# A practical computational protocol for photocatalytic reactions beyond ground-state DFT approximations

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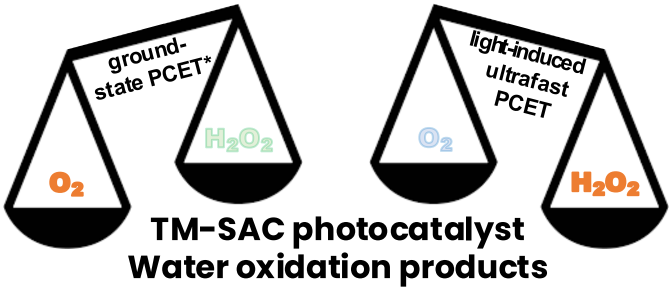
## Summary

Computational studies of heterogeneous photocatalysts typically discuss the band level alignment obtained by regular DFT, which does not capture the physics of light-driven processes. In a new computational protocol, excited states are explicitly considered in the Gibbs free energy diagrams. Applied to prototypical reactions on a single-atom cocatalyst, the protocol allows for the correct prediction of reaction products seen in experiment.

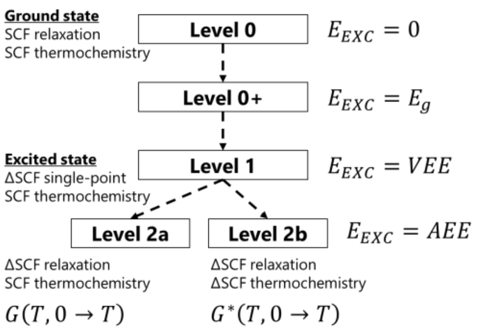
## DFT | DFT-ΔSCF



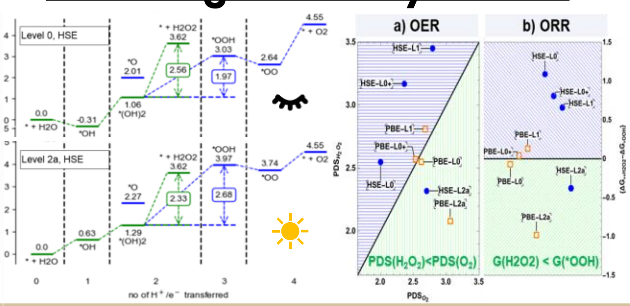

*proton-coupled electron transfer

## The protocol

$$G^* = E_0 + G(T, 0 \to T) + E_{EXC}$$




## Resulting thermodynamics




## Excitation energy $E_{EXC}$

**Level 0: No excitation**

**Level 0+: Electronic band gap**

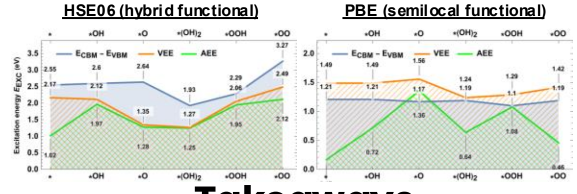
$E_g = ECBM - EVBM$

**Level 1: Vertical excitation energy**

(approx. optical band gap), $VEE = E^*_{0SP} - E_0$, SP – single point

**Level 2: Adiabatic excitation energy**

$AEE = E_{0REL} - E_0$, REL – excited state relaxation




## Takeaways

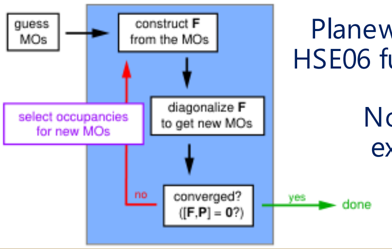
- PBE produces volatile, unphysical excitation energies. A hybrid functional should be used whenever possible
- The protocol at Level 2a predicts the correct majority product ($H_2O_2$) in both directions ($H_2O$ oxidation OER, $O_2$ reduction ORR)
- A minimal model was used. Extensions are planned for more realism:
  - environment interaction (solvent)
  - photoelectro catalysis with constant-potential approach (grand canonical kinetics)

## ΔSCF Method

**Occupancy selection:**

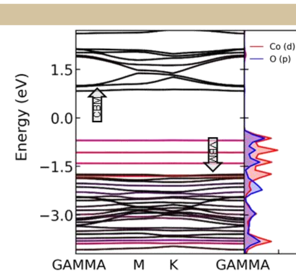
**SCF** (regular DFT): lowest-energy MOs are chosen as occupied according to the *aufbau* principle

**ΔSCF**: VBM -> CBM excitation is applied




Planewave DFT, HSE06 functional

No midgap excitations

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