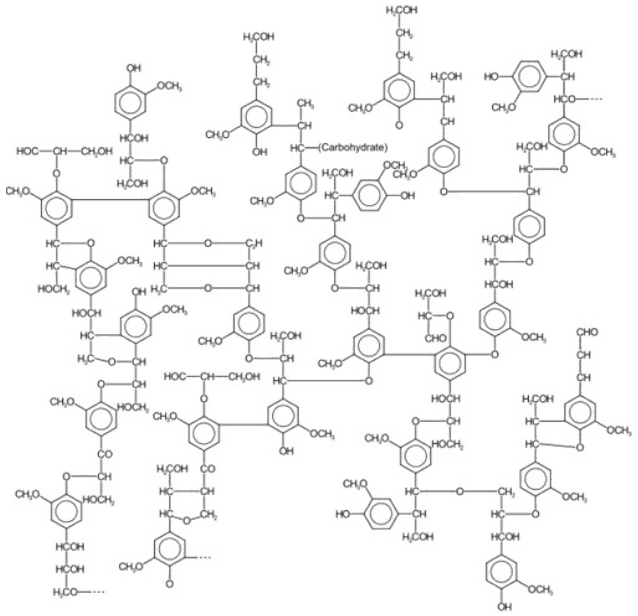
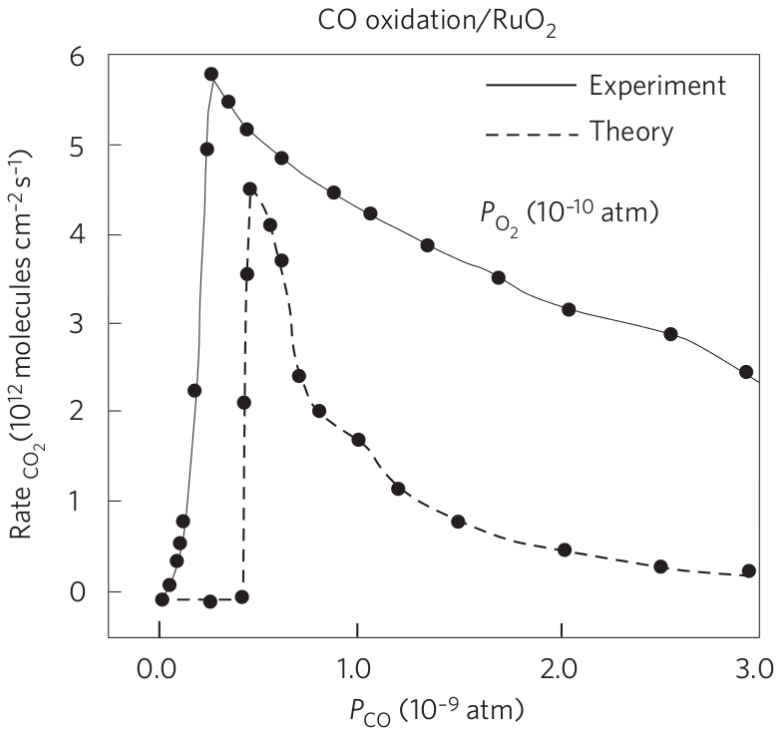
Designing catalysts for chemical production by density functional theory modeling

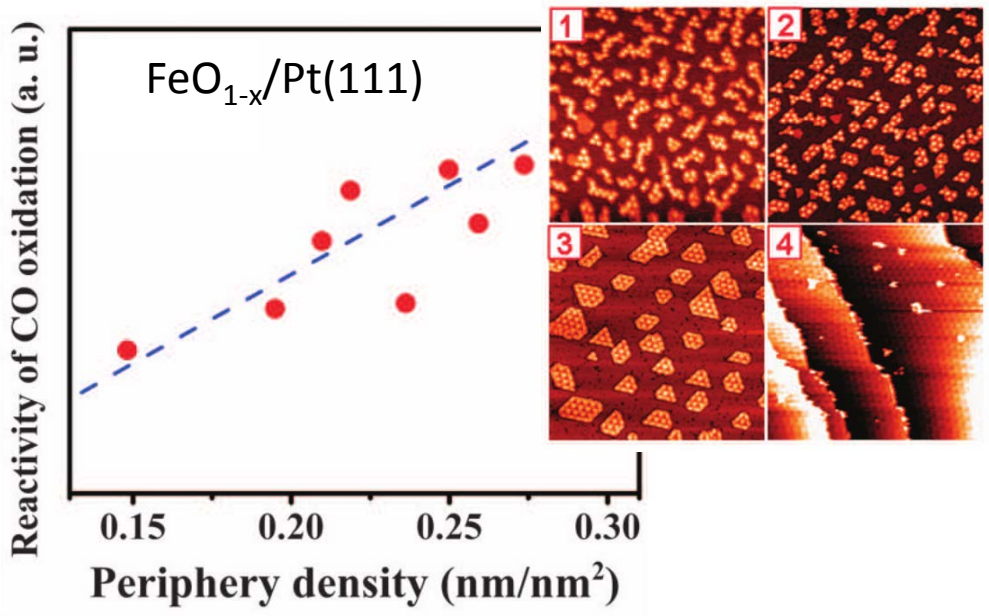
Bryan R. Goldsmith

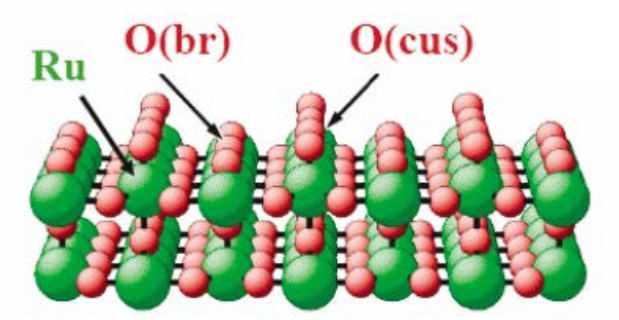
Catalysts make the world go round

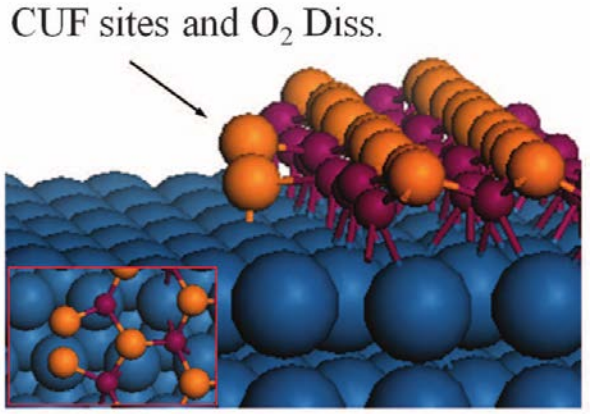


Computational modeling can be used to understand and design catalysts





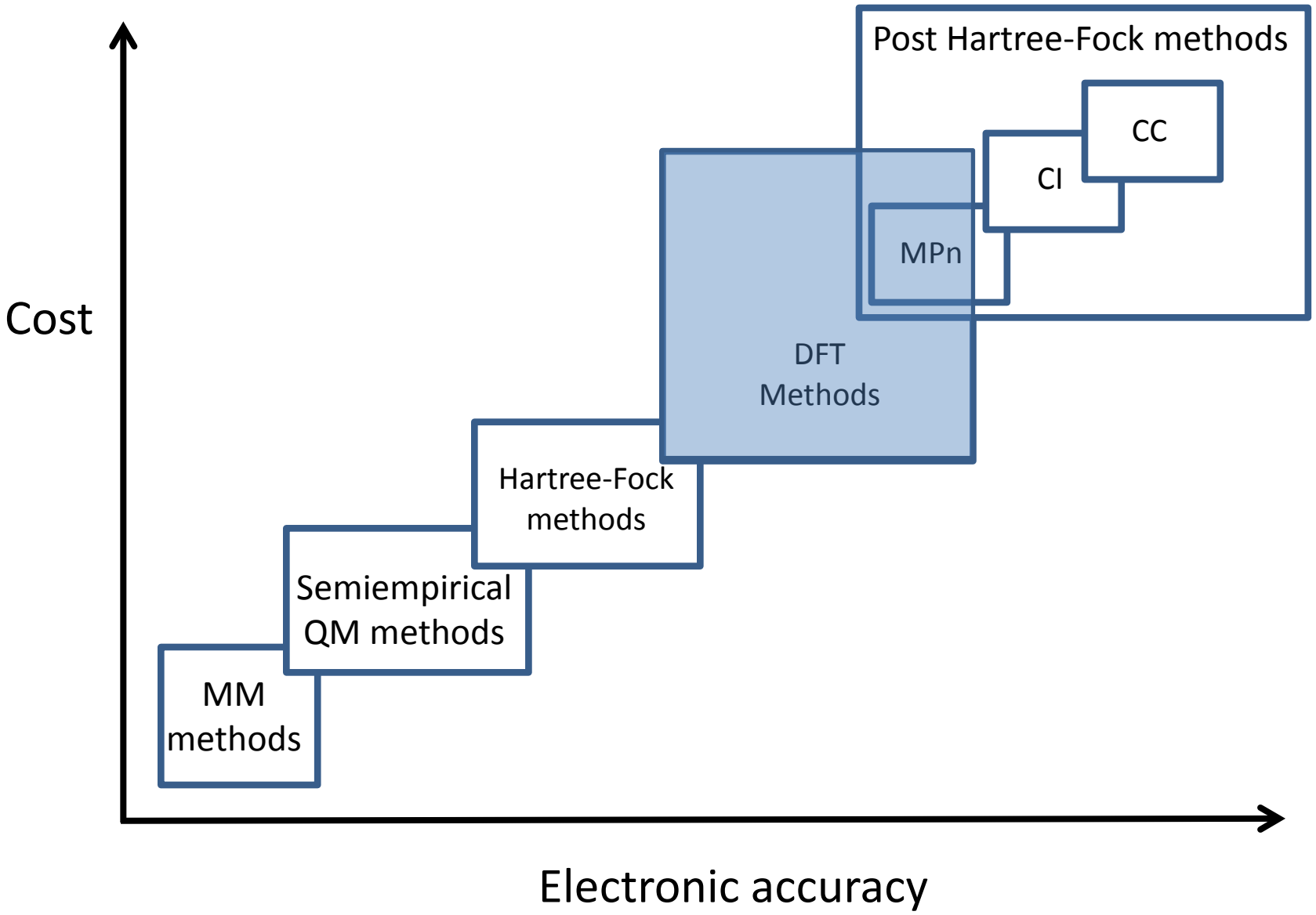




Reuter, K., Frenkel, D. & Scheffler, M. *Phys. Rev. Lett.* **93,** 116105 (2004).

Qiang Fu et. al.
Science **328**, 1141 (2010)

Accuracy vs. cost of modeling approaches



DFT is extremely popular and successful: See most cited papers in APS (from 1893)

	Journal	# cites	Title	Author(s)
1	PRB (1988)	39190	Development of the Colle-Salvetti Correlation-Energy ...	Lee, Yang, Parr
2	PRL (1996)	25452	Generalized Gradient Approximation Made Simple	Perdew, Burke, Ernzerhof
3	PRA (1988)	22904	Density-Functional Exchange-Energy Approximation ...	Becke
4	PR (1965)	20142	Self-Consistent Equations Including Exchange and Correlation ...	Kohn and Sham
5	PRB (1996)	13731	Efficient Iterative Schemes for Ab Initio Total-Energy ...	Kresse and Furthmuller
6	PRB (1976)	13160	Special Points for Brillouin-Zone Integrations	Monkhorst and Pack
7	PRB (1992)	10876	Accurate and Simple Analytic Representation of the Electron ...	Perdew and Wang
8	PRB (1999)	10007	From Ultrasoft Pseudopotentials to the Projector Augmented ...	Kresse and Joubert
9	PRB (1990)	9840	Soft Self-Consistent Pseudopotentials in a Generalized ...	Vanderbilt
10	PR (1964)	9789	Inhomogeneous Electron Gas	Hohenberg and Kohn
11	PRB (1981)	9787	Self-Interaction Correction to Density-Functional Approx. ...	Perdew and Zunger
12	PRB (1992)	9786	Atoms, Molecules, Solids, and Surfaces - Applications of the ...	Perdew, Chevary, ...
13	PRB (1986)	9313	Density-Functional Approx. for the Correlation-Energy ...	Perdew
14	PR (1934)	9271	Note on an Approximation Treatment for Many-Electron Systems	Moller and Plesset
15	PRB (1994)	9100	Projector Augmented-Wave Method	Blochl
16	PRL (1980)	7751	Ground-State of the Electron-Gas by a Stochastic Method	Ceperley and Alder
17	PRL (1987)	7663	Inhibited Spontaneous Emission in Solid-State Physics ...	Yablonovitch
18	PRL (1986)	7589	Atomic Force Microscope	Binnig, Quate, Gerber
19	PRB (1991)	7425	Efficient Pseudopotentials for Plane-Wave Calculations	Troullier and Martins
20	PRB (1993)	6925	Ab initio Molecular Dynamics for Liquid Meta	
21	PR (1961)	6467	Effects of Configuration Interaction on Intens	
22	PR (1957)	6260	Theory of Superconductivity	

Most cited physicists

Name: (Last, First)	Sum of Times Cited
Perdew, John P.	65,757
Smalley, Richard E.	63,354
Becke, Axel Dieter	62,581
Witten, Edward	59,157
Heeger, Alan J.	56,364

Hohenberg-Kohn Theorem (1964)

Assume two different external potentials give same electron density, $\rho(\vec{r}) = N\int\cdots\int|\Psi(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_N)|^2 ds_1 d\vec{x}_2 \ldots d\vec{x}_N$

$$\hat{V}_{ext} \Rightarrow \hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} \Rightarrow \Psi \Rightarrow \rho(\vec{r}) \Leftarrow \Psi' \Leftarrow \hat{H}' = \hat{T} + \hat{V}_{ee} + \hat{V}'_{ext} \Leftarrow \hat{V}'_{ext}$$

$$E_0 \neq E'_0$$

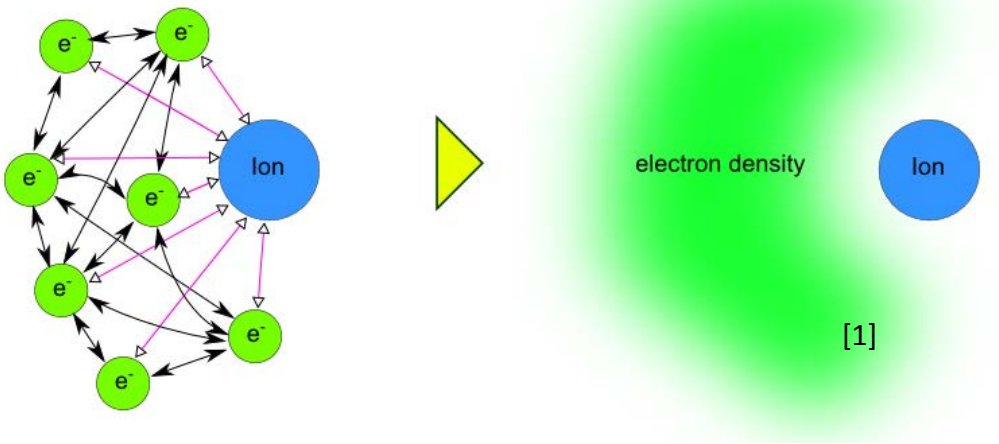
Impossible

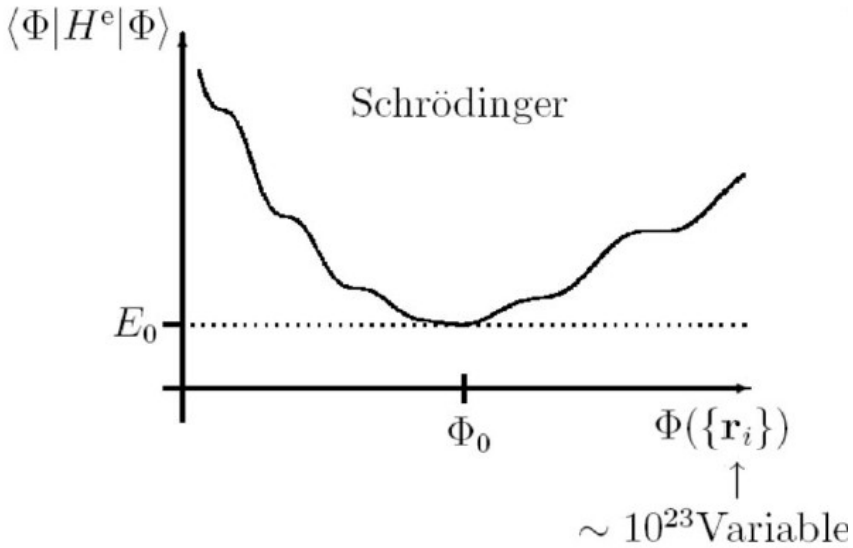
$$\Longrightarrow \quad E_0 + E'_0 < E'_0 + E_0 \text{ or } 0 < 0.$$

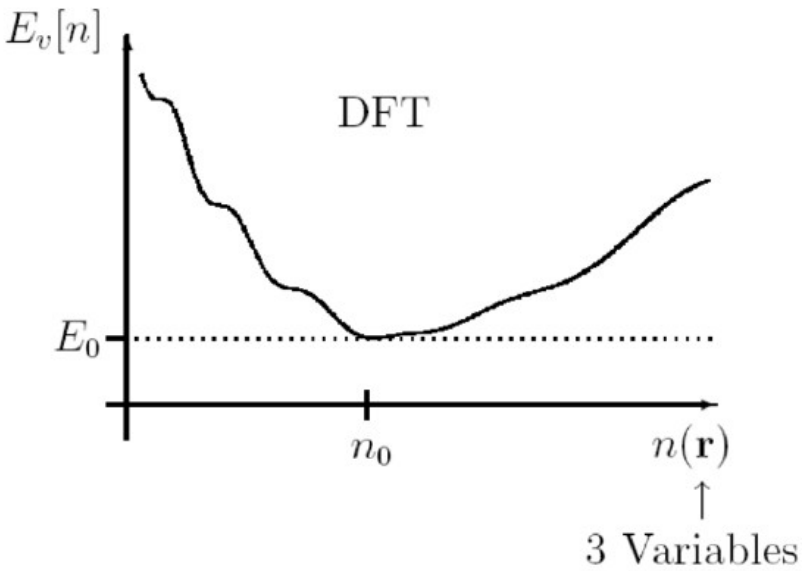
∴ The ground state density uniquely specifies the external potential

$$\rho_0 \Rightarrow \{N, Z_A, R_A\} \Rightarrow \hat{H} \Rightarrow \Psi_0 \Rightarrow E_0 \text{ (and all other properties).}$$

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

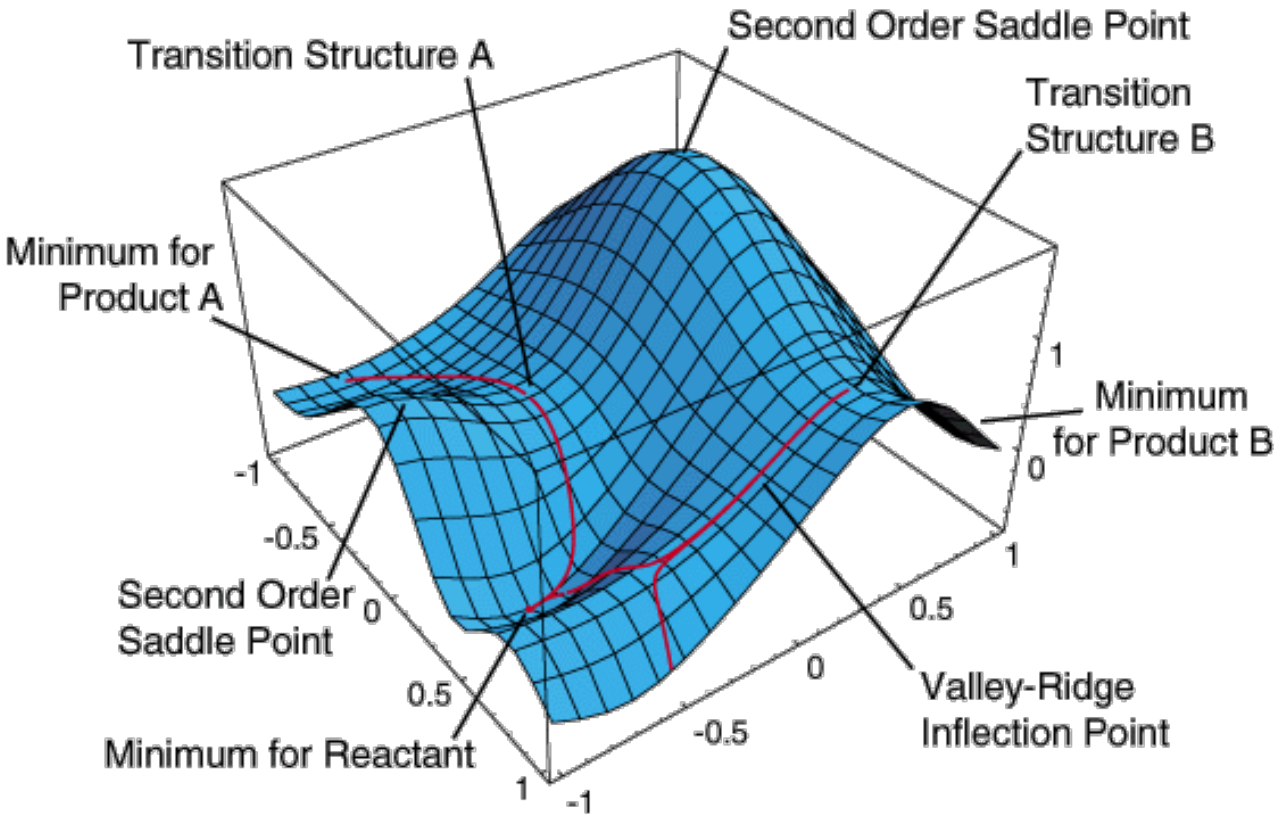






[1] http://www.magmat.org/theory/dft/

Exploring the potential energy surface is critical to compute system properties

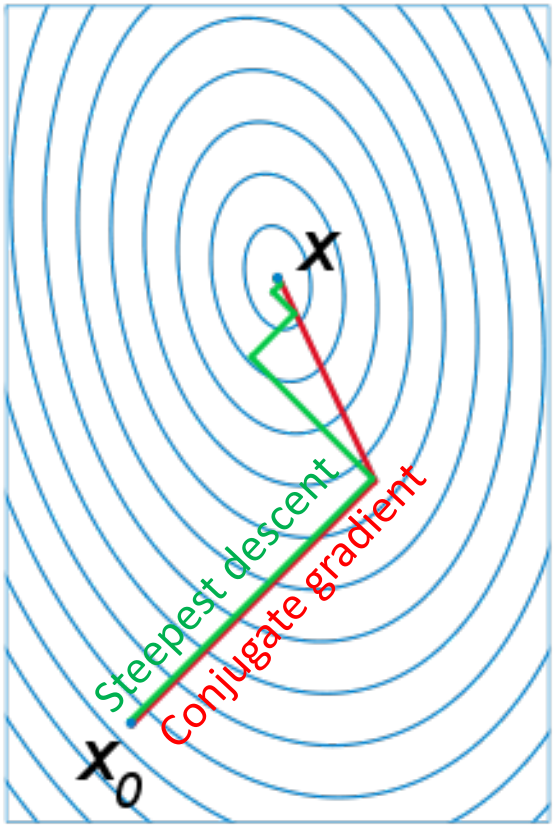


Common energy minimization algorithms

Gradient only methods

Example: Conjugate gradient

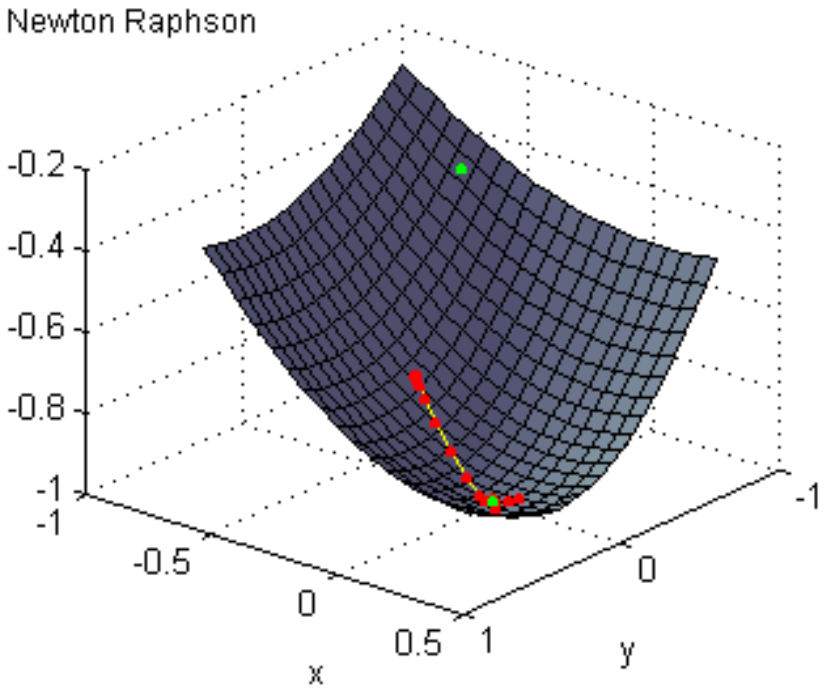
$x_{k+1} = x_k + \alpha p_k$



Second derivative based-methods

Example: Newton-Raphson

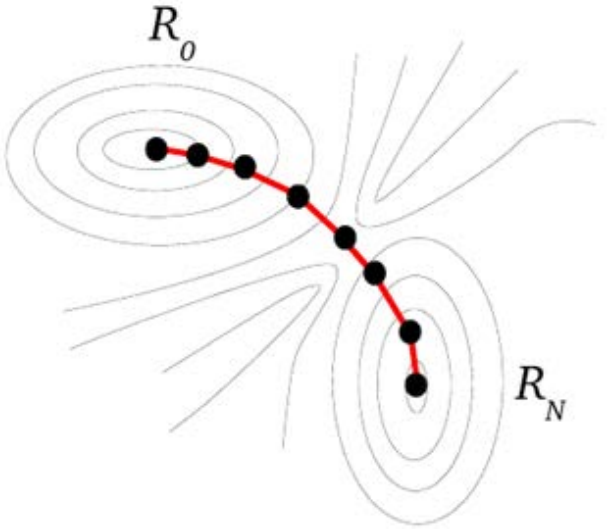
$$\Delta\varepsilon = E - E_o = g^t \Delta x + 1/2 \Delta x^t H \Delta x$$
$$\partial\Delta\varepsilon / \partial\Delta x = g + H\Delta x = 0$$
$$\Delta x = -H^{-1} g$$



Common transition state search methods

"Doubled-ended" searches

Example: Nudged elastic band

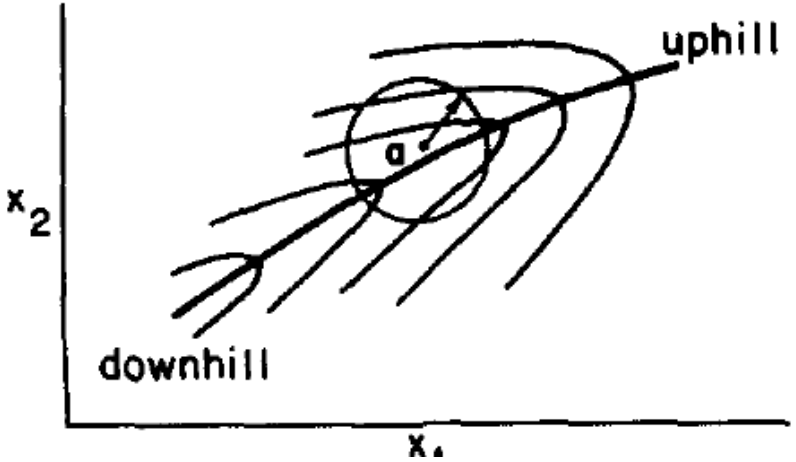


H. Jónsson, G. Mills, K. W. Jacobsen, NEB for Finding Minimum Energy Paths of Transitions, (World Scientific, 1998).

"Single-ended" searches

Example: min-mode following

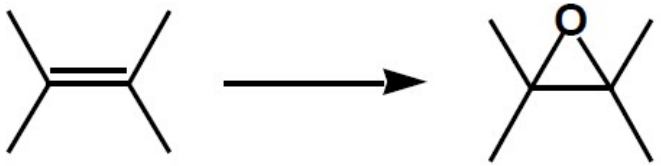
$$X = (\Lambda - H)^{-1} g$$

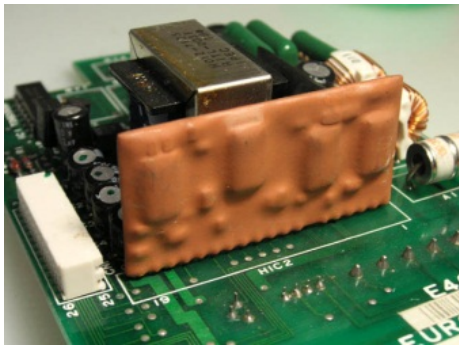


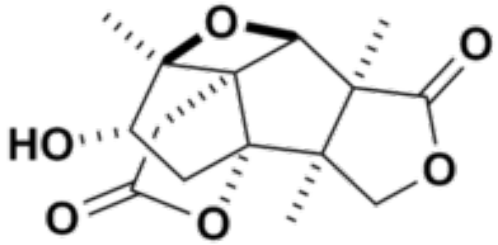
C. Cerjan, and W. Miller, J. Chern. Phys. 75(6), 1981

Applications of DFT to understand catalysts

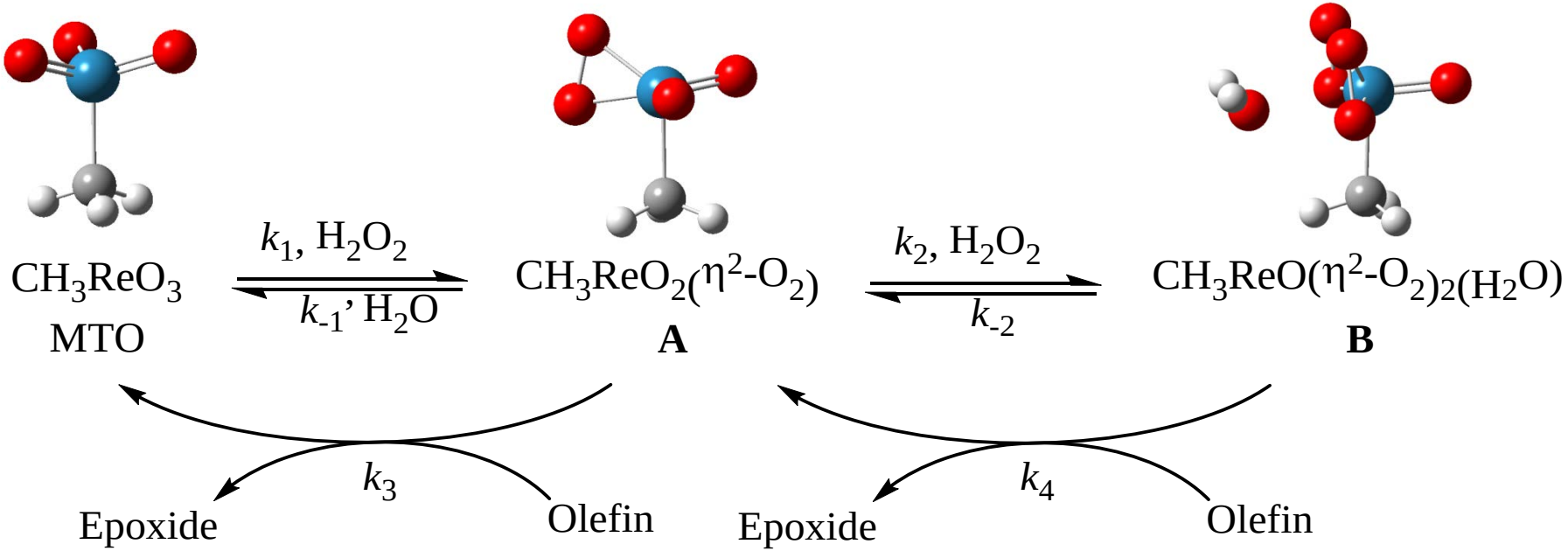
Olefin epoxidation plays a key role in chemical industry



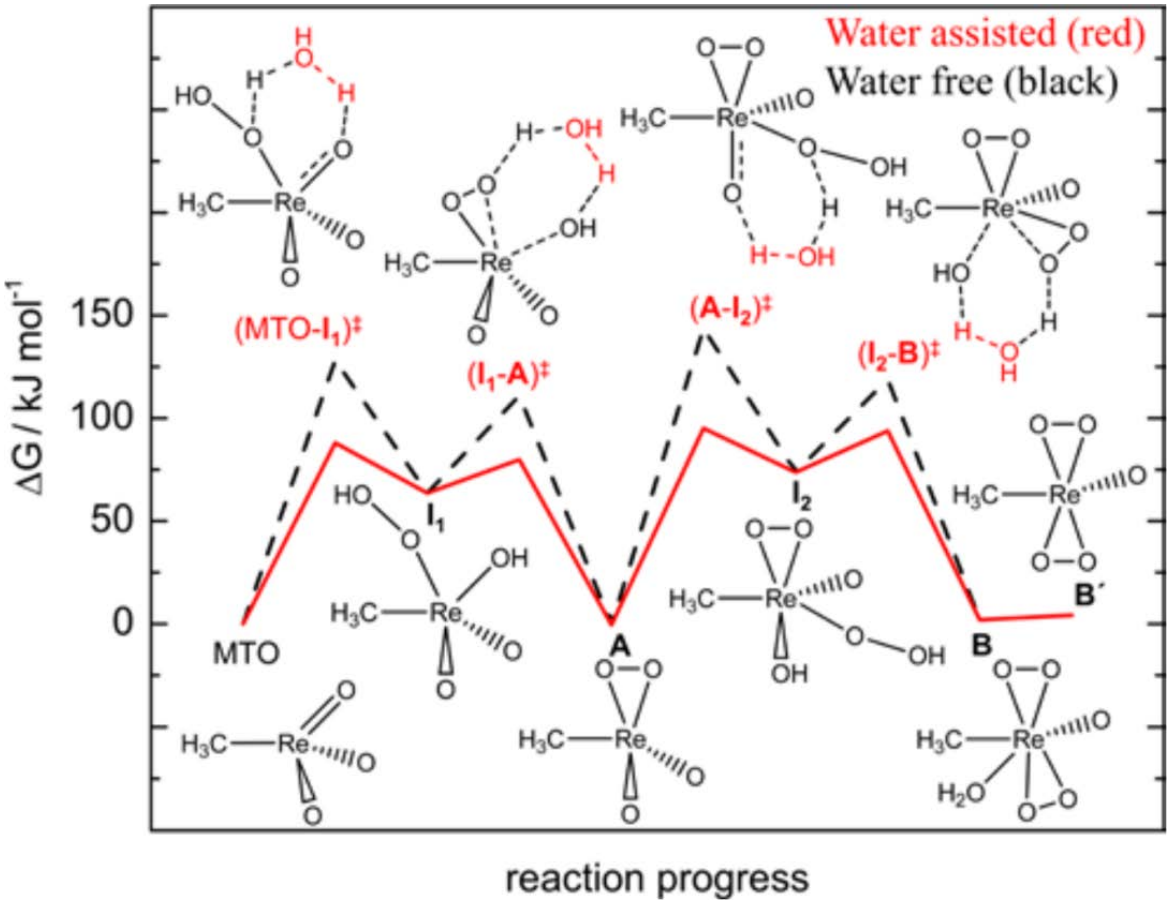




Methyltrioxorhenium is an active olefin epoxidation catalyst



Water-catalyzed activation of H_2O_2 by CH_3ReO_3 in aqueous acetonitrile

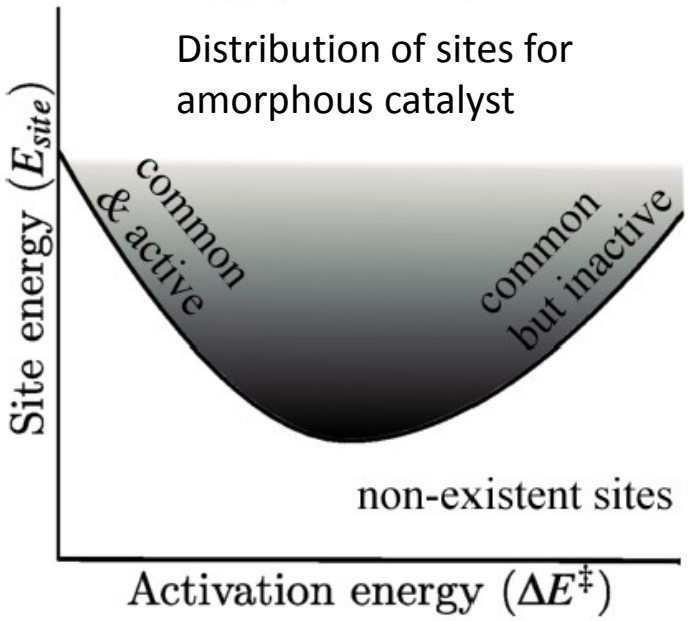


	Experiment	Calculated (water assisted)
$10^3\ k_1\ (M^{-1}\ s^{-1})$	471.4 (63)	18
$10^3\ k_{-1}'\ (s^{-1})$	2.84 (16)	24
$10^3\ k_2\ (M^{-1}\ s^{-1})$	34.7 (20)	0.61
$10^3\ k_{-2}\ (s^{-1})$	0.224 (72)	1.4

T. Hwang,* B. R. Goldsmith,* B. Peters, and S. L. Scott, Inorg. Chem. 52, 13904 (2013).

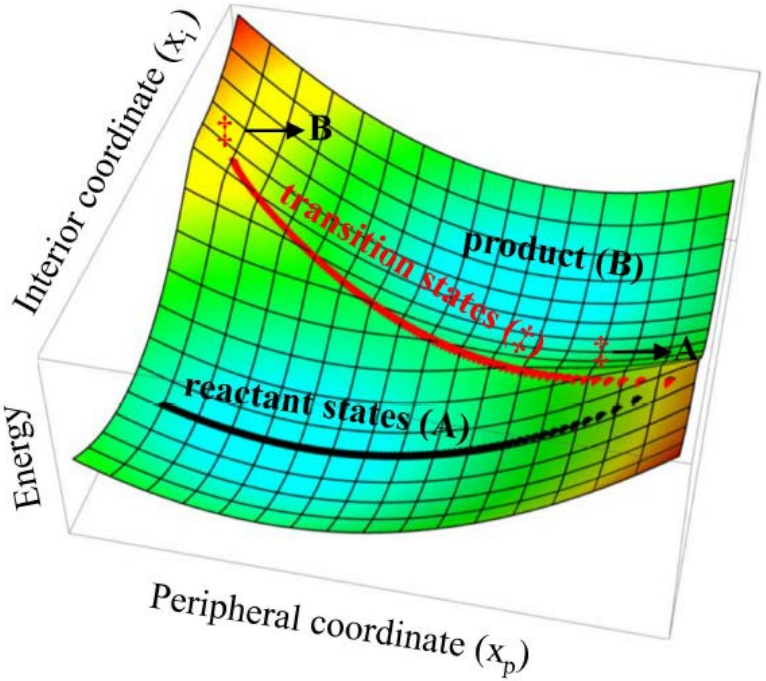
Structure-property relationships in *amorphous* catalysts

Amorphous catalysts are extremely difficult to model



Our approach

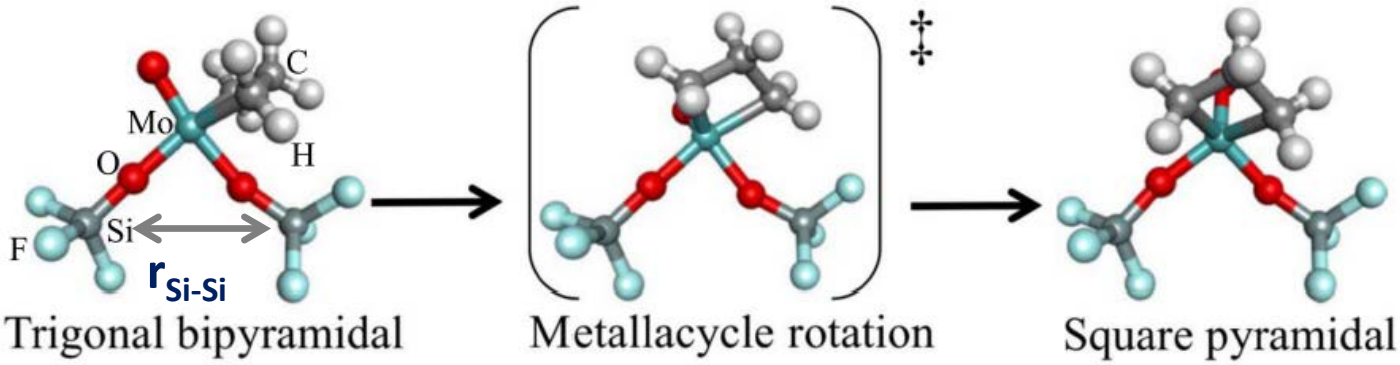
$$min_{\mathbf{x}_p} E^{A}_{red}(\mathbf{x}_p) \quad subject\ to \quad \Delta E^{\ddagger}(\mathbf{x}_p) = \Delta E^{\ddagger}$$



B. R. Goldsmith, E. D. Sanderson, D. Bean, B. Peters, J. Chem. Phys. 138, 204105 (2013).

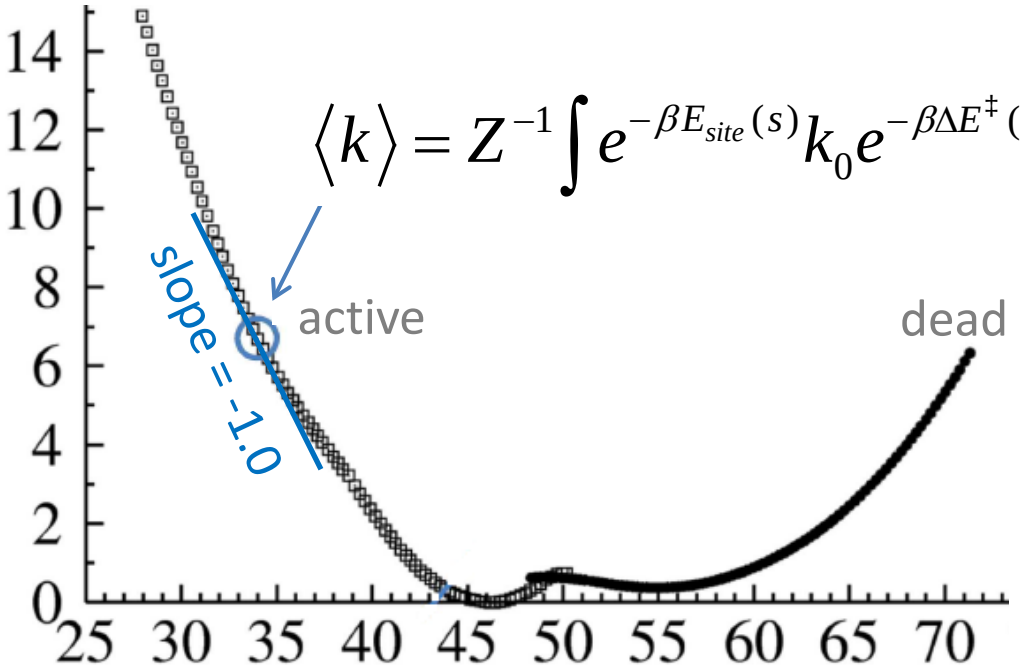
B. R. Goldsmith, A. Fong, and B. Peters (2013). *Reaction Rate Constant Computations,* Royal Society Chemistry.

Molybdenum/amorphous SiO_2 + C_2H_4

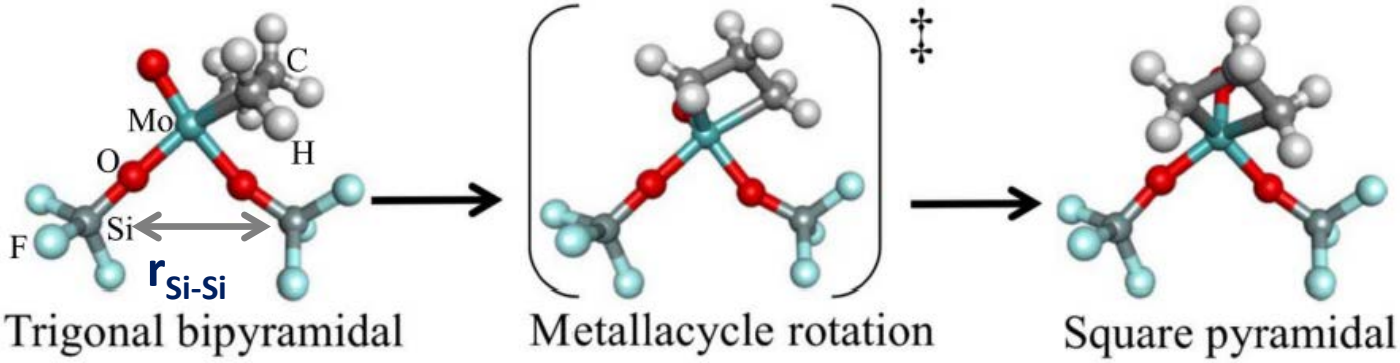


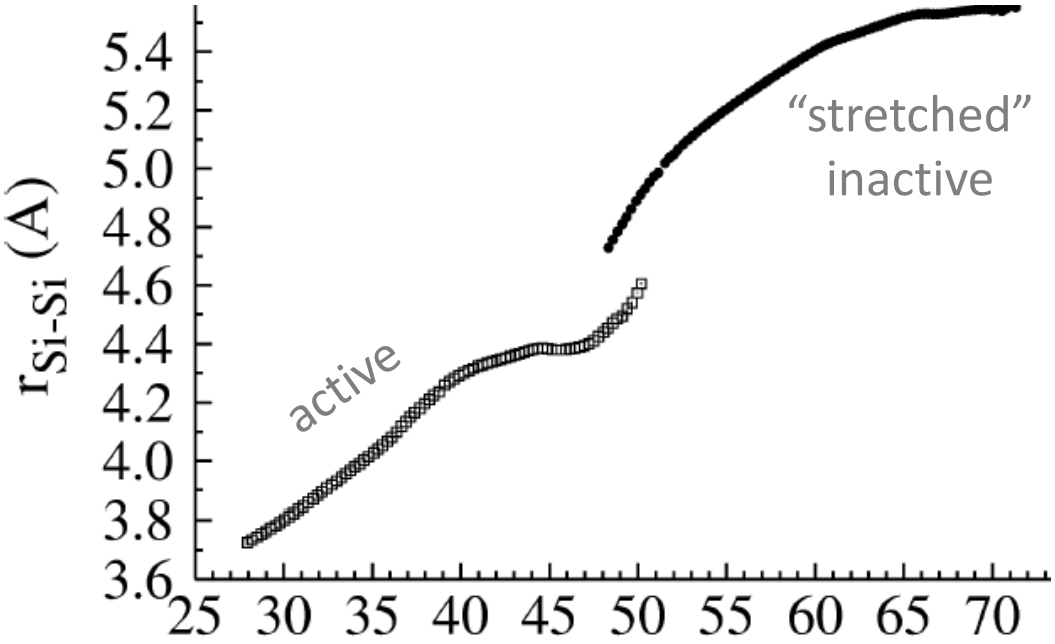
Site formation energy (kJ/mol)

$$\langle k \rangle = Z^{-1} \int e^{-\beta E_{site}(s)} k_0 e^{-\beta \Delta E^{\ddagger}(s)} ds$$



Molybdenum/amorphous SiO_2 + C_2H_4



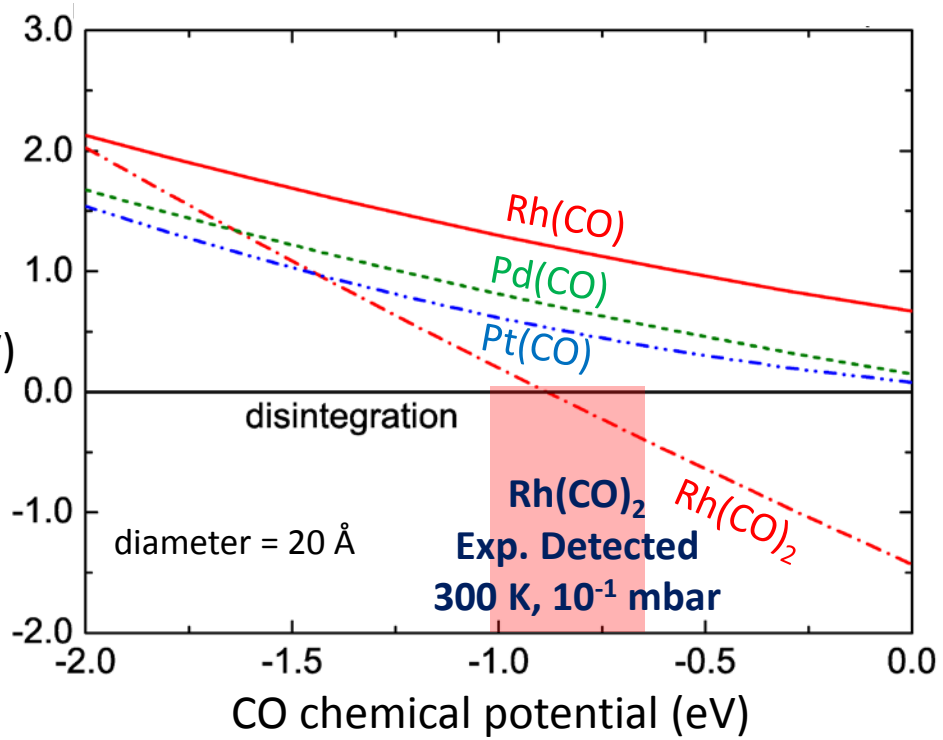


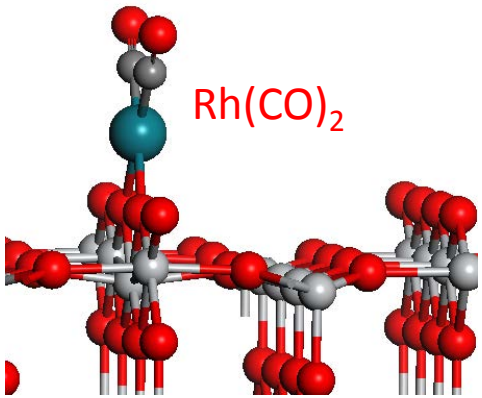
Predicting nanoparticle disintegration

$$\Delta G_{\text{disintegration}} < 0$$

Rh, Pd, or Pt nanoparticles supported on TiO_2(110) In the presence of CO

Gibbs free energy of disintegration (eV)





B. R. Goldsmith, E. D. Sanderson, R. Ouyang, and W.-X. Li, J. Phys. Chem. C 118, 9588 (2014).

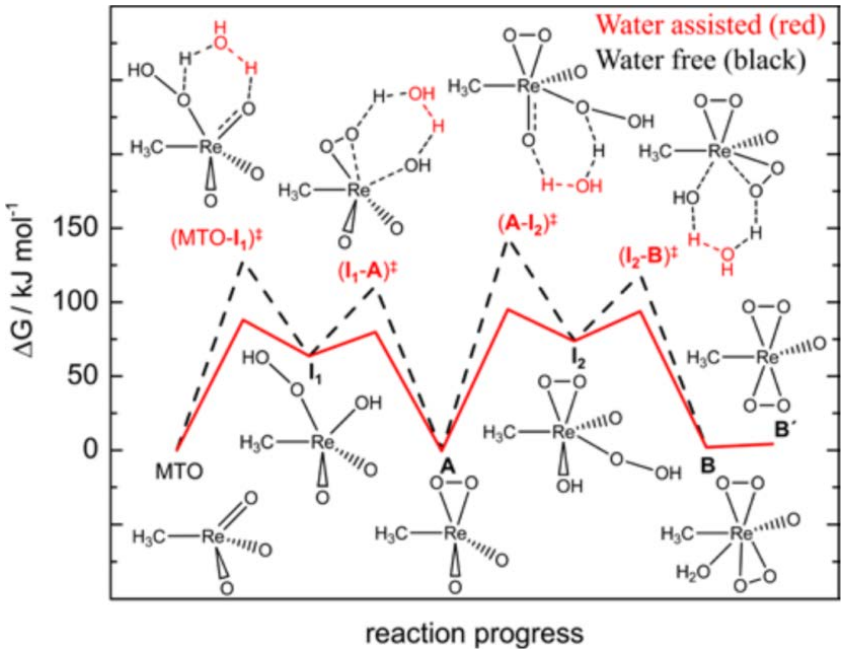
Density functional theory is a powerful method for helping to design new catalysts

Compute reaction mechanisms

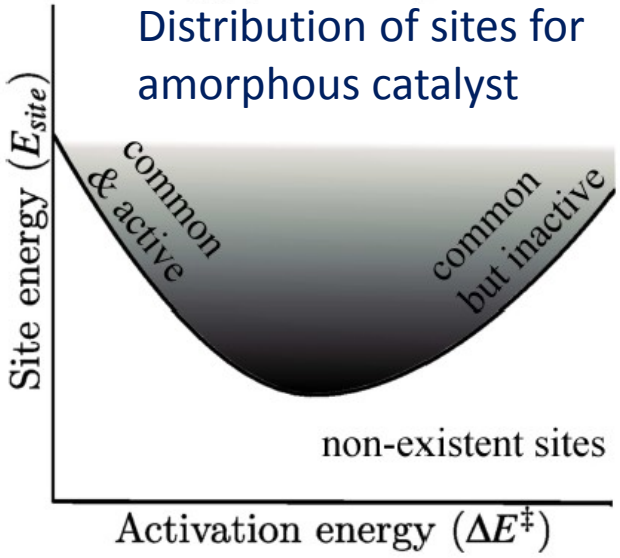
Structure-property relationships

Understand synthesis of catalysts

Reactions in solution



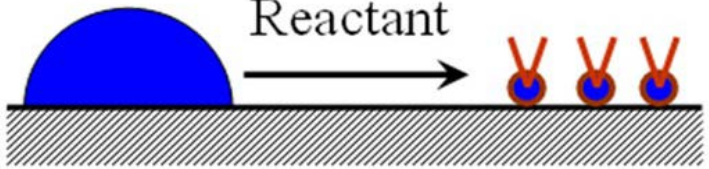
Distribution of sites for amorphous catalyst



$$min_{\mathbf{x}_p} E^{A}_{red}(\mathbf{x}_p) \quad subject\ to \quad \Delta E^{\ddagger}(\mathbf{x}_p) = \Delta E^{\ddagger}$$

Nanoparticle stability

$$\Delta G_{\text{disintegration}} < 0$$



Questions?

Acknowledgements
Prof. Baron Peters
Prof. Susannah Scott
Prof. Wei-Xue Li
Prof. Matthias Scheffler
Dr. Taeho Hwang
Colin Gardner
Evan D. Sanderson
Stefan Seritan
Chris Yuan
The Peters Group