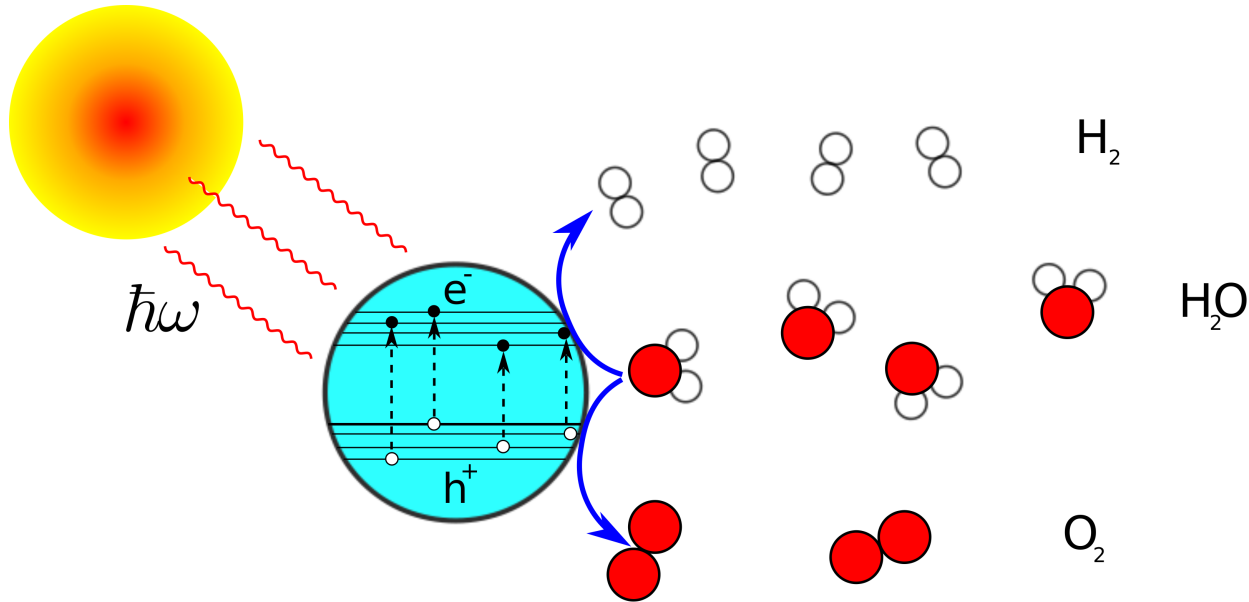
[1]Frankevich, Maruyamaa, Ogataa, CPL **214** 39, (1993)

PLAY

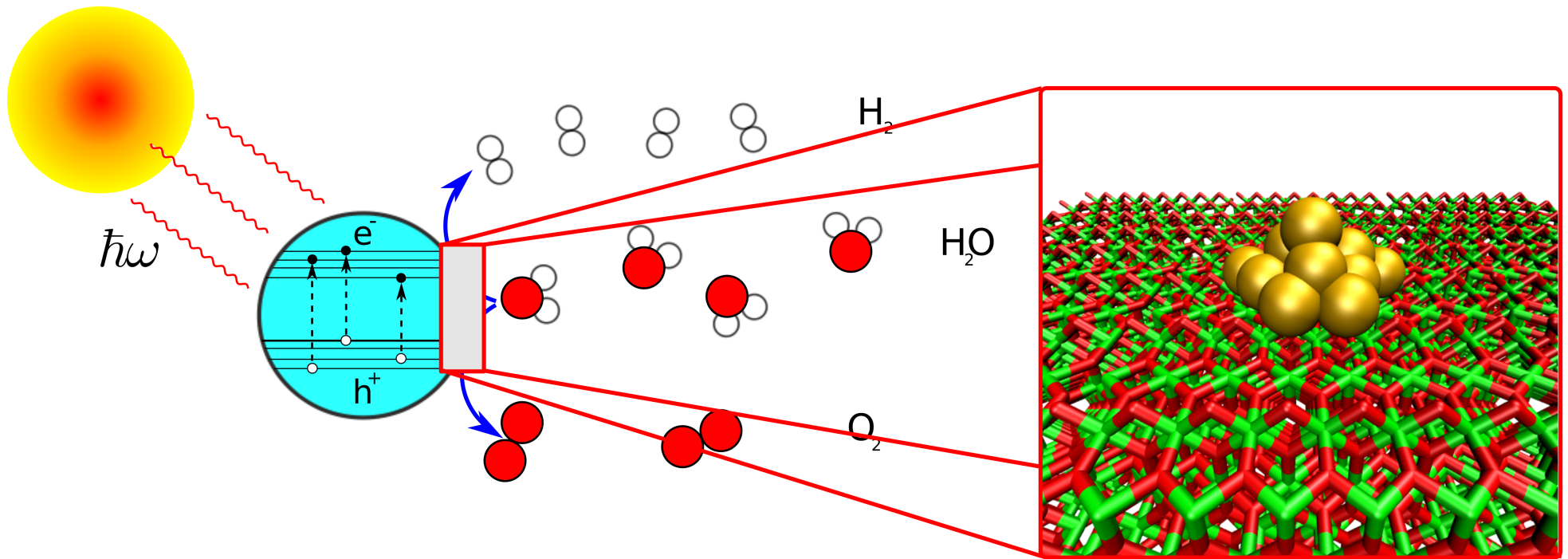# Part II: Photo-catalytic hydrogen production

Splitting water using visible light $\Rightarrow$ small(er) band-gap semiconductors $\Rightarrow$ less energy available for the reaction.
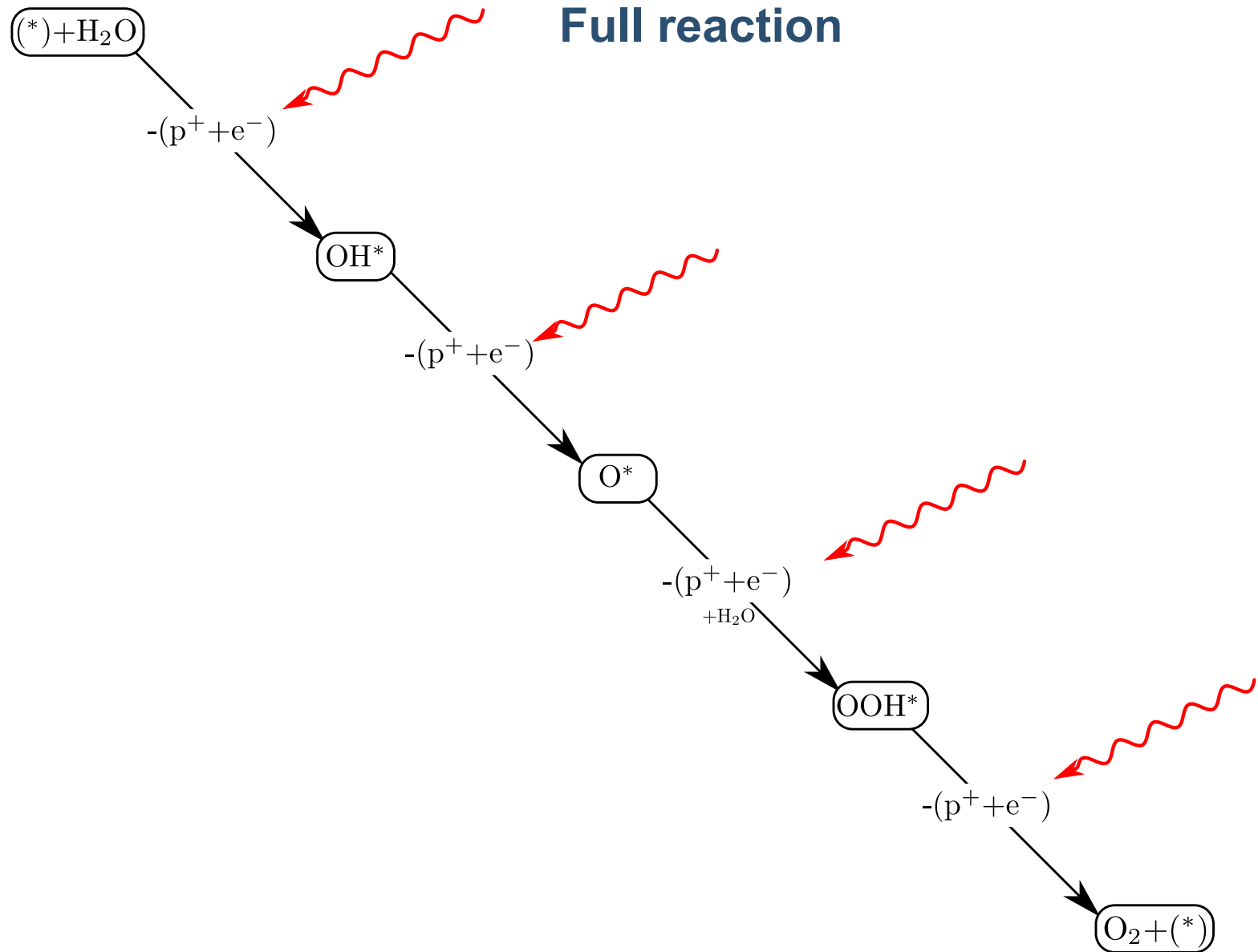
- $\rightarrow$ need catalysts with smaller overpotential

- $\rightarrow$ optimise reaction kinetics

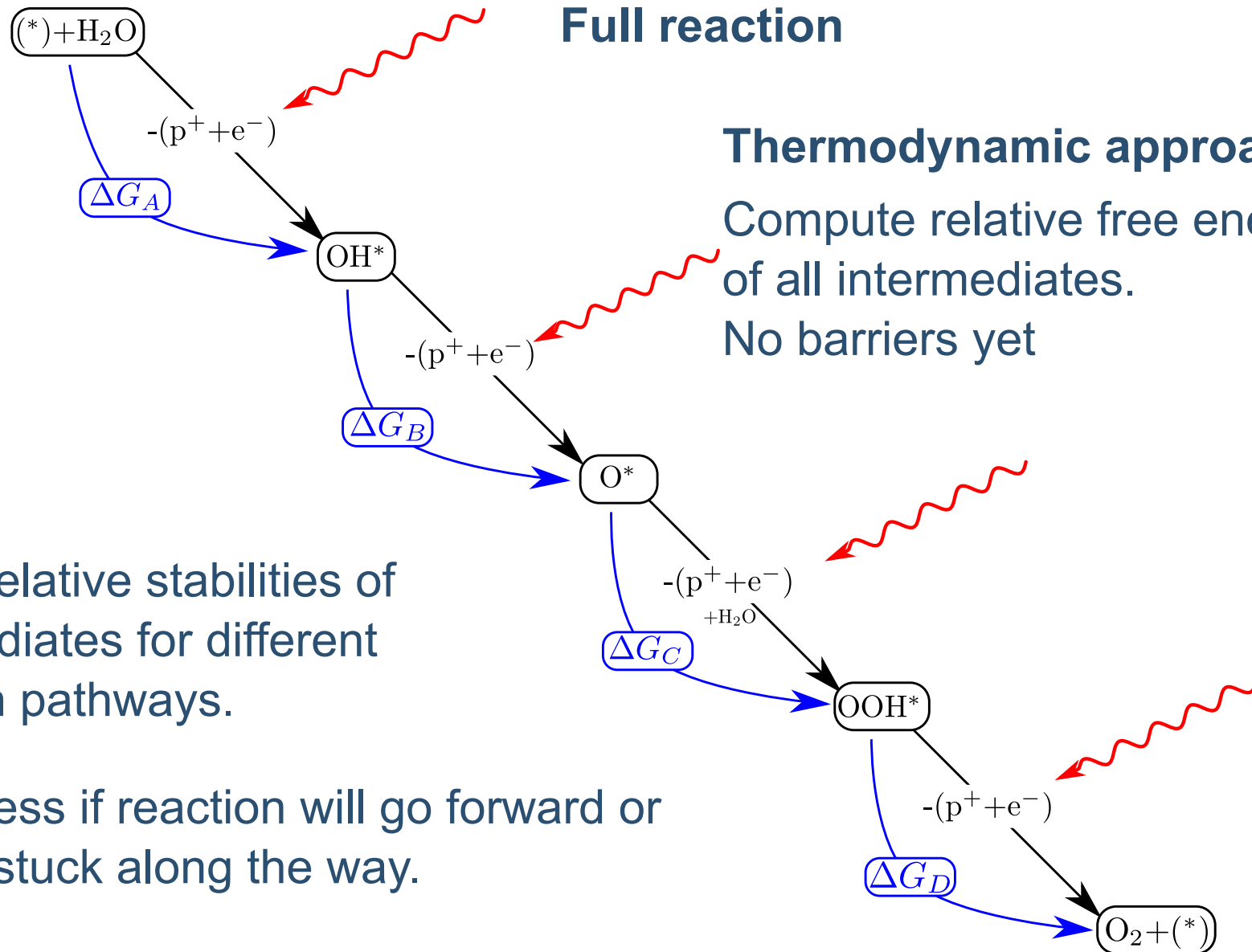All current water splitting approaches use co-catalysts.
Very often small metal clusters deposited on surface.

Full reaction

$(*)+H_2O$

$-(p^++e^-)$

OH^*

$-(p^++e^-)$

O^*

$-(p^++e^-)$

$+H_2O$

OOH^*

$-(p^++e^-)$

$O_2+(*)$

$(*)+H_2O$

$-(p^++e^-)$

ΔG_A

OH^*

$-(p^++e^-)$

ΔG_B

O^*

$-(p^++e^-)$
$+H_2O$

ΔG_C

OOH^*

$-(p^++e^-)$

ΔG_D

$O_2+(*)$

Full reaction

Thermodynamic approach:

Compute relative free energies of all intermediates.
No barriers yet

Yields relative stabilities of intermediates for different reaction pathways.

➤ Assess if reaction will go forward or get stuck along the way.
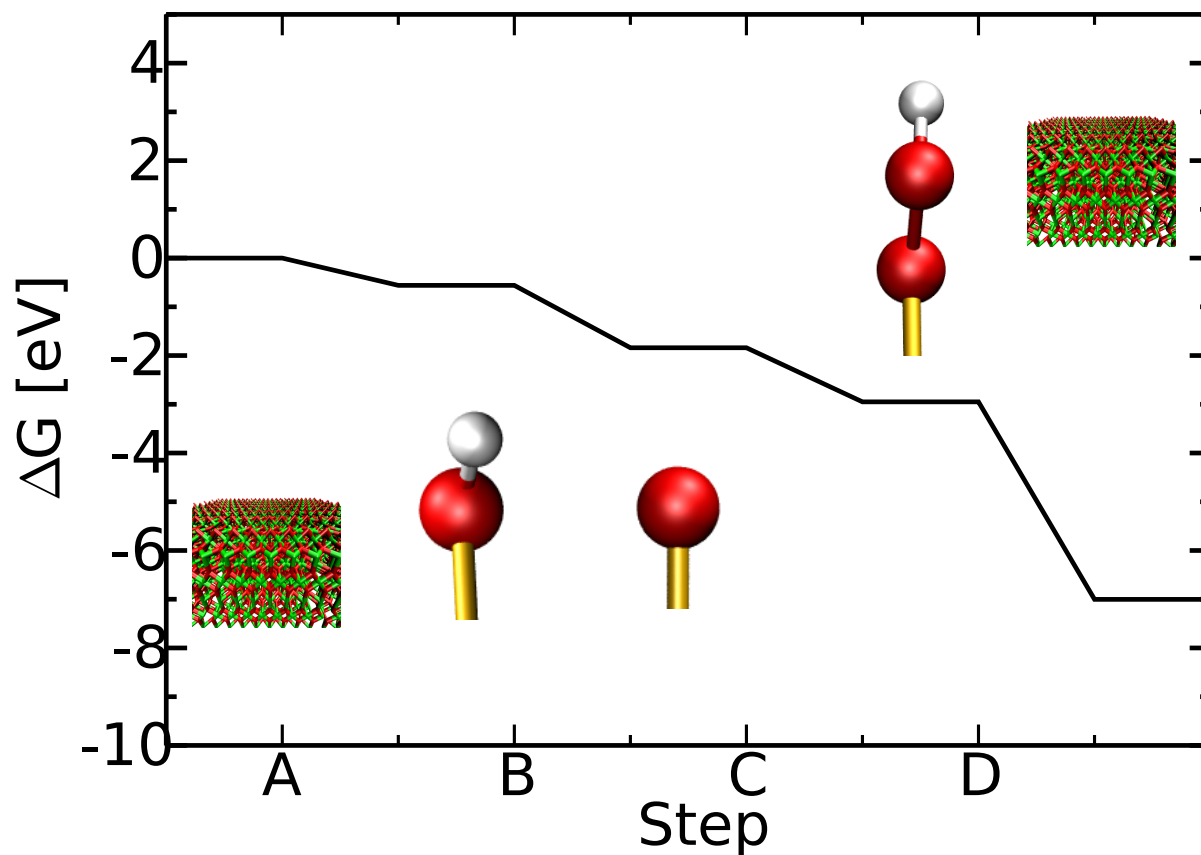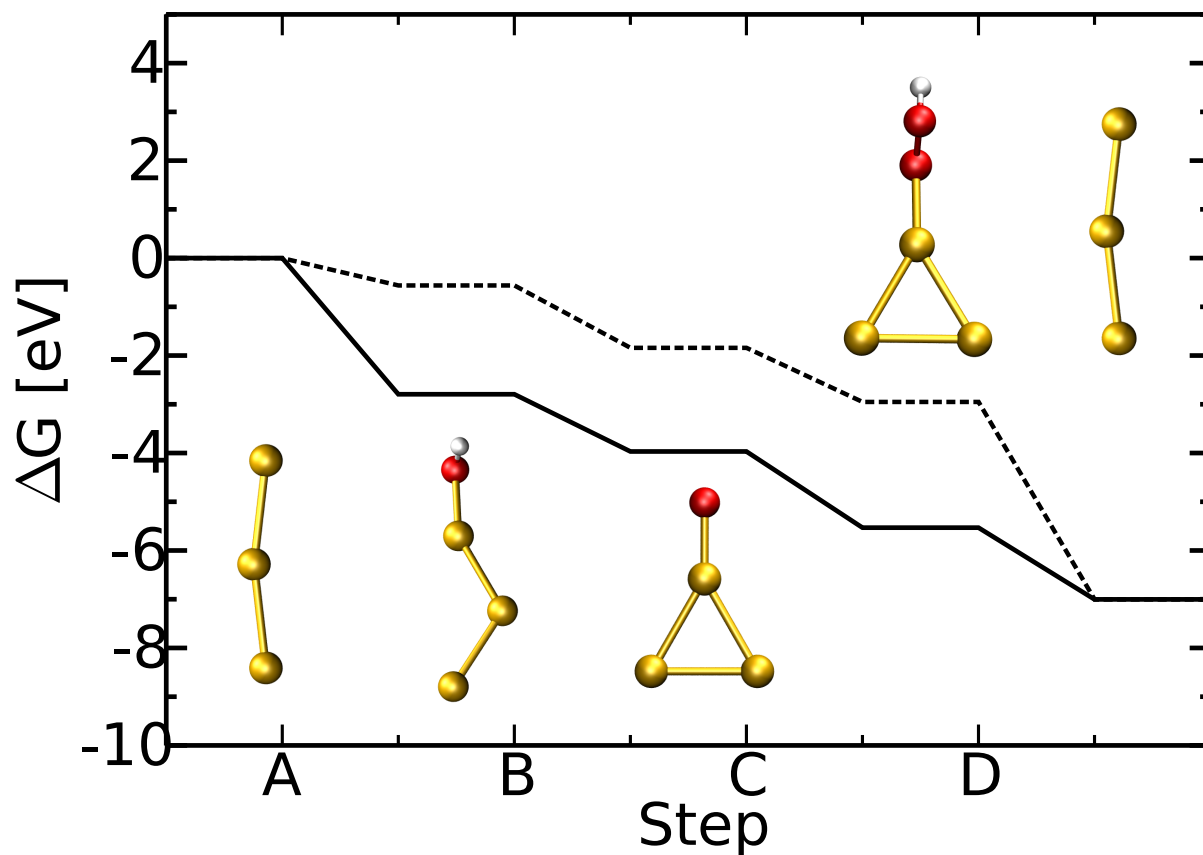
Reaction energetically possible but no information about barriers.

Only data on coupled pathway available, yet.

Data from: Valdés, *et. al.* , J. Phys. Chem. C **112**, 9872 (2008).

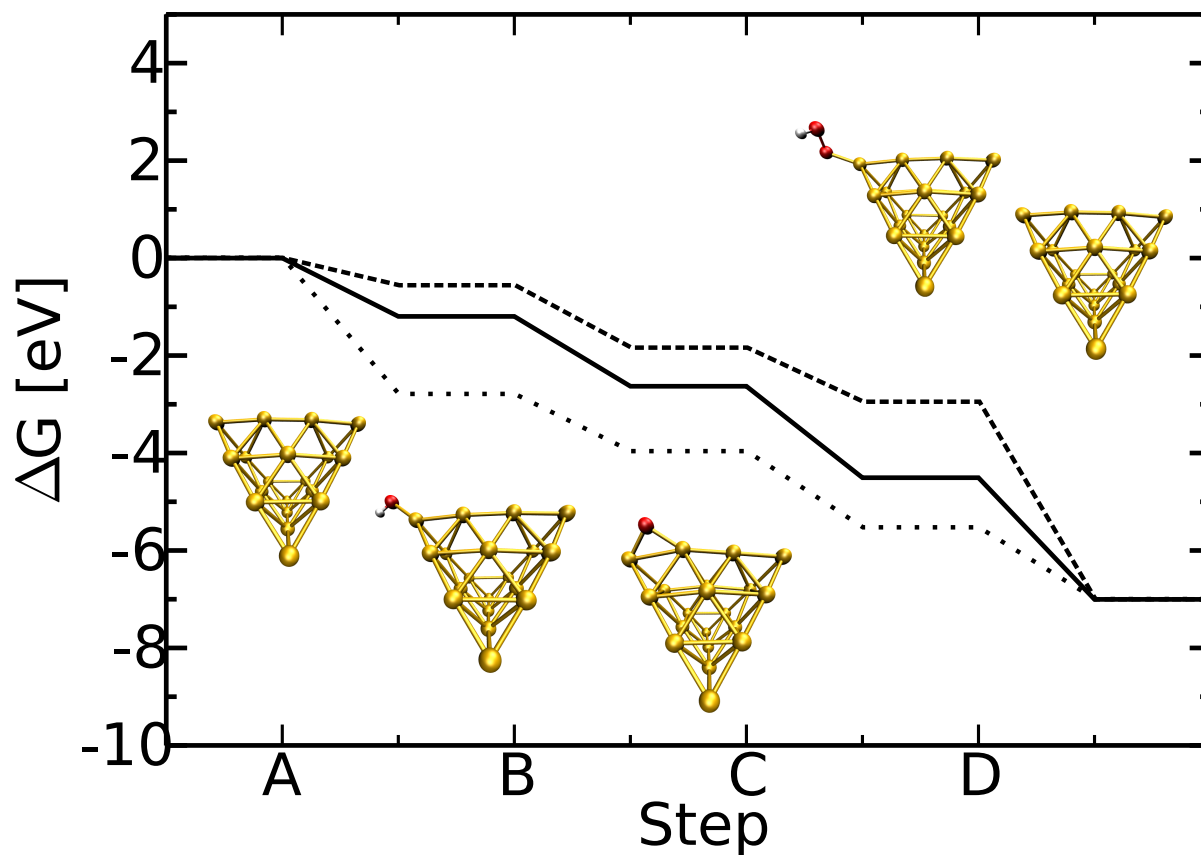# Results: water oxidation on Gold

Au$_3$

Reaction energetically much more favourable than on plain surface (dashed line).

Note:

Relative free energy of initial and final state is fixed.
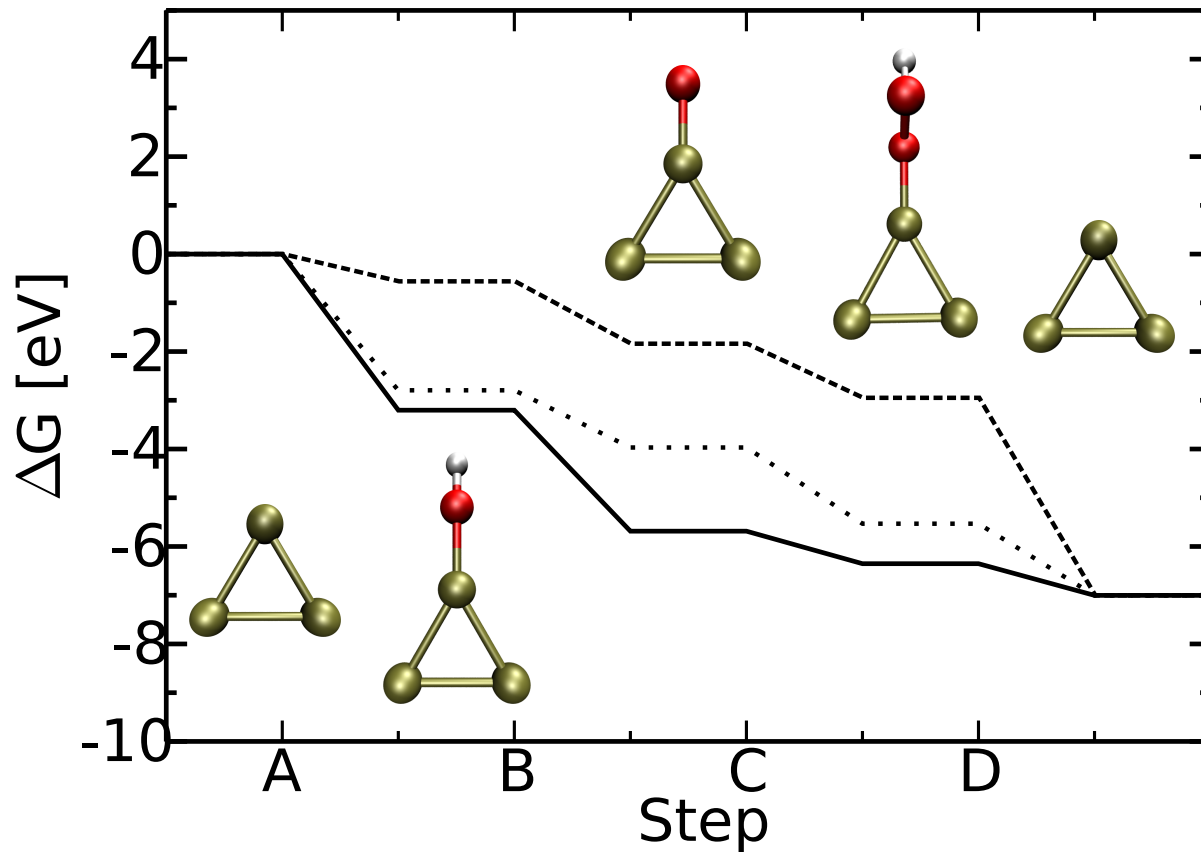Material only influences adsorbed intermediates.

Au$_{20}$
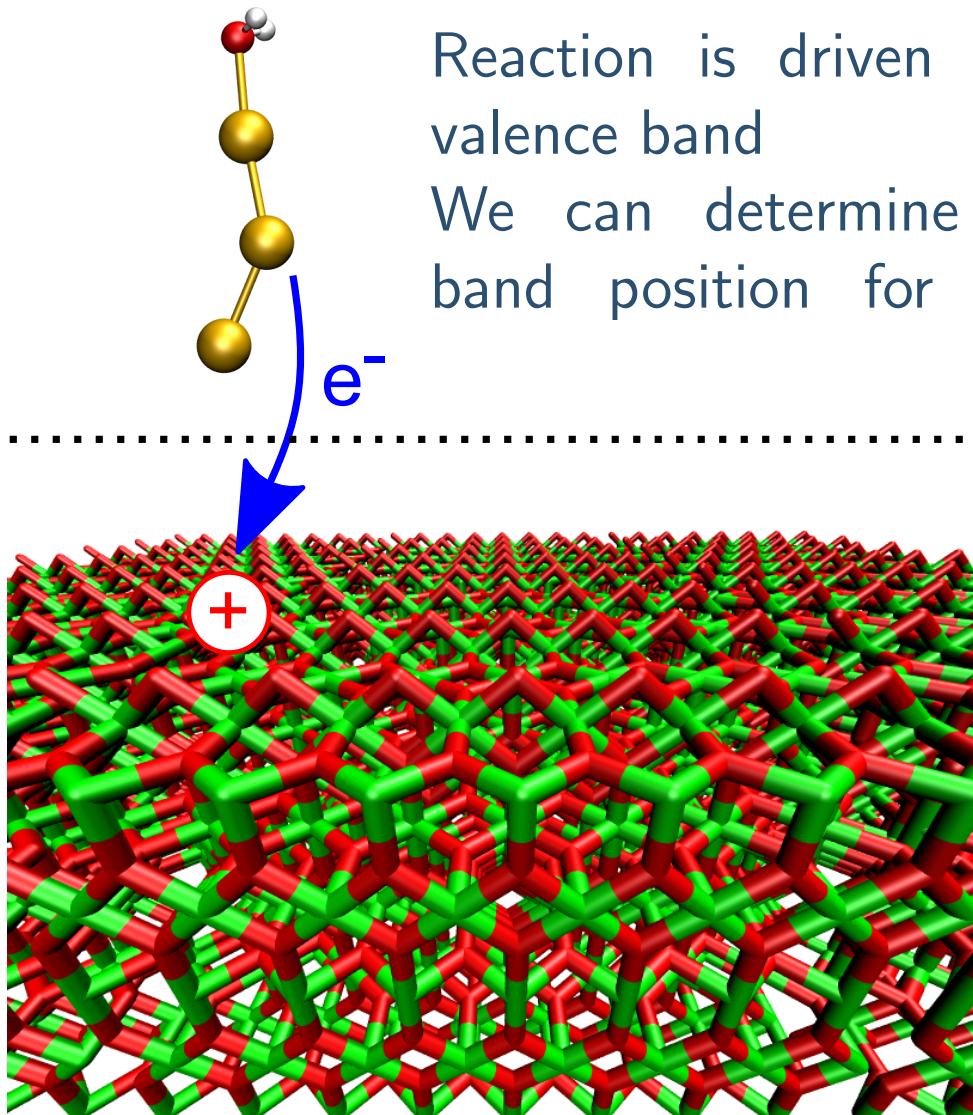Less steep than Au$_3$ (dotted) still more favourable than plain surface (dashed).

Trend towards reduced reactivity is expected to continue $\rightarrow$
plain Au surface is inert.

Pt$_3$
Energetically even more favourable than Au$_3$.

Reaction is driven by electron-holes in the surface's valence band

We can determine an upper limit to the valence band position for the reaction to still go ahead.

e^-

$+$

co-catalyst	VB versus vacuum
Au_3	-5.95 eV
Au_{20}	-5.97 eV
Pt_3	-6.45 eV

Note:
TiO_2 (111) surface has -7.1 eV.

Summary

- Simulation of electron mobilities needs a multi-scale approach

- Microscopic ET parameters calculated from DFT

- Hopping model not accurate enough $\rightarrow$ direct dynamics

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- Water oxidation on gold clusters in the non-scalable size regime is energetically possible (disregarding any barriers).

- Reaction with co-catalyst more favourable than on plain TiO_2 (increasingly important for small bandgap seminconductors).

- Small Pt clusters show even more promise than Au but need lower lying valence band of the substrate to work

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