Dr. Dennis Palagin :: Paul Scherrer Institut / ETH Zürich
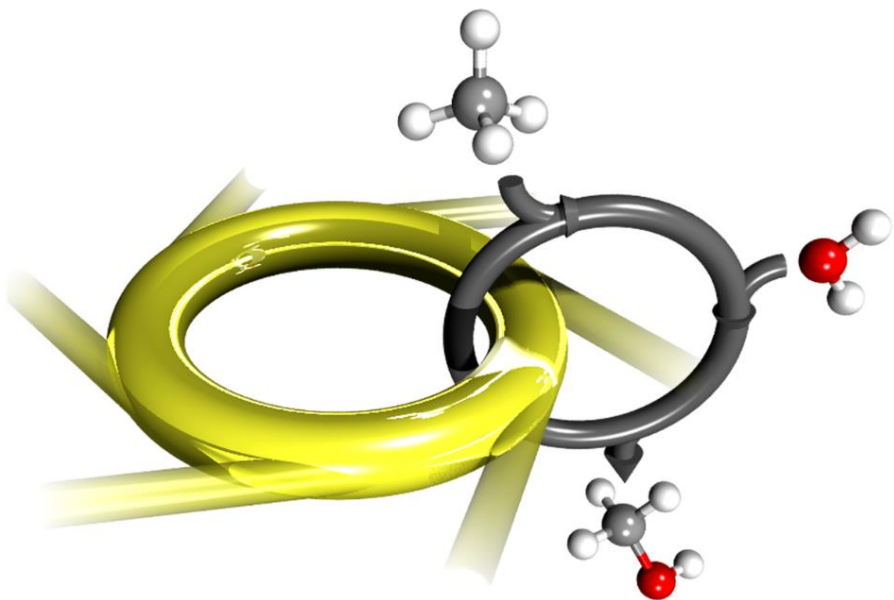
Introduction to first-principles modelling of catalysis at surfaces: Lecture 1

ETH Zurich, 14.10.2020

Who are we? What do we do?

Laboratory for Catalysis and Sustainable Chemistry

Two of the grand challenges of the 21st century are energy and sustainability. Within the Laboratory for Catalysis and Sustainable Chemistry, we combine synthetic chemistry with development and application of new (synchrotron-based) characterization tools to contribute to solving these challenges. Catalysis plays an essential role to energy conversion and storage as well as to achieving sustainable chemicals conversion.

An important part of our research therefore focuses on providing understanding of a functioning catalyst with the ultimate aim to be able to design better catalytic processes. This reflects the general research theme within the laboratory, which is to provide understanding of a functioning respectively functional material. The laboratory is in particular strong in the development and application of in situ / operando time- and space-resolved measurements. For that, we maintain strong links to the synchrotron. We apply methods based on X-ray absorption and emission and X-ray photoemission spectroscopies, in addition to ptychographic imaging. High space-resolution is achieved in both the hard and soft X-ray regimes and diffractive and spectroscopic imaging is explored.

The van Bokhoven Group

The Group | People | Education | Research | Publications | News | Gallery

ETH Zurich > D-CHAB > ICB > Van Bokhoven

The group
February 2019

News

22.08.2019

Completing the third dimension: Breakthrough method for transmission electron microscopy (TEM) published in Nature Communications!
Julian, Tim and co-workers published a patented method that tricks electrons to access complete space in TEM (*Nat. Commun.* DOI: 10.1038/s41467-019-11326-2). They overcame the so called "missing wedge problem" that impedes the breakthrough of many TEM techniques since ever. The simplicity while high impact of their approach was acknowledged by der Standard, die Presse and Phys.org. →

Featured Publications

Stable complete methane oxidation over palladium based zeolite catalysts
Andrey W. Petrov, Davide Ferri, Frank Krumeich, Maarten Nachtegaal, Jeroen A. van Bokhoven and Oliver Kröcher
Nature Communications, 9 (1): 2545, London: Nature Publishing Group, 2018
DOI ↓ Research Collection ↓

Theory division: TheoCat

Laboratory for Catalysis and Sustainable Chemistry (LSK)

Groups

Projects ∧

Theocat Project ∧

Theocat Team

Theocat Research

Theocat Publications
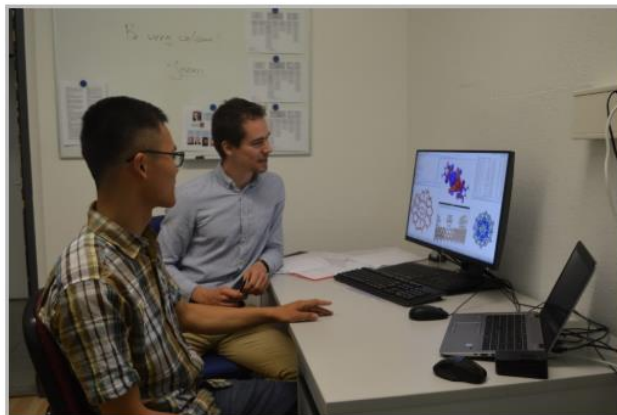
NAPP ∨

Time Resolved XAS ∨

People

Scientific Highlights

Publications

Books / Book Chapters

News

Theocat Project

https://www.psi.ch/lsk/theocat-project

Theoretical Catalysis Project led by **Dennis Palagin** was started in June 2016 as a theory division of LSK, and is focused on applying state-of-the-art *ab initio* methods to study the interplay between the structure and the chemical properties of novel catalytic materials. We aim at understanding the chemical nature of the catalytic processes to be able to facilitate rational design of novel engineered materials.

People in our project

Research

List of publications

News

2019

02/10: Our paper on the mechanism of the hydrogen release in the anaerobic oxidation of methane to methanol has been accepted to **ACS Catalysis** ☑!

23/09: Swiss National Supercomputing Centre (CSCS) just awarded us 100'000 node hours on their new hybrid Cray XC50 system. Happy number crunching!
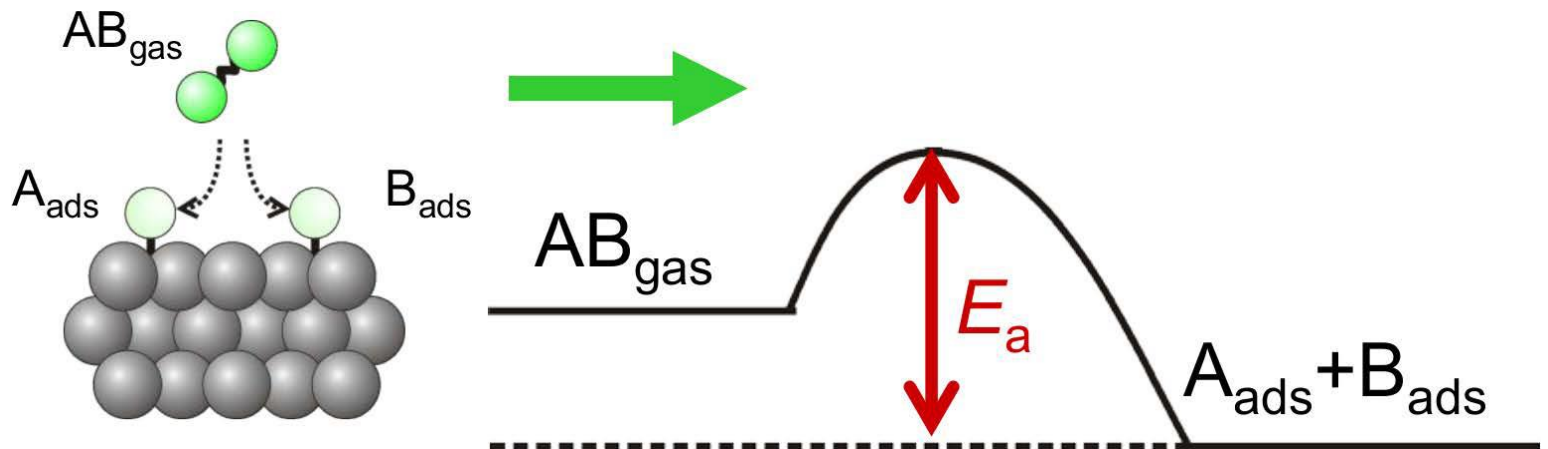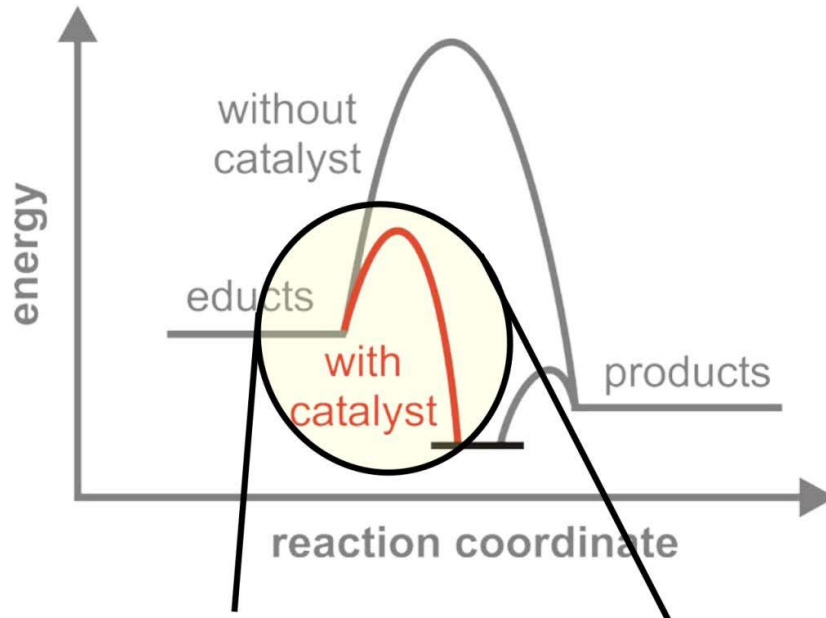
Theoretical Catalysis

1) **Intro**

2) Computational catalysis and first-principles modelling

3) Structure optimization

4) "*ab initio*" thermodynamics

5) "Descriptors" and catalysts screening

Catalysis is a multibillion-dollar industry with a profound influence on everyday life
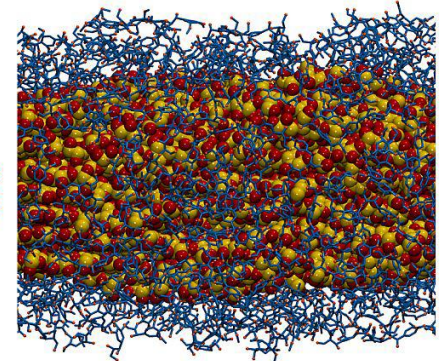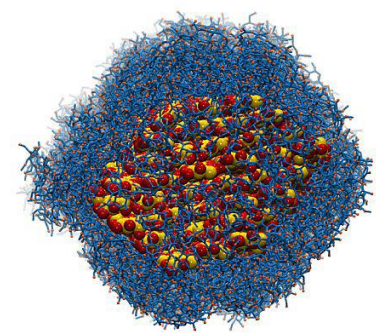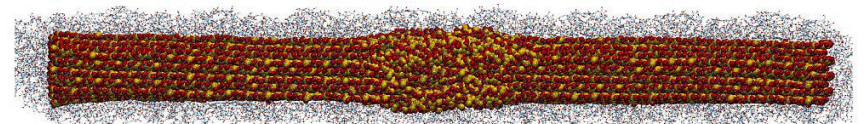
Catalysts lower the activation barrier of a reaction without being consumed

Wilhelm Ostwald, 1909
"investigations into fundamental principles governing chemical equilibria and rates of reaction"

Paul Sabatier , 1912
"for his method of hydrogenating organic compounds in the presence of finely disintegrated metals"

Fritz Haber, 1918
"for the synthesis of ammonia from its elements"

Irving Langmuir, 1932
"for discoveries and investigations in surface chemistry"

Cyril Hinschelwood, 1956
"for researches into mechanism of chemical reactions"

Walter Kohn, 1998
"for his development of the density-functional theory"
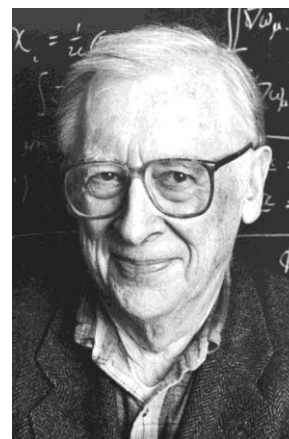
John Pople, 1998
"for his development of computational methods in quantum chemistry"

2013 Nobel Prize in Chemistry
Martin Karplus, Michael Levitt and Arieh Warshel

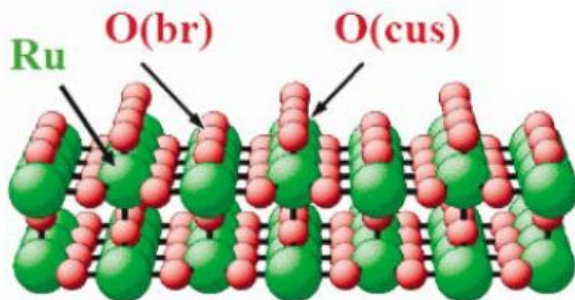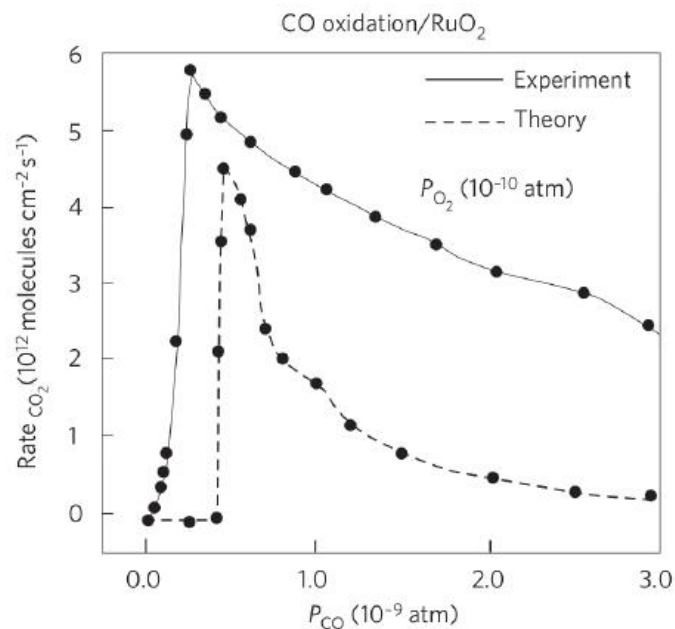"for the development of multiscale models for complex chemical systems"

Theoretical Catalysis

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Computational modeling can assist in understanding catalysis

CO oxidation at RuO$_2$

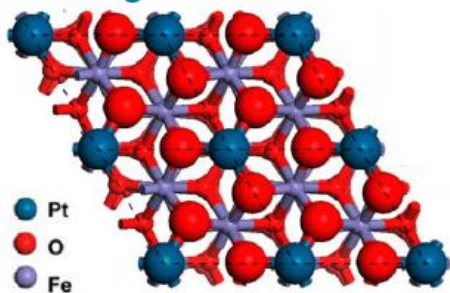Ru   O(br)   O(cus)

[1] K. Reuter, *et al.*
Phys. Rev. Lett. 93, 116105 (2004)

Many opportunities for improving catalysts remain

CO oxidation/RuO$_2$

— Experiment
- - - Theory

P_{O_2} (10^{-10} atm)

Rate $_{CO_2}$ (10^{12} molecules cm^{-2} s^{-1})

P_{CO} (10^{-9} atm)

Single atoms

Pt
O
Fe

Single Pt atoms
dispersed on FeO$_x$

Nanoclusters
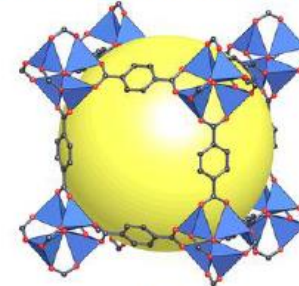

Rh
O
H
Al   Si
H
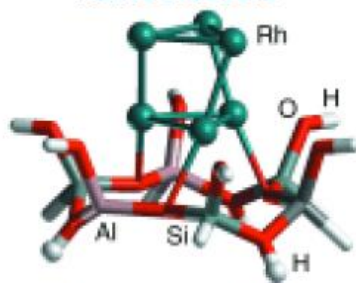
Rh$_6$ nanocluster
supported by a zeolite

Nanoparticles
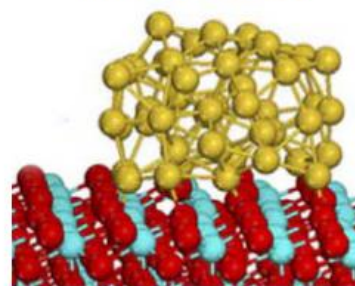
Gold nanoparticle
supported by CeO$_2$

Metal-organic frameworks

The MOF-5
lattice structure

Catalyst characterization

- Computational spectroscopy
- First-principles thermochemistry & kinetic parameters
- First-principles microkinetic modeling

Active sites

Reaction mechanism

Mechanistic understanding
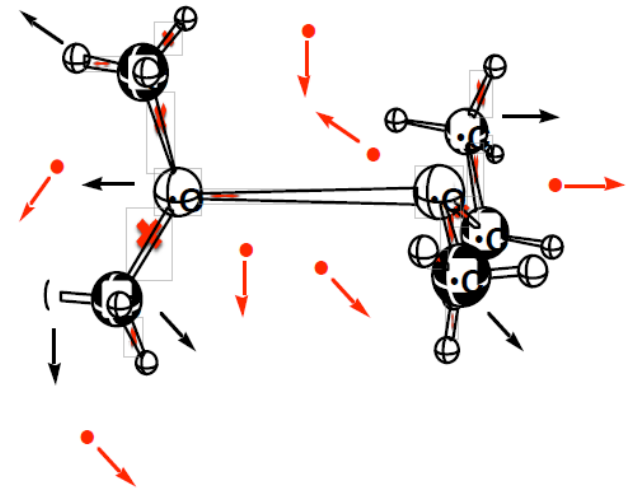
Catalyst design

Ascertained descriptor

Computational screening
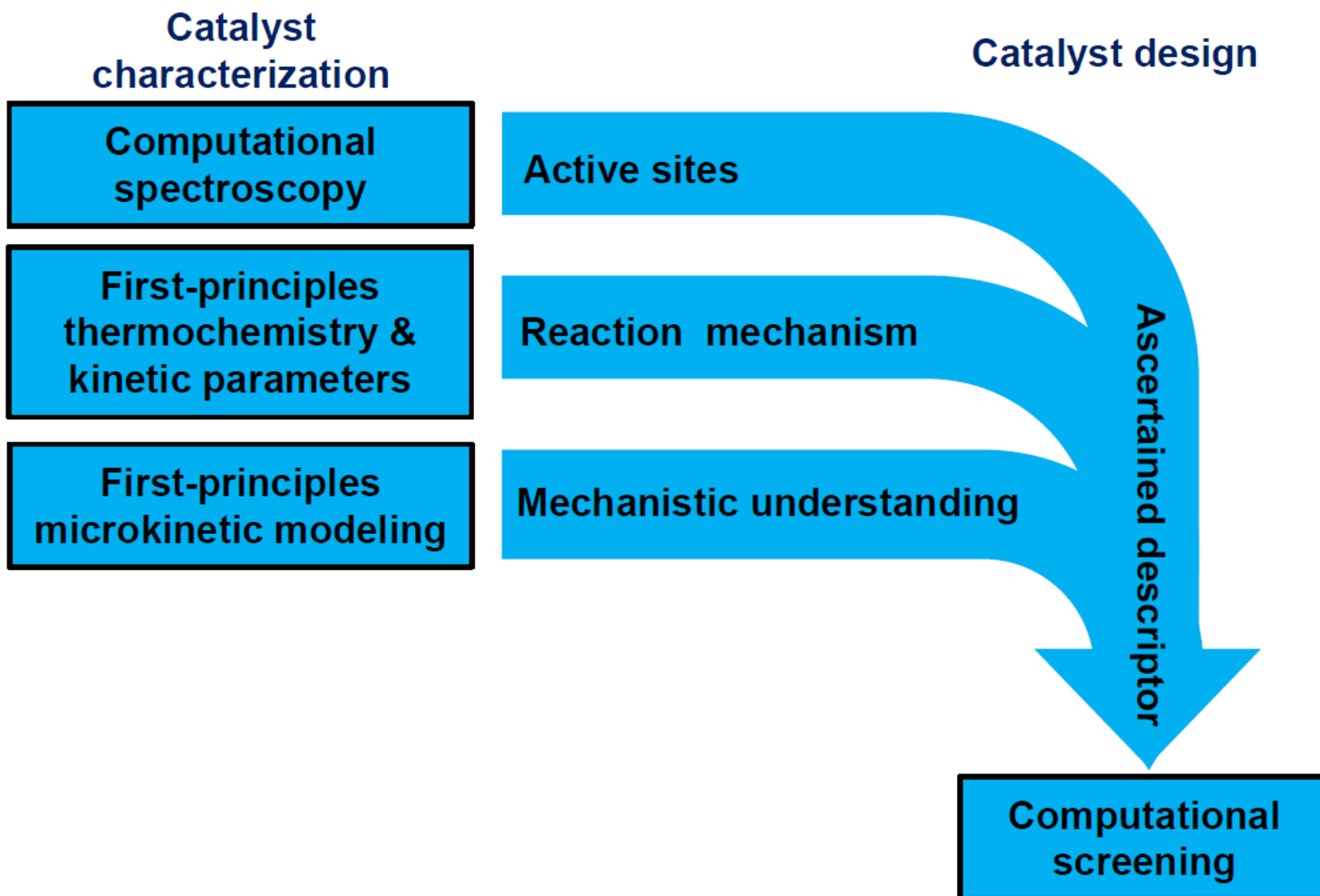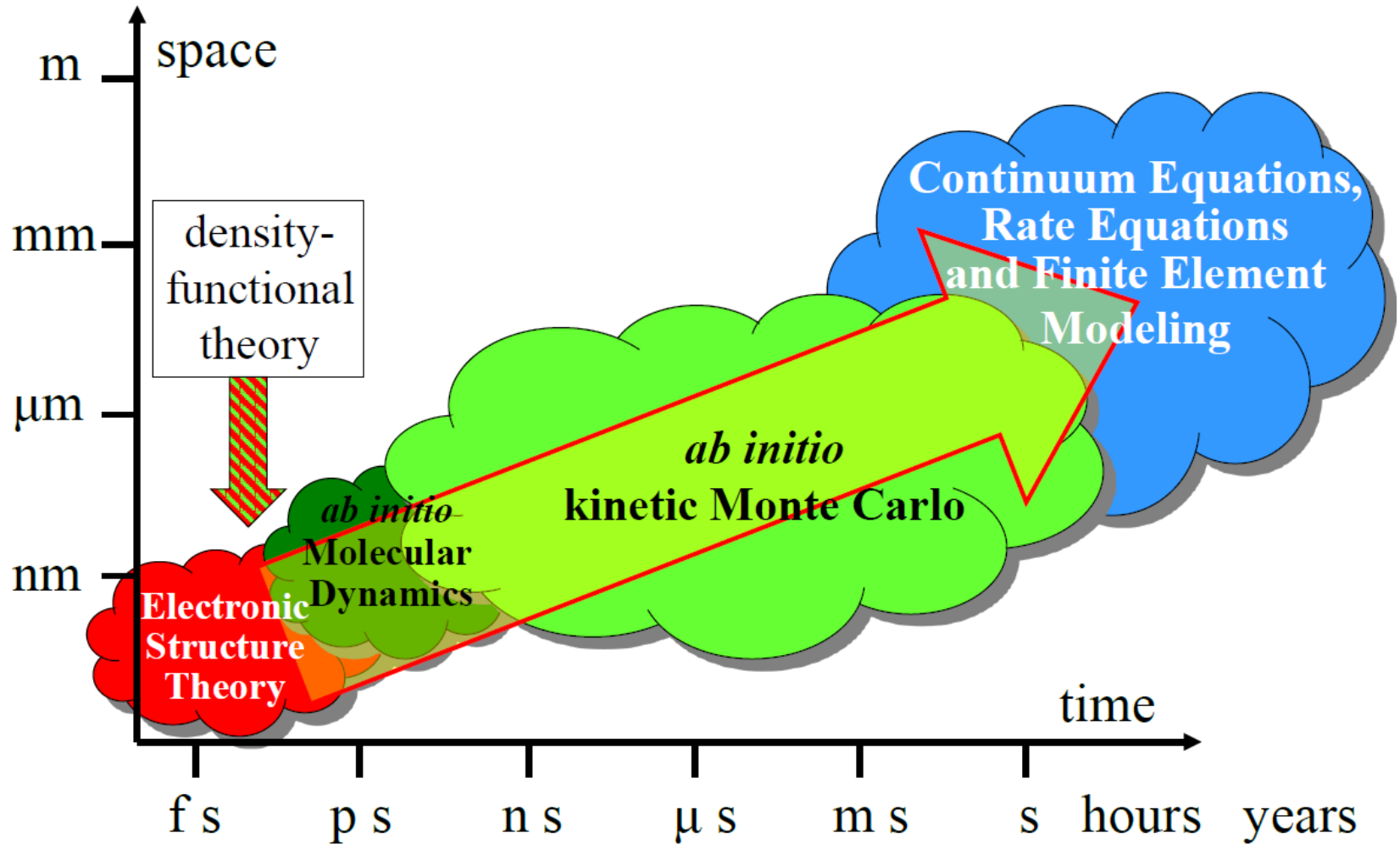
- *p* nuclei

- *n* electrons

- N body problem (N=n+p)

Calculate the total energy

$$E_{\text{tot}} = \langle \psi | \hat{H} | \psi \rangle$$

in order to find stable states (minimum energy configurations).

ψ — the system's total eigenfunction

$\hat{H}$ — total Hamiltonian

In general solvable ⇒ Born Oppenheimer Approximation

$$\psi = \psi_{\text{electrons}} + \psi_{\text{nuclei}}$$

Nuclei mostly treated as classical point particles R_l

⇒ only ψ_e (and thus $\hat{H}_e$) to consider.

$$\hat{H}_e = \hat{T}^e + \hat{V}^{e-e} + \hat{V}^{e-I}$$

$$\hat{T}^e = \sum_i^{N_e} \frac{p_e^2}{2m} \qquad \text{kinetic energy of electrons}$$

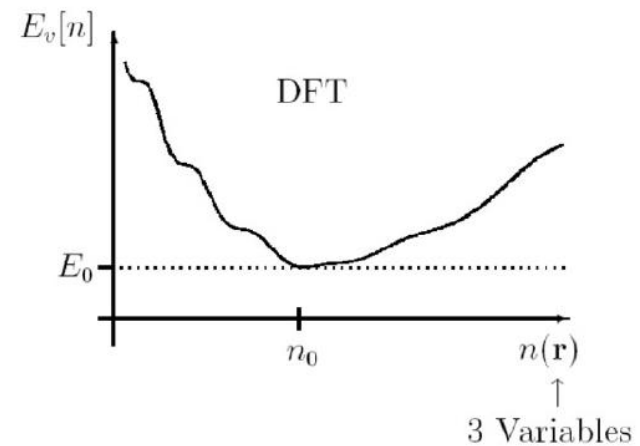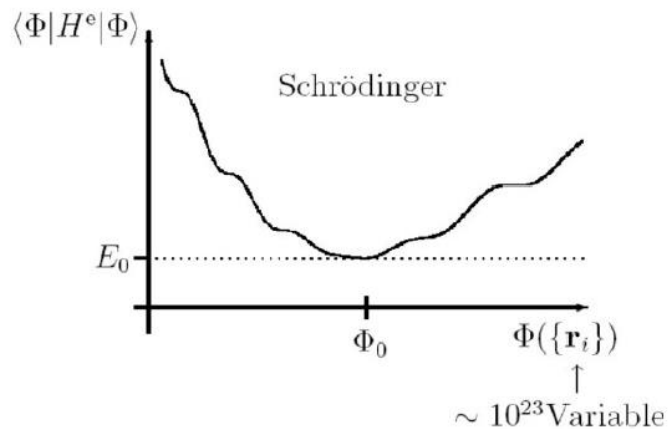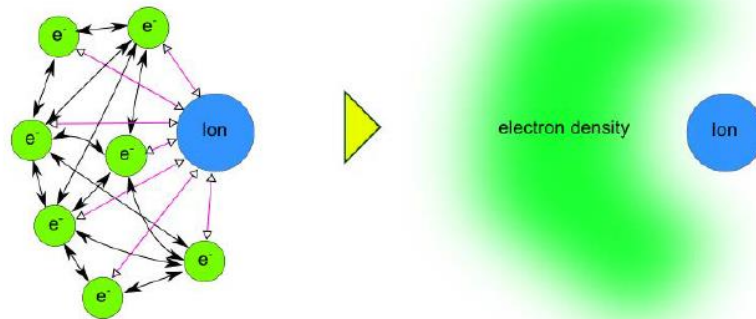$$\hat{V}^{e-e} = \sum_i^{N_e} \sum_{i'}^{N_e} \frac{1}{|r_i - r_i'|} \qquad \text{electron-electron interaction}$$

$$\hat{V}^{e-I} = \sum_i^{N_e} \sum_j^{N_I} \frac{q_j}{|r_i - R_j|} \qquad \text{electron-nuclei interaction}$$

Everything known but too complicated to solve.

The electron density contains all the information and is more tractable than the wave function

For a fixed set of nuclear coordinates R_I

$$E_e(R_I) = \langle \psi_e | \hat{H}_e(R_I) | \psi_e \rangle$$

Idea:

Express total electronic energy as a functional of the electronic density $\rho(R_I)$.

$$E_{\{R_I\}}[\rho] = T[\rho] + \int d^3r \rho(\mathbf{r}) v_{\{R_I\}}^I(\mathbf{r}) + \frac{1}{2} \iint d^3r d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E^{\text{XC}}[\rho]$$

| kinetic energy of system with non-interacting electrons | potential energy of electron-nuclei interaction | inter-nuclei repulsion | Exchange-correlation: Non-classical interactions |

$\Rightarrow$ density that minimizes $E_{\{R_I\}}[\rho]$ is the ground state electron density.

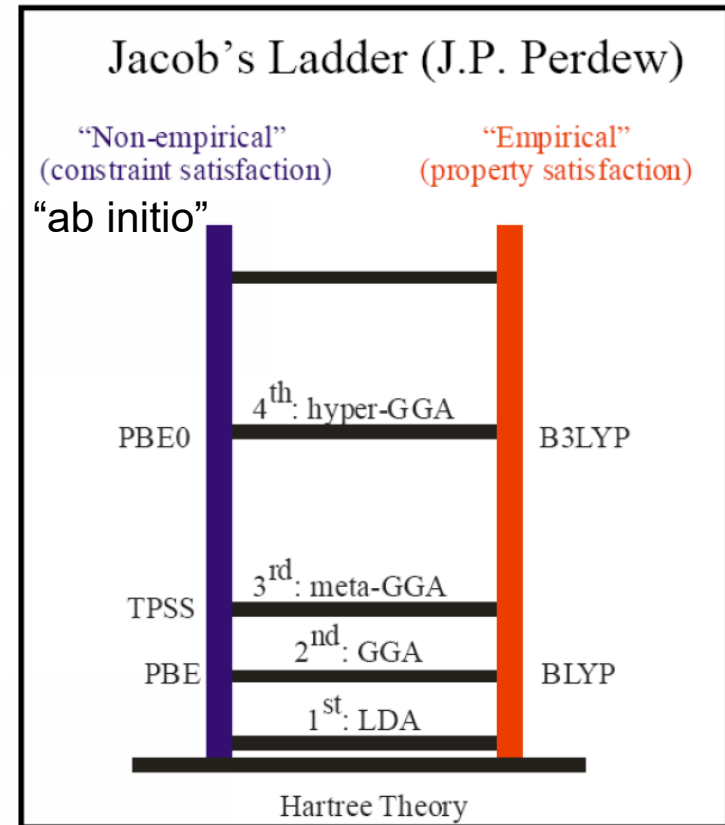Short answer: we don't know.
Long answer: we can try to approximate it.

as a function of the density:

$$E^{XC}_{LDA}[\rho] = \int d^3r\ \rho(\mathbf{r})\varepsilon^{XC}(\rho_0)\big|_{\rho_0=\rho(r)}$$

of density and its gradient:

$$E^{XC}_{GGA}[\rho] = \int d^3r\ \rho(\mathbf{r})\varepsilon^{XC}(\rho_0, \nabla\rho_0)\big|_{\rho_0=\rho(r)}$$

and much, much more complex

Jacob's Ladder (J.P. Perdew)

"Non-empirical"
(constraint satisfaction)

"Empirical"
(property satisfaction)

"ab initio"

PBE0	4th: hyper-GGA	B3LYP
TPSS	3rd: meta-GGA	
PBE	2nd: GGA	BLYP
	1st: LDA	

Hartree Theory

Density Functional Theory (DFT)
is widely applied to model catalysis at surfaces

The choice of the exchange-correlation (XC) functional
is critical for accurate predictions!

DFT IN PRINCIPLE
EXACT

$$V_{XC} \equiv \frac{\delta E_{XC}}{\delta \rho}$$

DFT IN PRACTICE
APPROXIMATE E_{XC}

Practitioner level

GGA (metals)

Hybrids (molecules, insulators)

Major problems

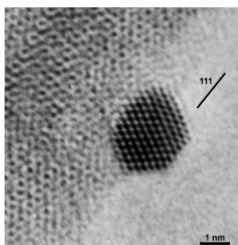Self-interaction error

van der Waals interaction

Inaccuracies in binding
energies and activation
barriers of ~0.2–0.4 eV!

J. P. Perdew and K. Schmidt,
AIP Conf. Proc. **557**, 1 (2001)
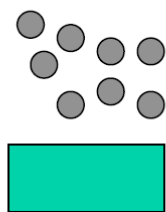
Heterogeneous Catalysis

Surface of solid catalyst

Surface structure
Reconstruction
Segregation
Steps, defects
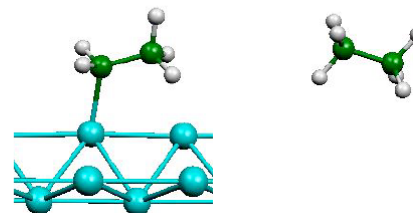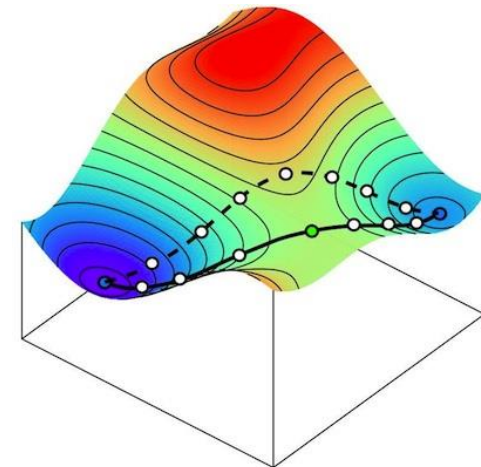
Gas pressure   Temperature

?

Active sites ?

### Chemical reaction

**Reaction pathways,
kinetics and selectivity**

Theoretical Catalysis

1) Intro

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3) **Structure optimization**

4) "*ab initio*" thermodynamics

5) "Descriptors" and catalysts screening

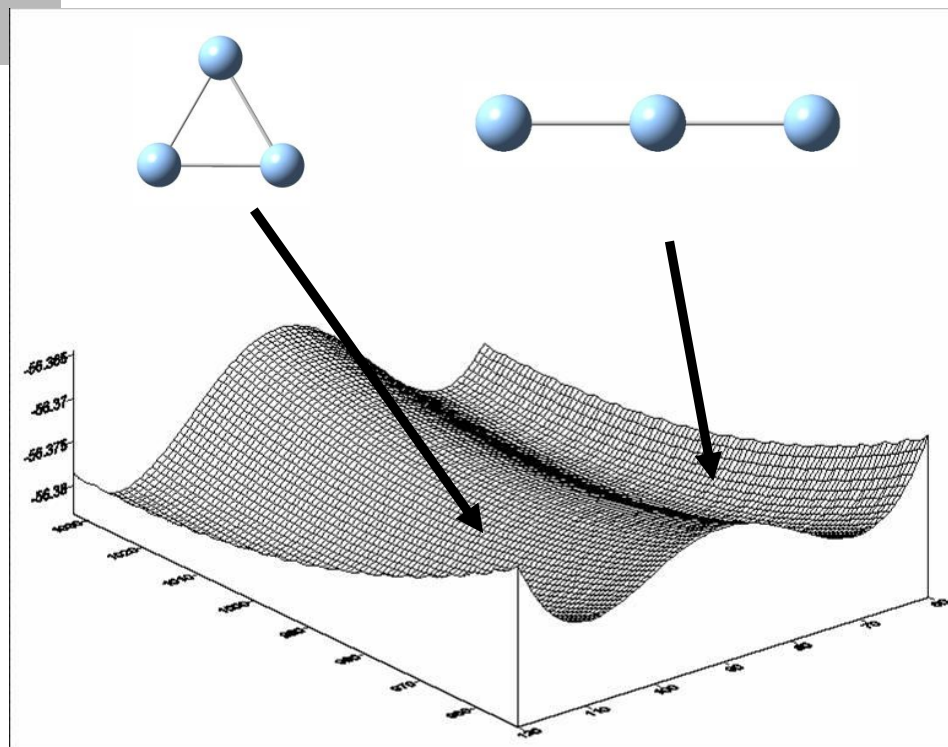## Potential energy diagrams amount to finding the relevant minima and transition states for a given reaction

Potential Energy Surface (E, $\boldsymbol{R}_i$)   (3N+1) dimensional
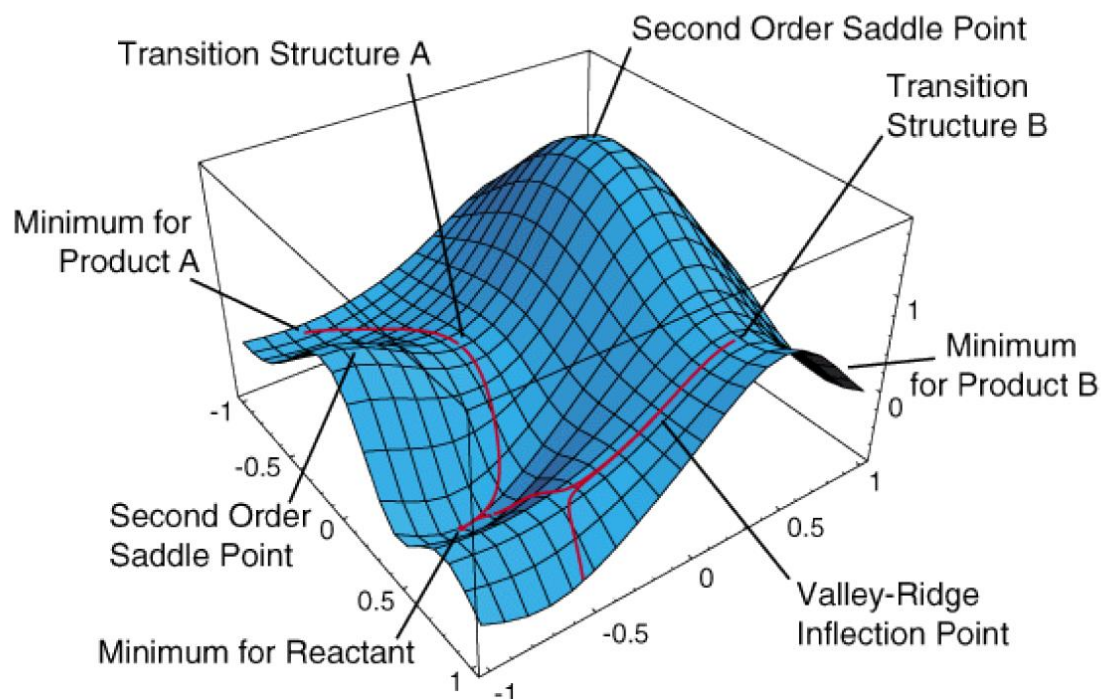
Knowledge of the minima and transition states enables the estimation of reaction rates

PES is a function of 3N–6 coordinates

Very smooth for clusters

Exploring configurational space

Local optimization   Global optimization

- Steepest descent
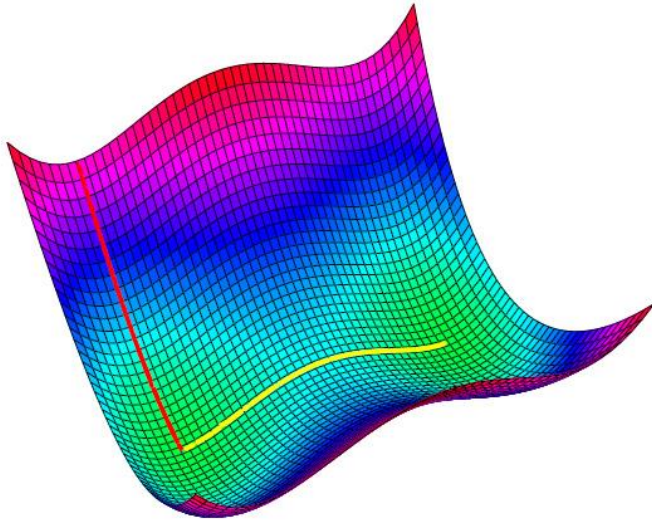
- Conjugate gradient

- Broyden-Fletcher-Goldfarb-Shanno

Next local minimum

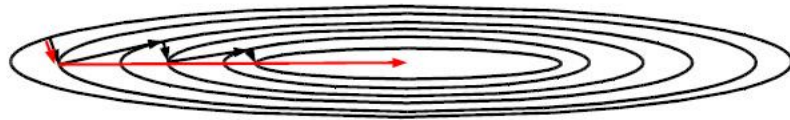- Simulated annealing

- Basin-hopping

- Genetic algorithms

Global minimum

- Steepest descent:

- Conjugated gradient:

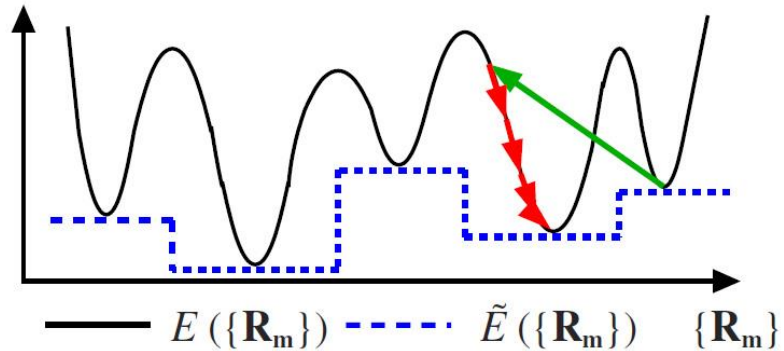 fraction of the previous search direction to the atomic forces

- Broyden-Fletcher-Goldfarb-Shanno:

  adding Hessian information

$$R_{\alpha, i+1} = R_{\alpha, i} + \gamma_i F_\alpha(\{R_{\alpha, i}\})$$

Strictly downhill to local minimum

- Basin hopping:

$$\tilde{E}\{\mathbf{R}_m\} = \min E\{\mathbf{R}\}$$
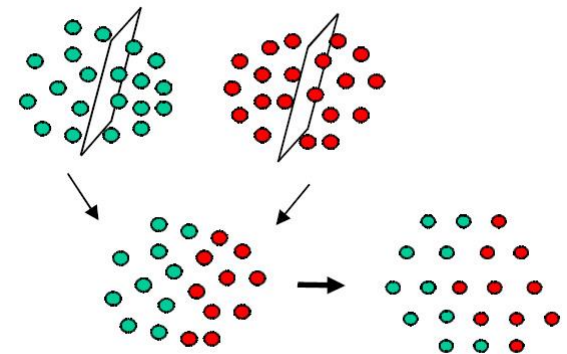
Transform PES into set of staircases

- Simulated annealing:

acceptance criterion

$$P(\Delta E) = exp(-\Delta E/k_B T)$$

- Genetic algorithms:

"survival of the fittest"

- Intermediate configurations are bonded together with springs, so that they are always constrained to remain between the configurations that precedes and follow them. Then the configurations act as an elastic chain.

- Of the true force that applies to atoms, only the component normal to the reaction path is used. Along the reaction path it is the force due to the springs that applies to atoms.
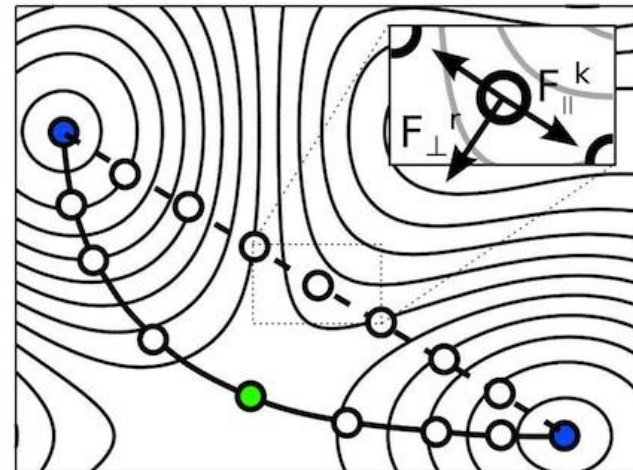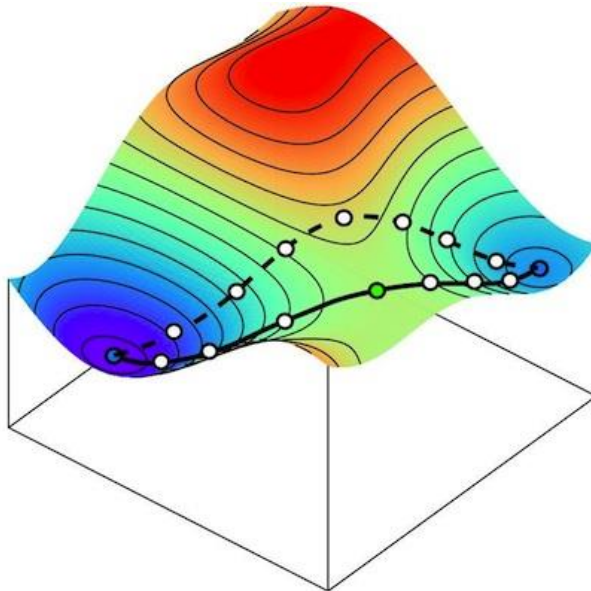
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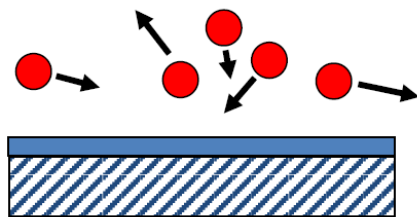5) "Descriptors" and catalysts screening
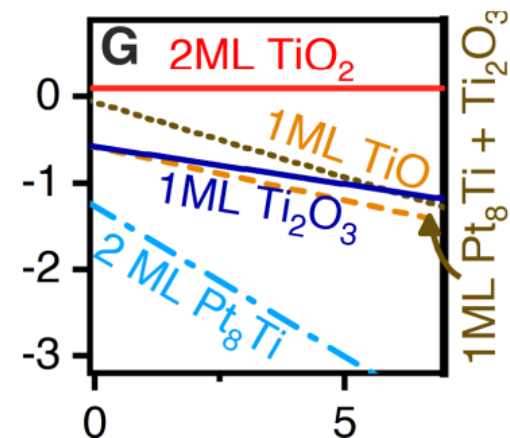
A DFT calculation corresponds to $T = 0$ K

Real materials may be full of defects (vacancies, dislocations, dopants)

Material's structure and composition can strongly depend on preparation

Impurities and adsorbates can influence the surface morphology

A surface cannot be separated from a gas (or liquid) above it
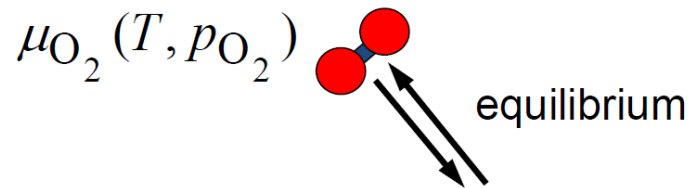

$$v = \frac{p}{\sqrt{2\pi m k T}}$$

Requires $p \leq 10^{-12}$ atm to keep a "clean" surface clean

For $T = 300$ K, $p = 1$ atm

$v \approx 10^{8}$ site^{-1} s^{-1}

Ab initio thermodynamics provides a connection between the microscopic and macroscopic regimes

Predict the preferred structure of a material as a function of environmental conditions

$$\mu_{O_2}(T, p_{O_2})$$

equilibrium

$$G(T,p) = E^{\text{total}} + F^{\text{vibration}} - TS^{\text{configurational}} + pV$$

DFT

[1] C.M. Weinert and M. Scheffler, *Mater. Sci. Forum* 10-12, 25 (1986)
[2] G.-X. Qian, R.M. Martin, and D.J. Chadi, *Phys. Rev. B* 38, 7649 (1988)
[3] K. Reuter and M. Scheffler, *Phys. Rev. B* 65, 035406 (2002)

From statistical thermodynamics we know:

$$G(T,p) = E(\text{electr.}) +$$ electronic

$$+ \sum_i \left\{ N_A \frac{h\nu_i}{4\pi} + RT\ln\left[1 - \exp\left(\frac{-h\nu_i}{k_B T} \right) \right] \right\}$$ vibrational
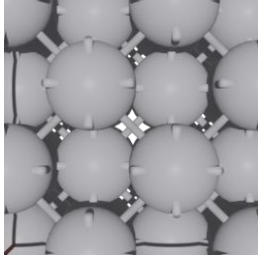
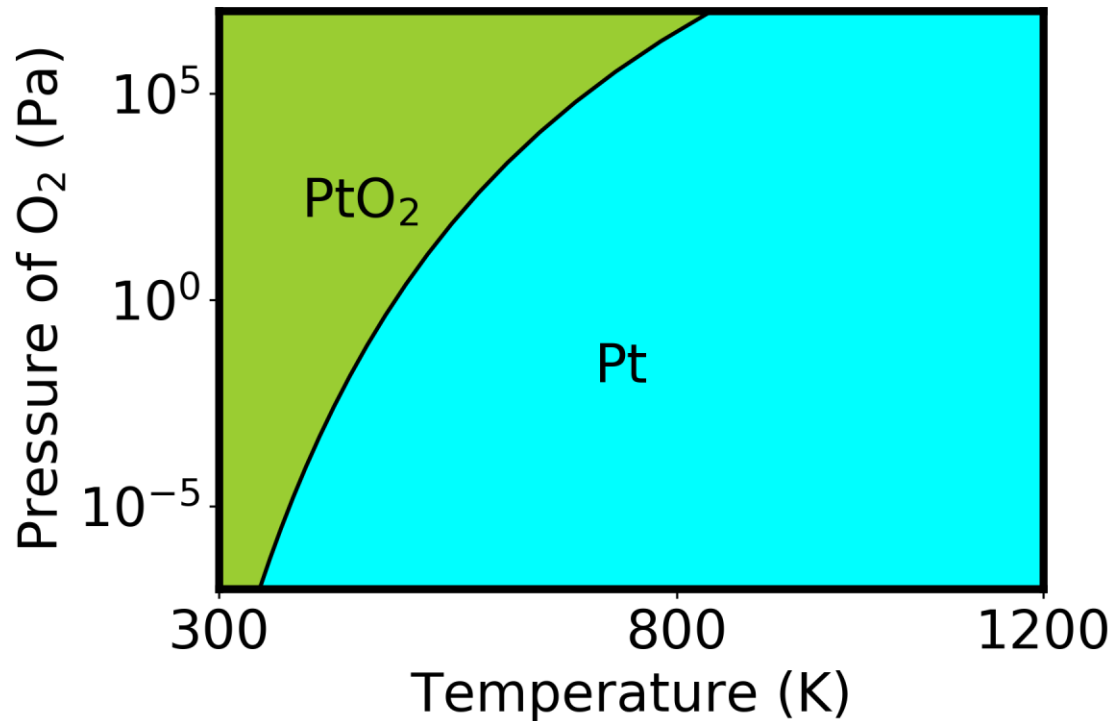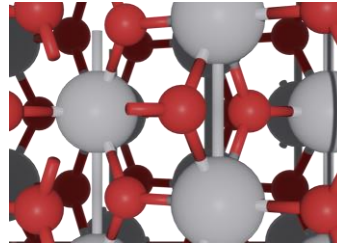$$-RT\ln\left(\frac{(2\pi k_B T m)^{\frac{3}{2}}}{h^3} \cdot \frac{k_B T}{p} \right)$$ translational

$$-RT\ln\left[\frac{8\pi^2}{\sigma} \left(\frac{2\pi k_B T}{h^2} \right)^{\frac{3}{2}} \cdot (I_A I_B I_C)^{\frac{1}{2}} \right]$$ rotational
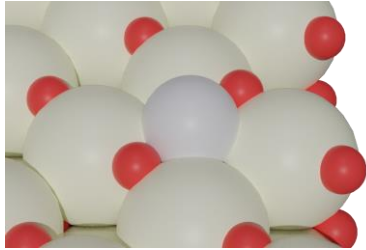
Phase diagram for Pt-O system

Pt

PtO_2

$$Pt + O_2 \quad \rightleftharpoons \quad PtO_2$$

$(Pt)_{ads}$

$(PtO)_{ads}$
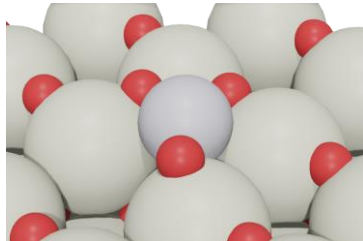
$(PtO_2)_{ads}$
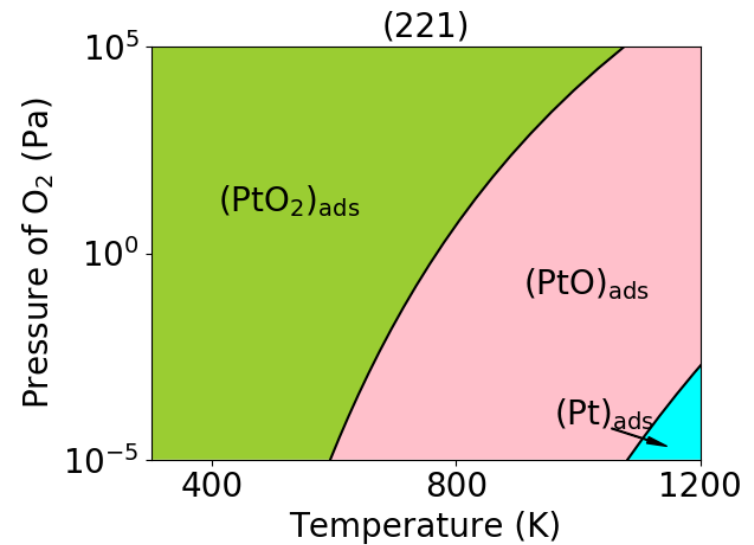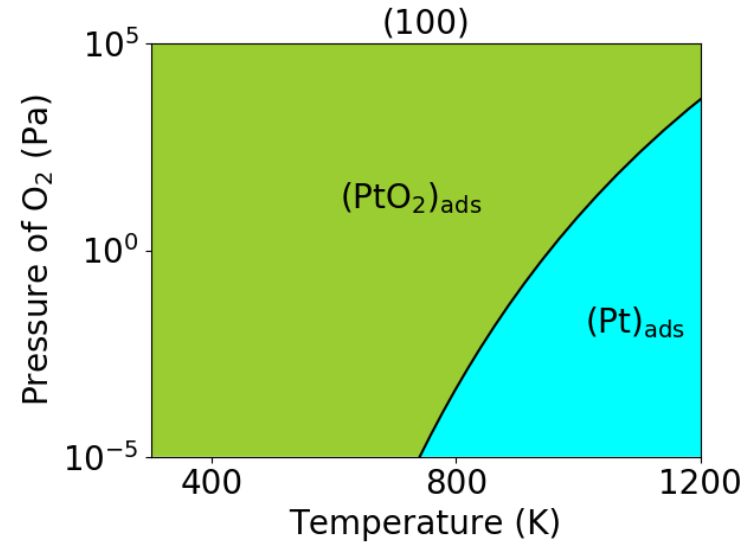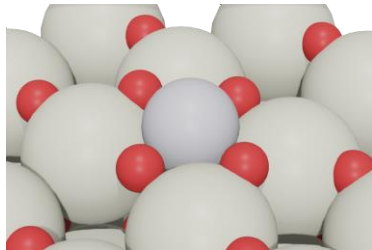
Surface phase diagram for the Pd(100) surface with an environment consisting of O_2 and CO
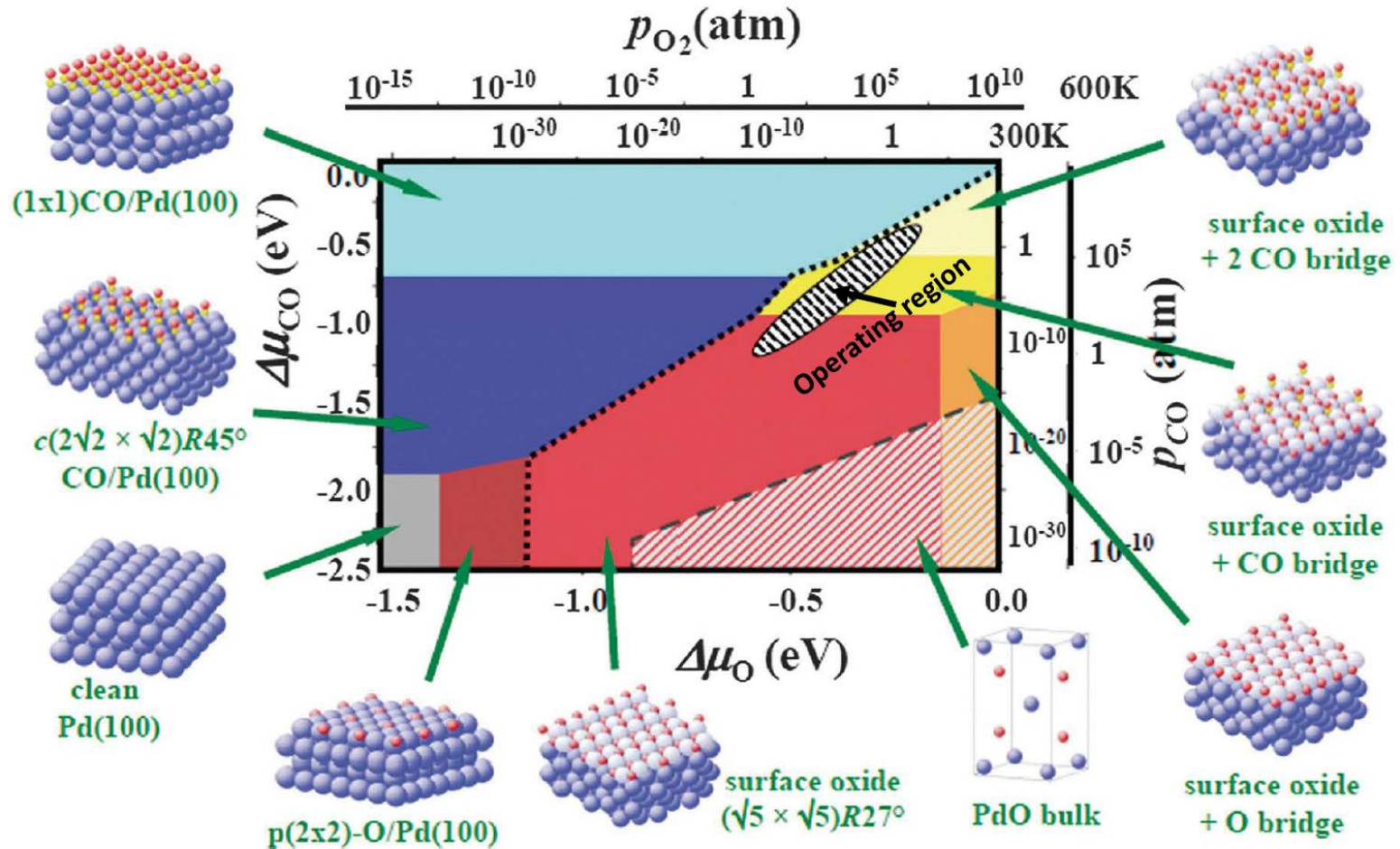
Pd: large blue spheres, O: small red spheres, C: white spheres

[1] K. Reuter and M. Scheffler, *Phys. Rev. Lett.* 90, 4 (2003)
[2] J. Rogal, K. Reuter, M. Scheffler, *Phys. Rev. Lett.,* 98, 046101 (2007)

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The Sabatier principle

- The rate is given by the ability of a catalyst to activate reactants

- The rate of a catalytic reaction is a maximum when the interaction between reactant and catalyst is at an optimum value

P. Sabatier, Ber. Dtsch. Chem. Ges. **1911**, *44*, 1984.

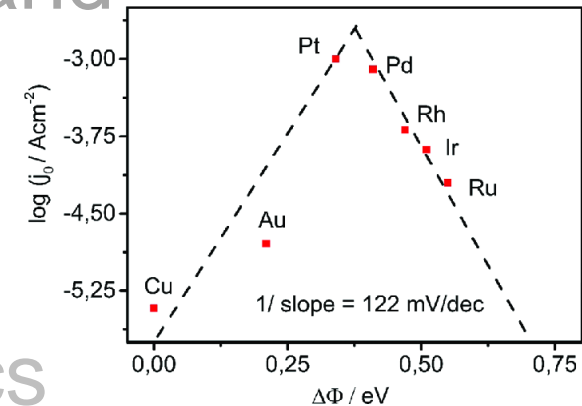At least one of the reacting molecules forms a complex with the catalyst. When the complex is too stable, the catalyst will become poisoned. When it is too unstable, the reaction will not proceed.

Mitteilungen.

258. **Paul Sabatier**: Hydrogénations et déshydrogénations par catalyse.

[Vortrag, gehalten vor der Deutschen Chem. Gesellschaft am 13. Mai 1911.]

Volcano plots

- A quantity related to the reaction under consideration is plotted against a measure of the stability of the intermediate compound (heat of adsorption, position of the catalytic element in the periodic table, deprotonation energy,…)

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

Volcano plots

- A quantity related to the reaction under consideration is plotted against a measure of the stability of the intermediate compound (heat of adsorption, position of the catalytic element in the periodic table, deprotonation energy,…)

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$
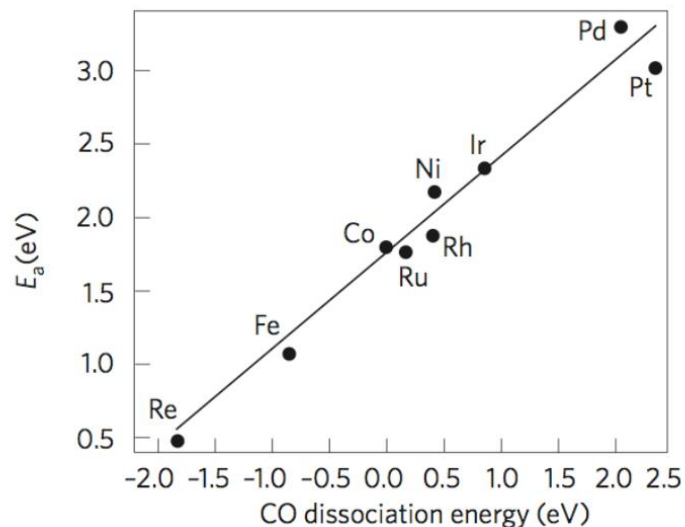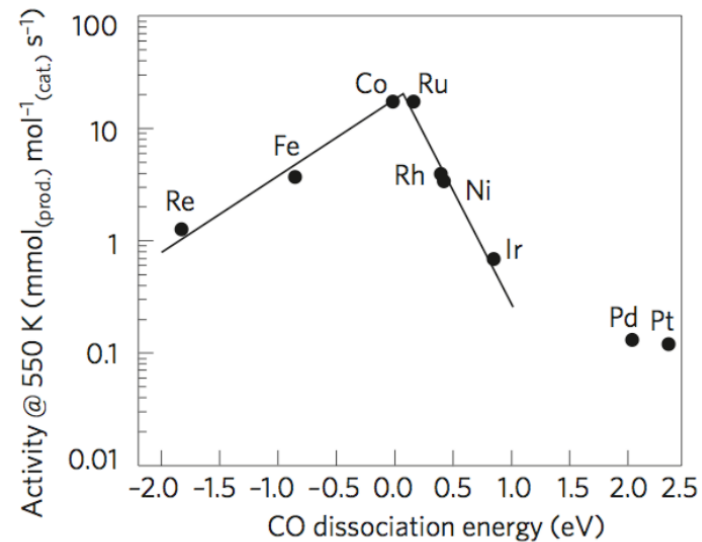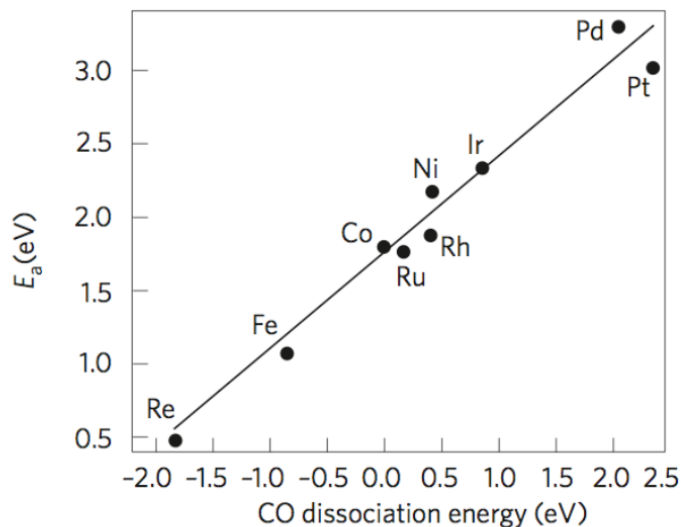
Dissociation of CO easy, C and O interact strongly with the metal

CO molecularly adsorbed

M. P. Andersson, T. Bligaard, A. Kustov, K. E. Larsen, J. Greeley, T. Johannessen, C. H. Christensen, J. K. Nørskov, *Journal of Catalysis* **2006**, *239*, 501-506.

Linear free energy relationships

- Brønsted-Evens-Polanyi reaction rate expression relations (BEP relationships) – relate the rate of a reaction with a thermodynamic quantity of the reaction (dissociation constant, reaction enthalpy) in reactions where dissociation is the essential step in the reaction mechanism

- More general, valid when one compares related elementary reaction steps that proceed through nearly the same intermediate structures and have similar reaction coordinates

- Empirical relations supported by calculations based on density functional theory

Linear free energy relationships

- Shown for activation of a diatomic molecule (NH_3 synthesis, methanation of CO)

- Reactions consist of two main parts

1. Dissociation of the reacting molecules determined by the activation barrier for dissociation, E_a

2. Removal of the dissociation products largely given by the stability, ΔE, of the intermediates on the surface

- Hydrogen also needs to dissociate, but this reaction is fast and hydrogen binds more weakly to the surface than N, C, or O

- A good catalyst is characterized by a low activation energy **and** weak bonding of the intermediates

structure/energy → TS barriers → reaction rates → probabilities of system evolution
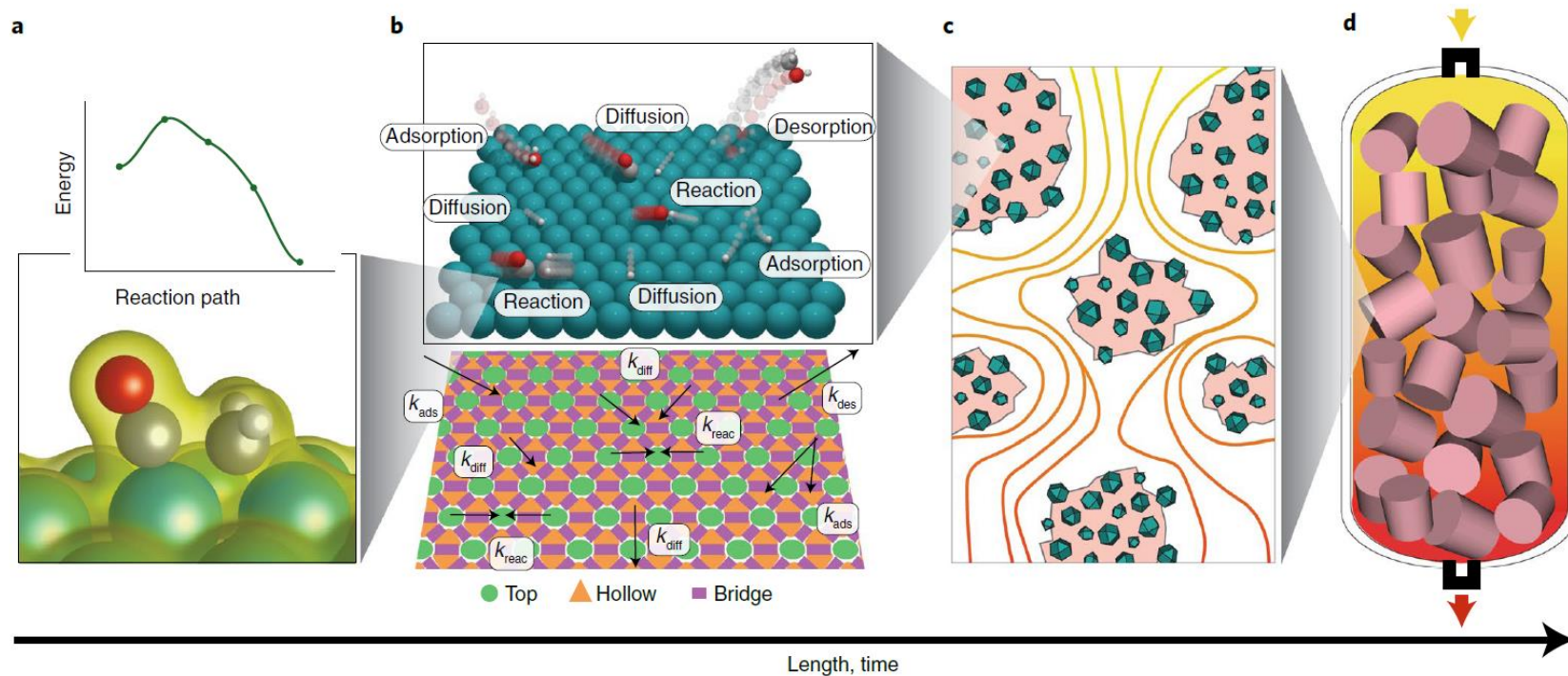

Fig. 1 | Different levels in a multiscale modelling framework from electrons to a reactor, or electrochemical cell. a, Electronic structure calculations provide predictive-quality information on individual elementary processes in the catalytic cycle, such as energetic barriers. **b,** First-principles microkinetic models use this information to evaluate the interplay between all elementary processes and establish the intrinsic catalytic activity. **d,** The integration into transport models determines how this activity interfaces with the overall macroscopic flow of heat and mass. **c,** For real catalysts, this integration requires an intermediate step appropriately coarse-graining over the catalyst microstructure.

A. Bruix *et al.*, *Nature Catalysis* **2**, 659 (2019)

Computational modeling is a powerful method for understanding catalysis at surfaces

Mechanistic hypothesis testing

Structure-property relationships

Catalyst screening and design
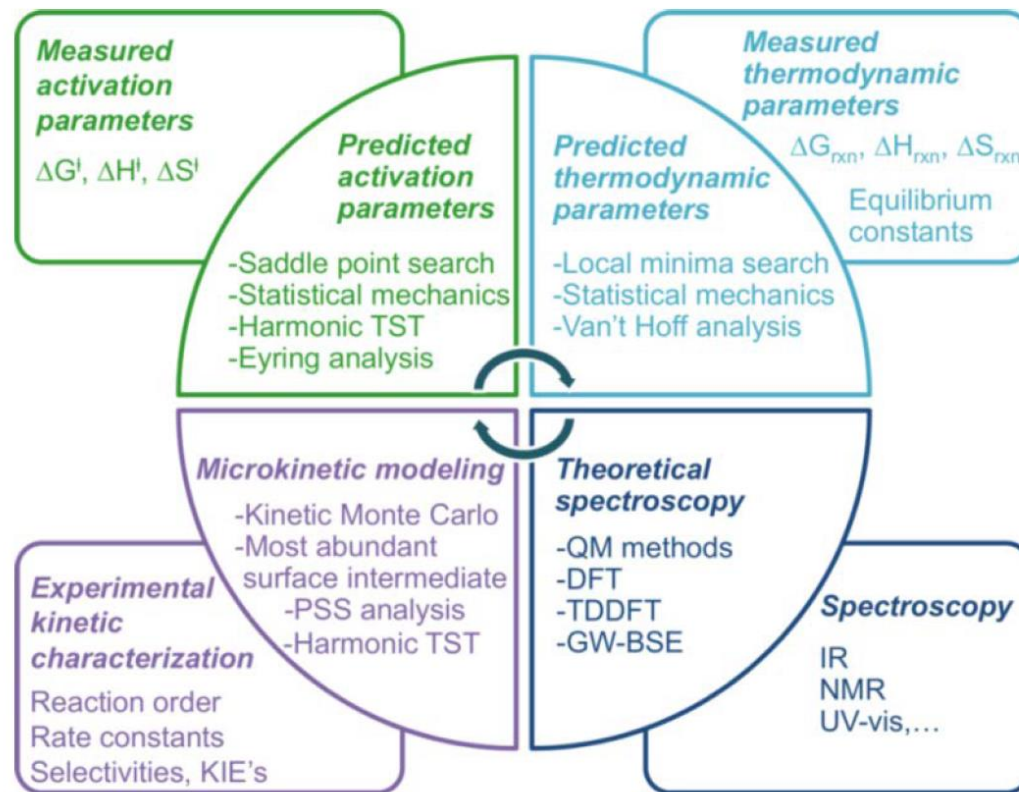
DFT:

"The ABC of DFT" by Kieron Burke:

http://chem.ps.uci.edu/˜kieron/dft/book/

ab initio thermodynamics:

"Ab Initio Atomistic Thermodynamics for Surfaces: A Primer" by Karsten Reuter:

https://th.fhi-berlin.mpg.de/th/publications/EN-AVT-142-02.pdf

Volcano plots:

"Towards the computational design of solid catalysts" by Jens Nørskov:

https://www.nature.com/articles/nchem.121

Theoretical catalysis:

"First-principles-based multiscale modelling of heterogeneous catalysis" by
Karsten Reuter:

https://www.nature.com/articles/s41929-019-0298-3

**Interested in a
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dennis.palagin@psi.ch

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