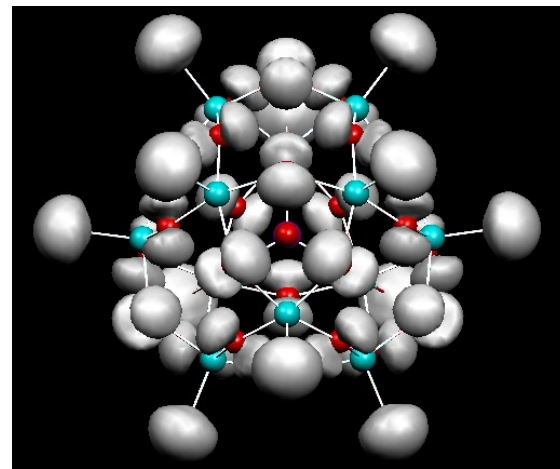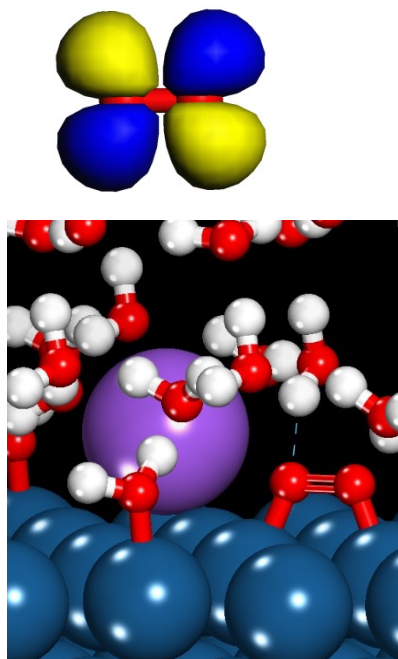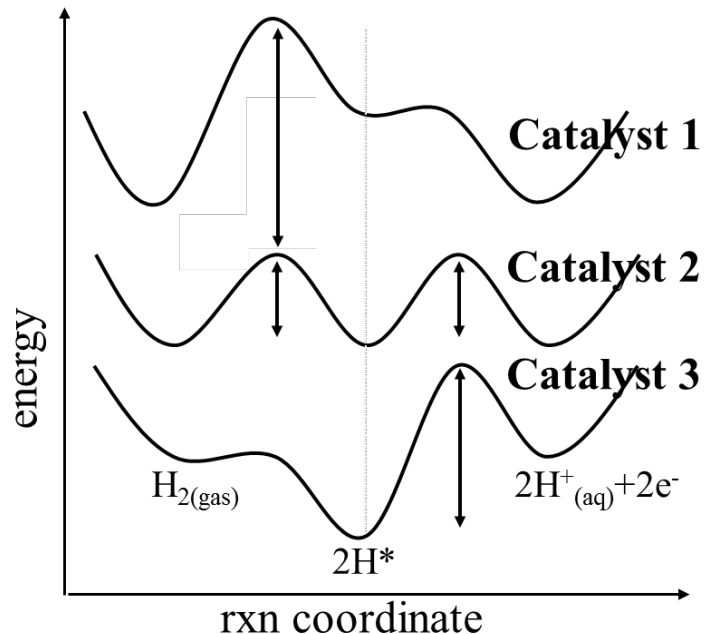# The potential energy surface for catalytic reactions: an overview of computational catalysis

Michael Janik

Department of Chemical Engineering, Pennsylvania State University
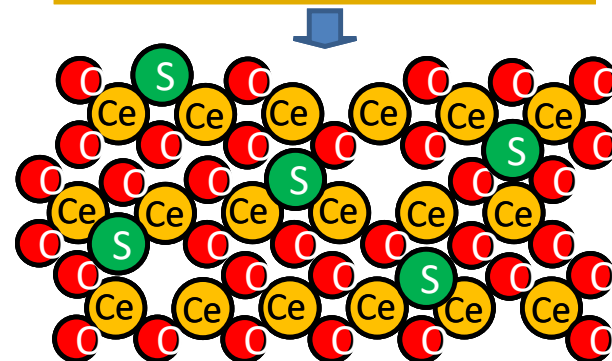
mjanik@psu.edu

Mississippi State University
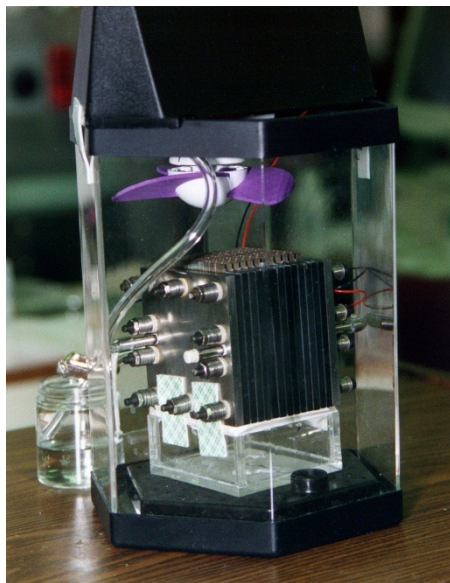**June 15, 2022**

Catalysis plays many roles in our energy future

- **Enable new energy feedstocks:**
  - biomass to fuels and chemicals
  - renewable electricity to fuels
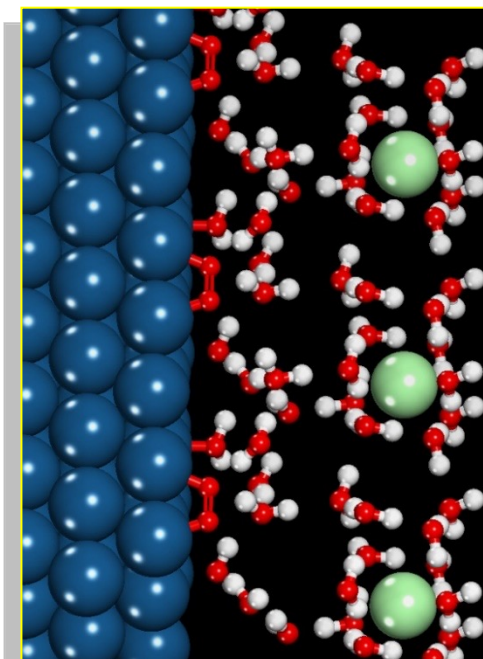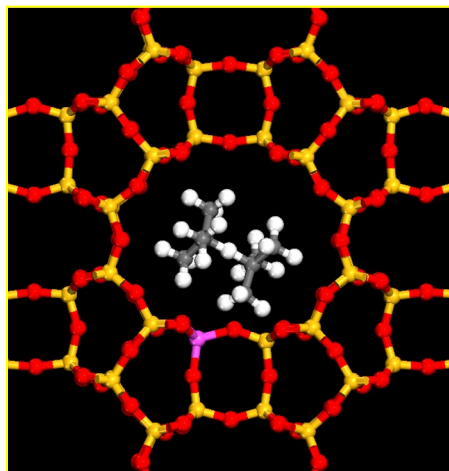 - solar fuels - photoelectrolysis

$M_xCe_{1-x}O_2$

- **Fossil fuel efficiency and diversification**
  - petroleum use efficiency
  - methane to chemicals, liquid fuels
  - coal to liquids

- **Flexible and efficient energy conversion**
  - Hydrogen production
  - Electrocatalysis in fuel cells
  - Electrolysis of CO_2 for fuel production
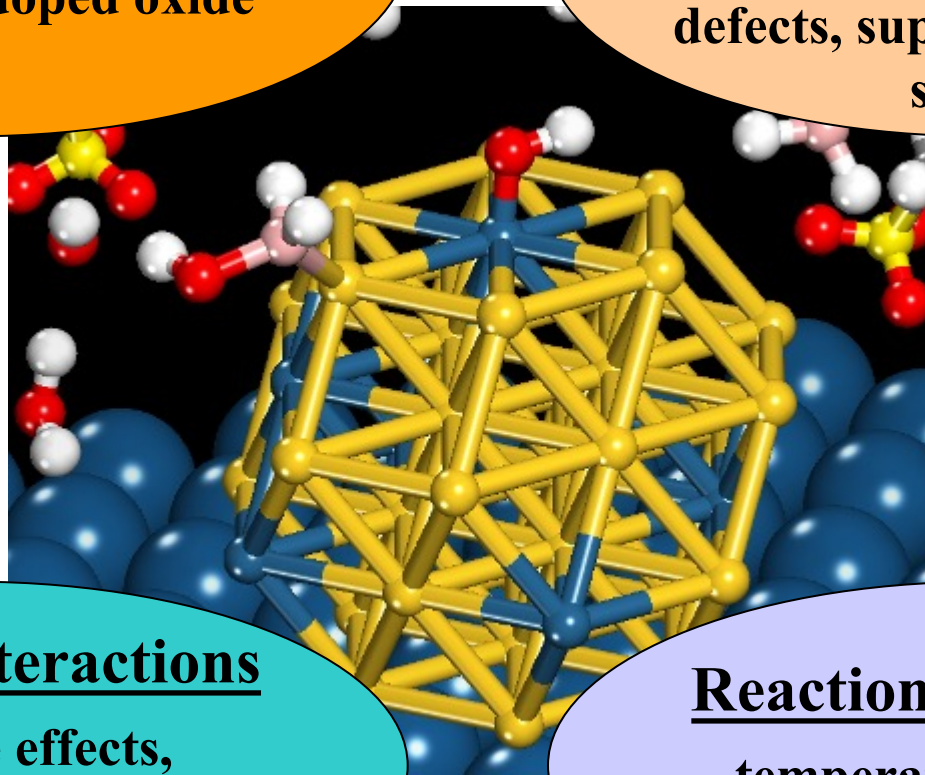
Catalyst activity and selectivity are controlled at the molecular scale:

Site composition
bimetallics, doped oxide

Structure and morphology
particle size, surface structure, defects, support interactions, stability
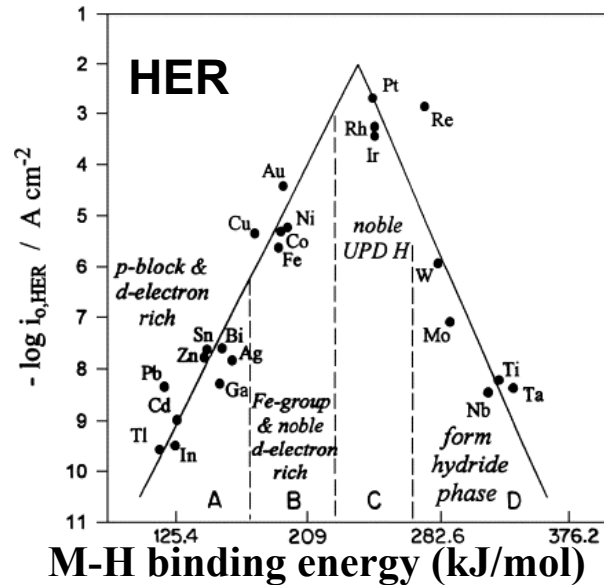
Surface interactions
coverage effects, intermolecular interactions, poisons, promoters
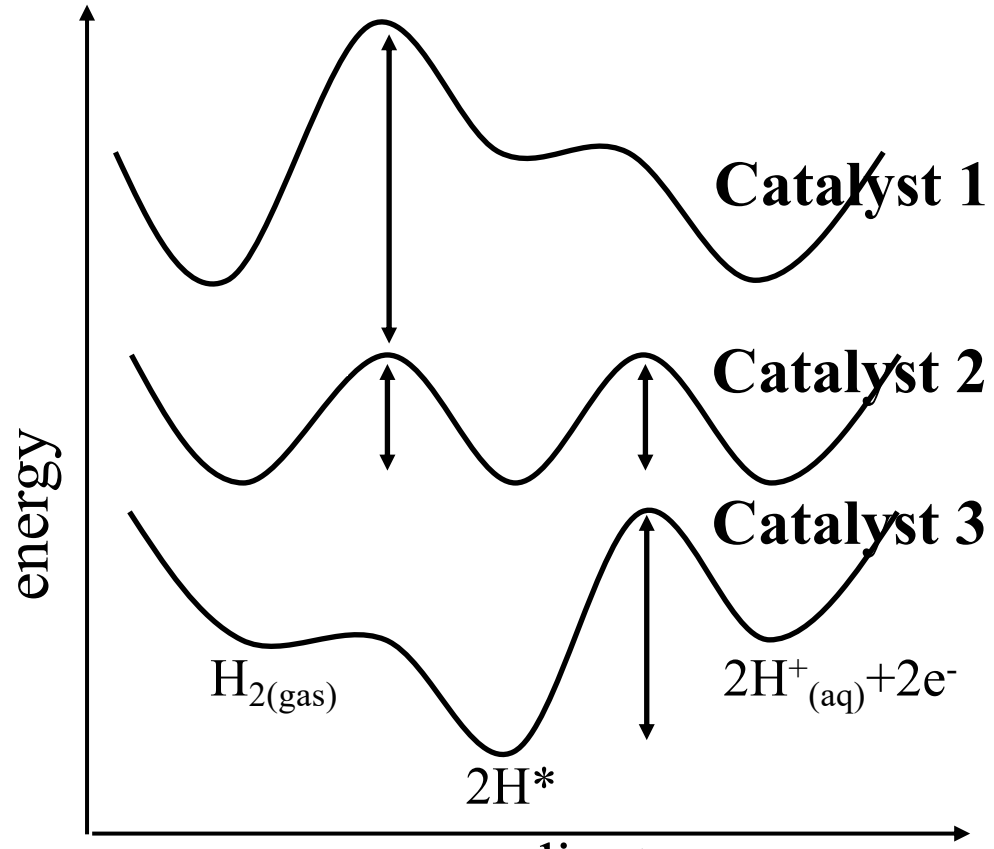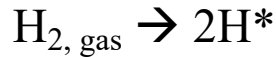
Reaction environment
temperature, pressure, solution, electric field

First-principles guided catalyst design

Explain at an atomic level what controls catalyst performance

HER

Pt
Rh
Ir
Re
Au
Cu
Ni
Co
Fe

noble UPD H

p-block & d-electron rich

W
Mo
Sn Bi
Zn Ag
Pb
Cd Ga
Tl In
Ti
Ta
Nb

Fe-group & noble d-electron rich

form hydride phase

A   B   C   D

$-\log i_{o,HER}$ / A cm^{-2}

M-H binding energy (kJ/mol)

125.4   209   282.6   376.2

S. Trasatti. *Electrochim. Acta* 39 (1994) 1739.
B. E. Conway, G. Jerkiewicz. *Solid State Ionics* 152 (2002) 93.

$H_{2, gas} \rightarrow 2H*$

energy

Catalyst 1

Catalyst 2

Catalyst 3

$H_{2(gas)}$
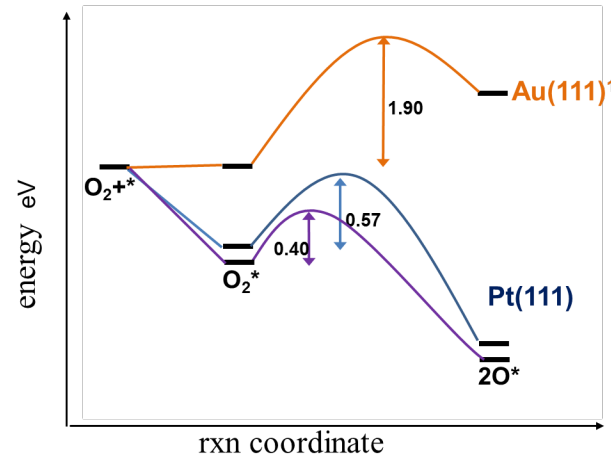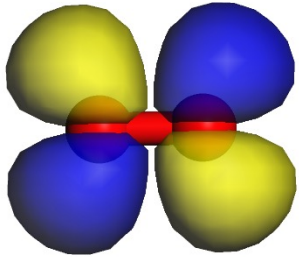
$2H*$

$2H^+_{(aq)} + 2e^-$

Catalyst Design Procedure:
- **Detailed studies on reaction steps, path, environment effects**
- **Identify key parameters (energetics) that dictate performance**
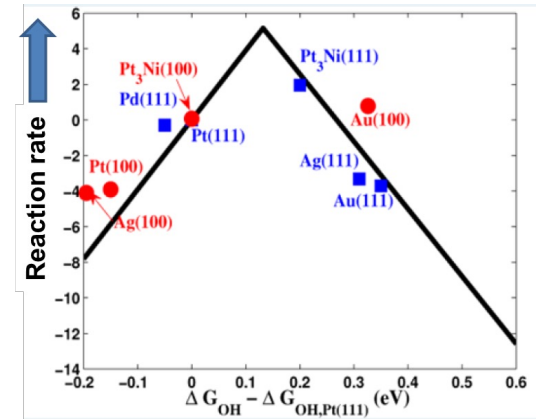- **Evaluate parameters over a design space for improved performance**

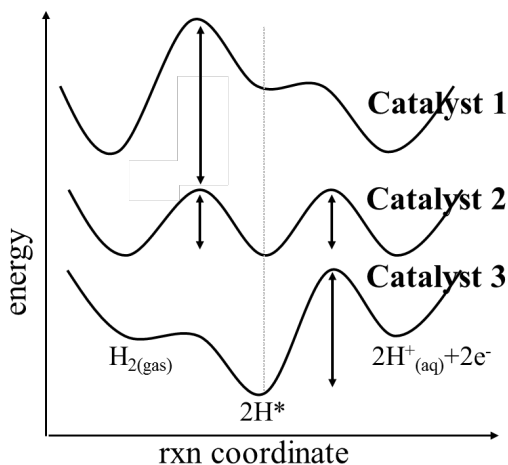# Oxidation catalysis by metals: DFT for O_2 activation

O_2 molecular orbitals

Oxidation "volcano" curves

O_2 binding to metals and activation

Oxidation using molecular oxygen on metals

How does a metal catalyst activate O_2 to participate in oxidation reactions?

What is the key energetic parameter to dictate activity to reduce O_2?

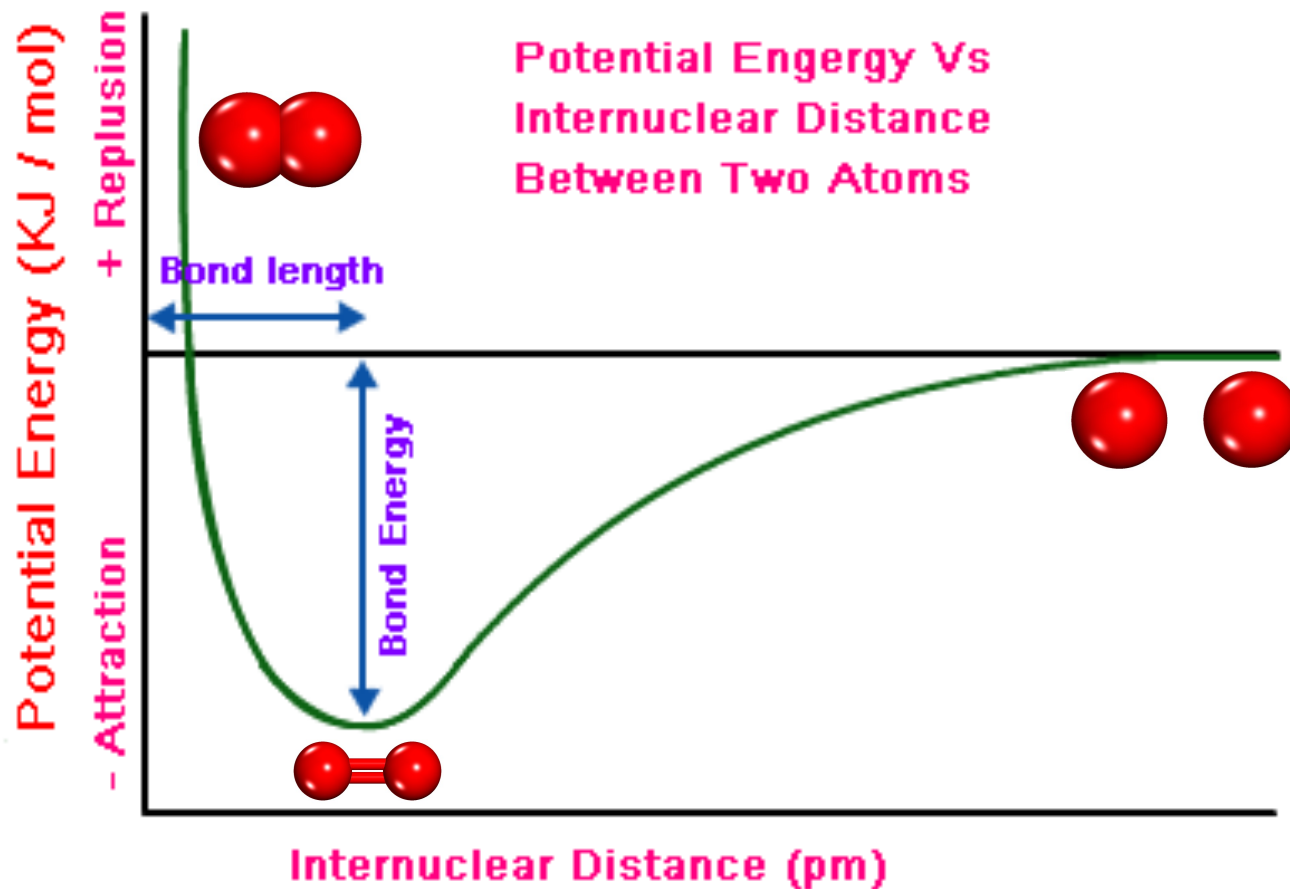**DFT calculation to first examine the electronic structure of O_2**

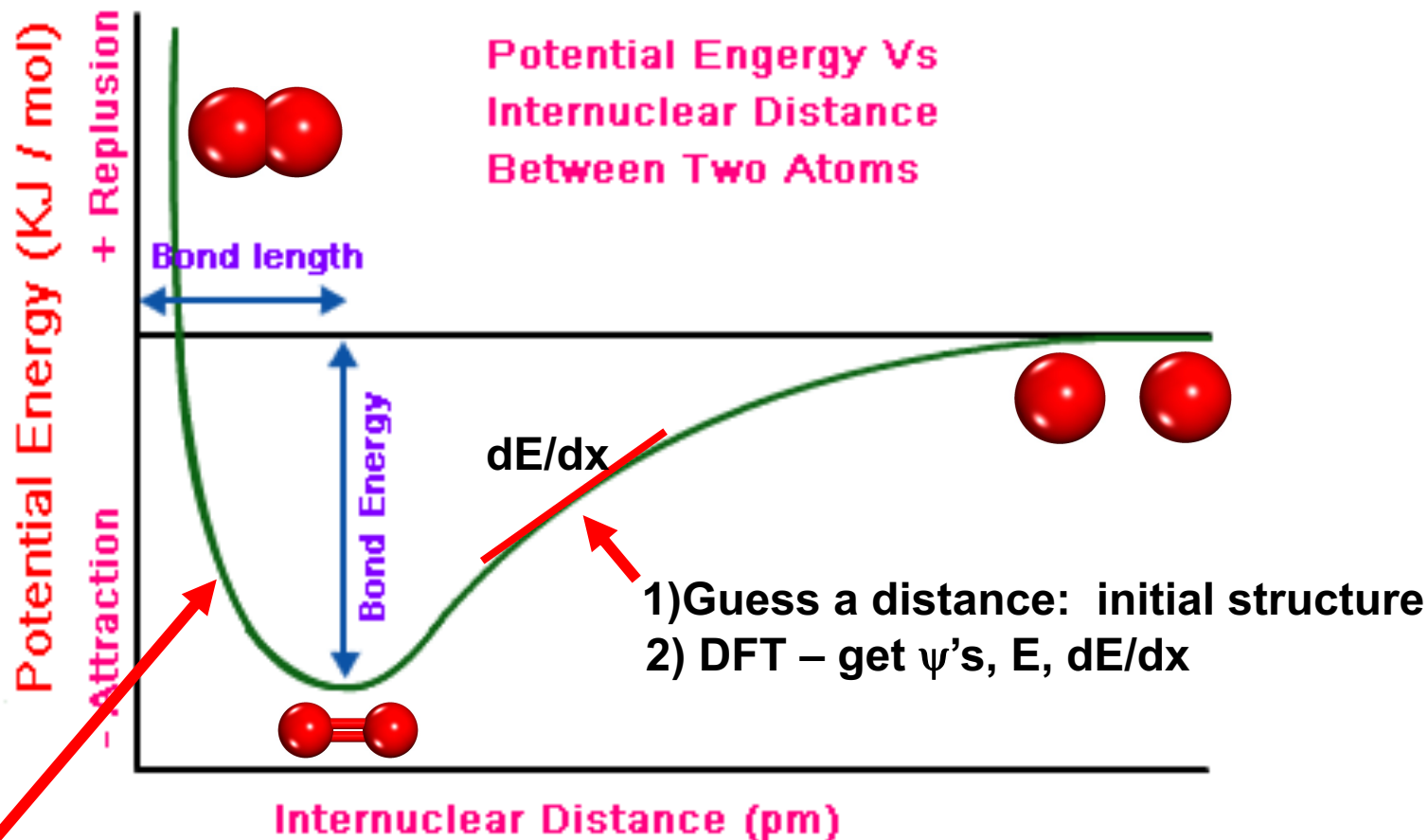1) **Build O_2**

2) **Set-up geometry optimization calculation**

3) **DFT – solve for wavefunctions (orbitals), energy, minimum energy structure**

4) **Analyze results**

Geometry optimization of O₂

Potential Engergy Vs
Internuclear Distance
Between Two Atoms

Geometry optimization of O₂

Potential Engergy Vs Internuclear Distance Between Two Atoms

dE/dx

1) Guess a distance: initial structure
2) DFT – get ψ's, E, dE/dx

3) Move to new distance
4) Repeat until dE/dx ~ 0
Gives optimal structure and final E, ψ's

Geometry optimization of O$_2$

Potential Engergy Vs Internuclear Distance Between Two Atoms

Potential Energy (KJ / mol)

+ Replusion

− Attraction

Bond length

Bond Energy

Internuclear Distance (pm)

O VASP energy = -1.84 eV

O$_2$ VASP energy = -9.823 eV
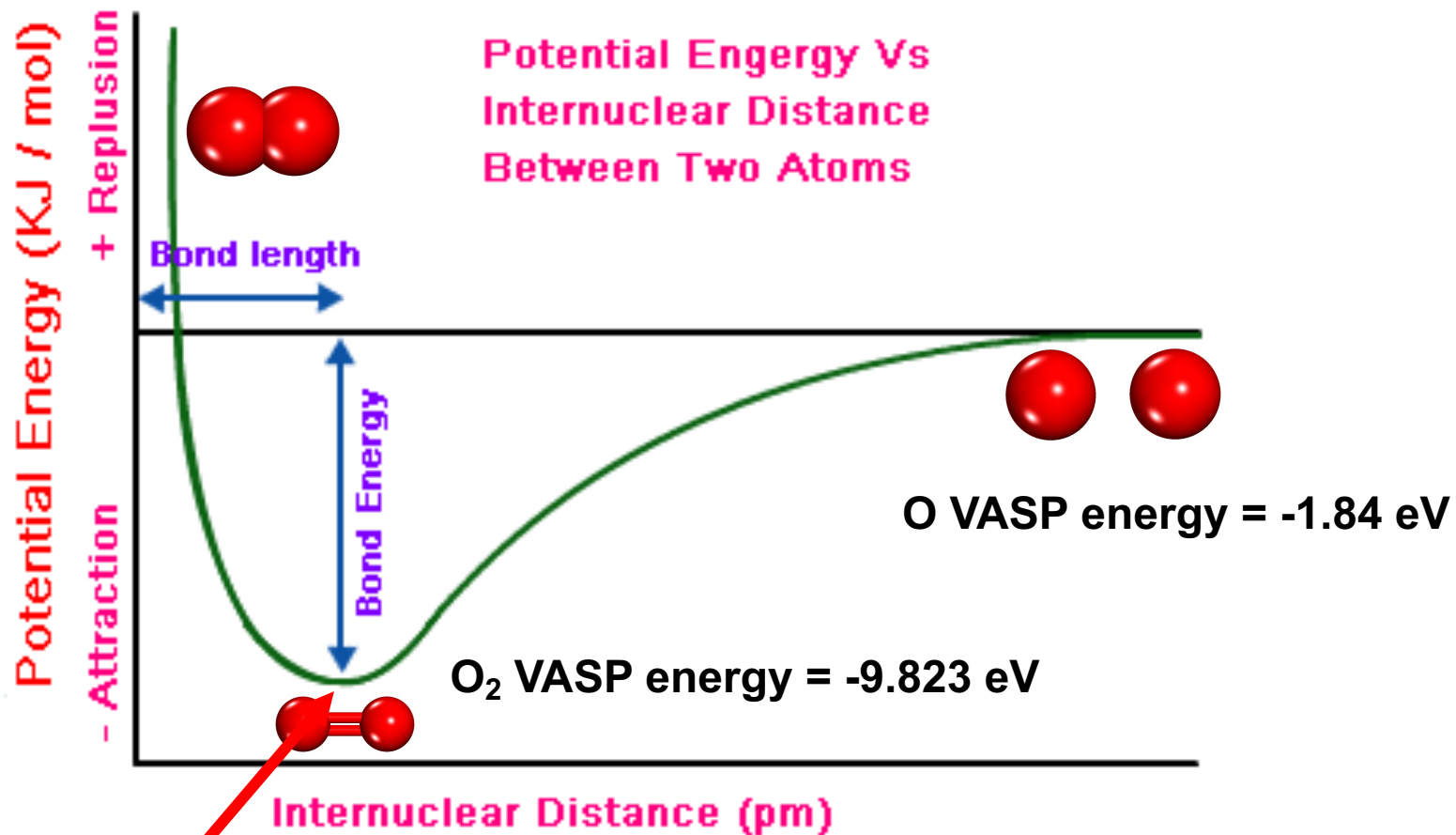
Optimal bond distance 1.23 Å

Bond energy = E(O$_2$)-2E(O)
= -6.15 eV = -593 kJ/mol

Molecular orbital diagram of O_2
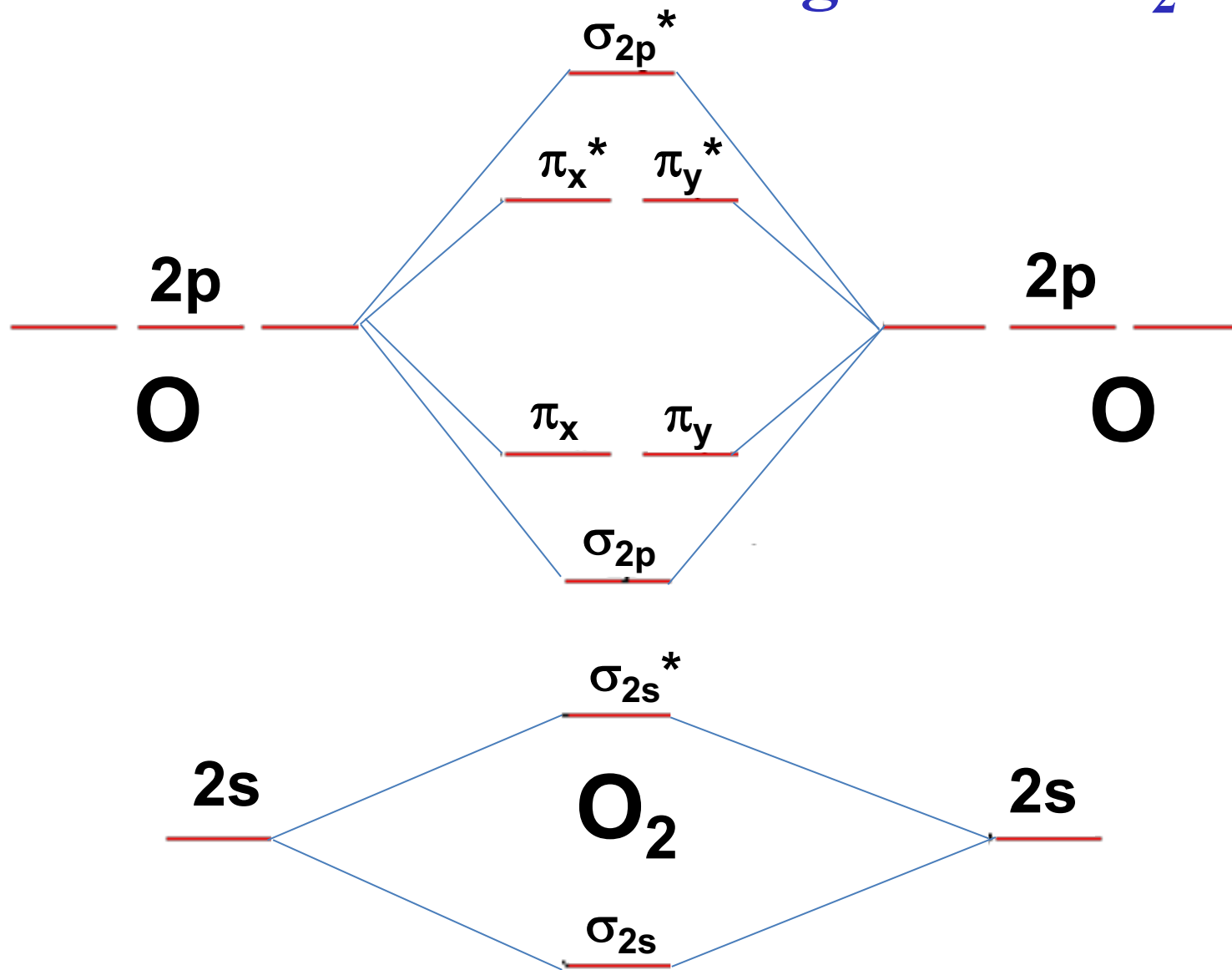
O—O bond distance 1.23 Å

O_2 energy from VASP   -9.82 eV

O energy from VASP   -1.84 eV

Bond energy

$E(O_2) - 2E(O) = -6.15$ eV $= -593$ kJ/mol

Molecular orbital diagram of O_2
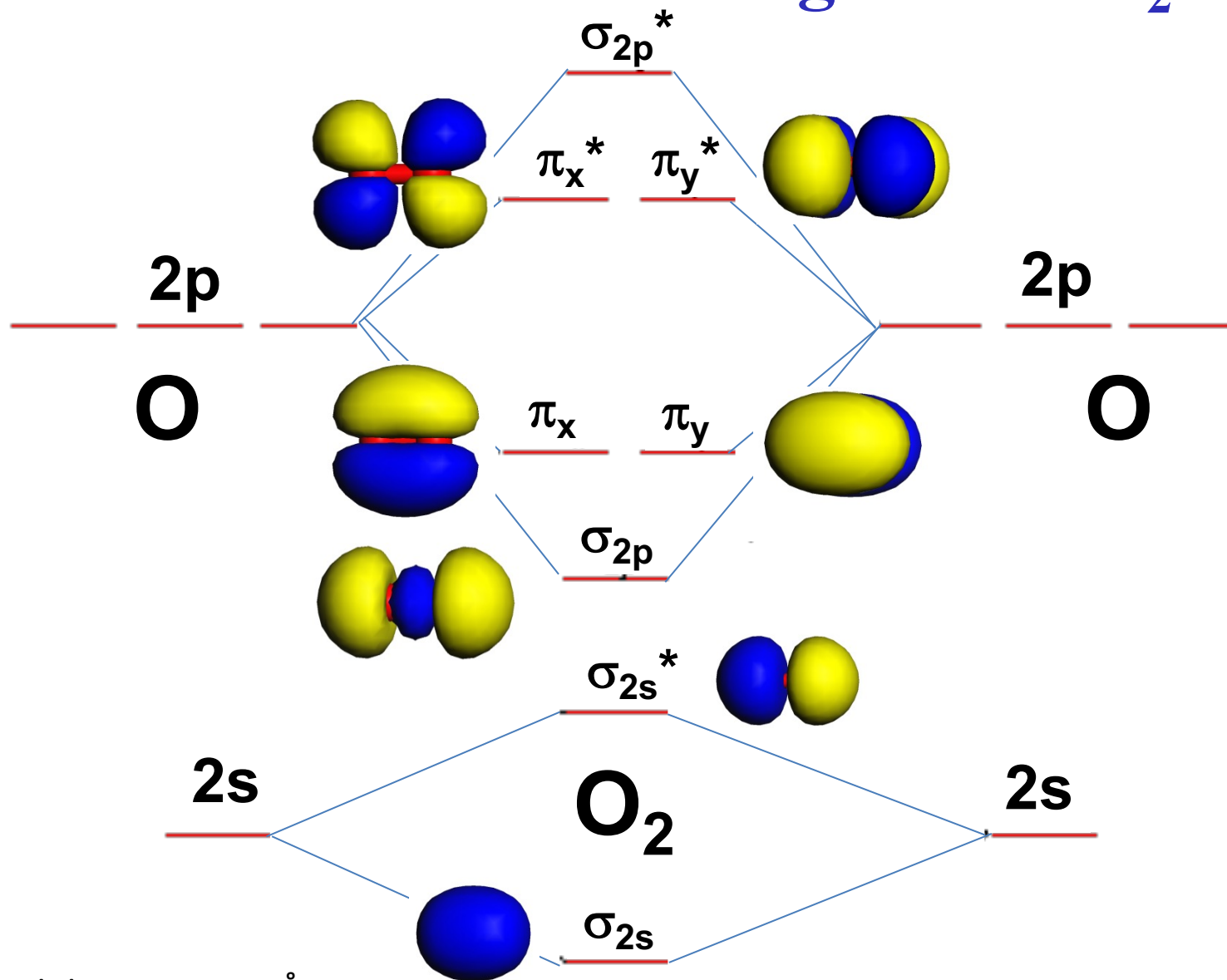
O—O bond distance 1.23 Å

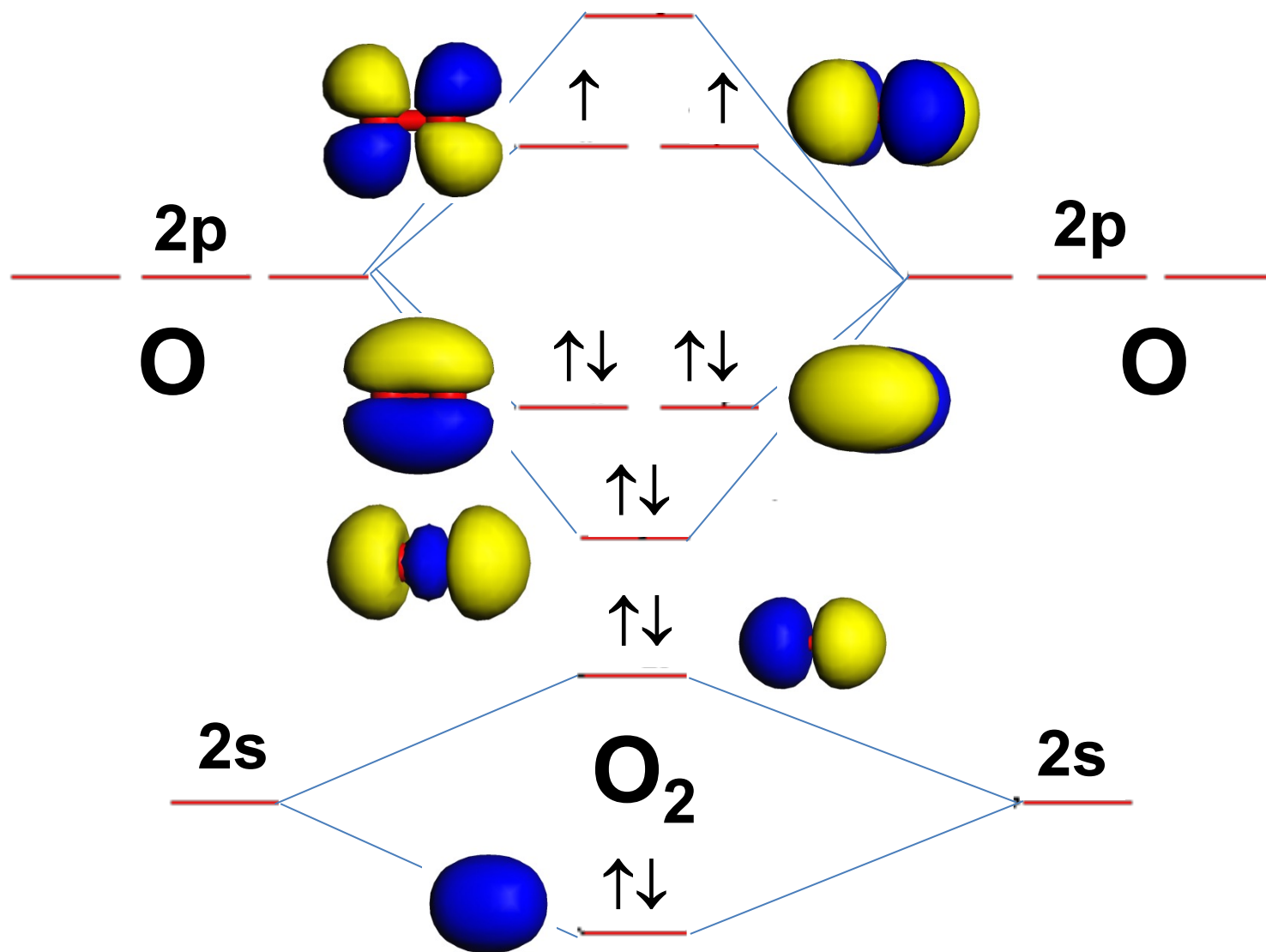O_2 energy from VASP   -9.82 eV

O energy from VASP   -1.84 eV

Bond energy

$E(O_2)-2E(O) = -6.15$ eV $= -593$ kJ/mol

Molecular orbital diagram of O_2

Ground state (lowest energy electron occupation of orbitals) is a triplet
2 unpaired electrons in π^* orbitals.

Now I want to put O_2 on a surface and calculate the energy change to adsorb it.

What DFT calculations do I need to run?

?

Now I want to put O_2 on a surface and calculate the energy change to adsorb it.

What DFT calculations do I need to run?

O2(gas) + surface → O2 on the surface

$\Delta E_{ads} = E_{O2\ on\ surface} - E_{O2\ in\ gas\ phase} - E_{surface\ with\ nothing\ on\ it}$

DFT calculations
O2 gas
Surface (*)
O2 on surface (O2*)

O2 + * → O2*

# Woody will show you how to build (cut) a surface later today, and how to put an adsorbate on that surface.

Let's take a look at O2 on a surface.
Choices – how many layers?
What is frozen?
What is my supercell size (I am showing you a 3x3 surface cell – 9 Pt atoms per layer). Surface cell size dictates "fractional coverage"

O$_2$ on metal surface – bonding is between O$_2$ π^* orbital and metal d orbitals

O$_2$ π^*
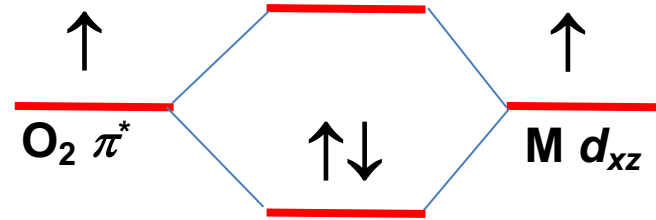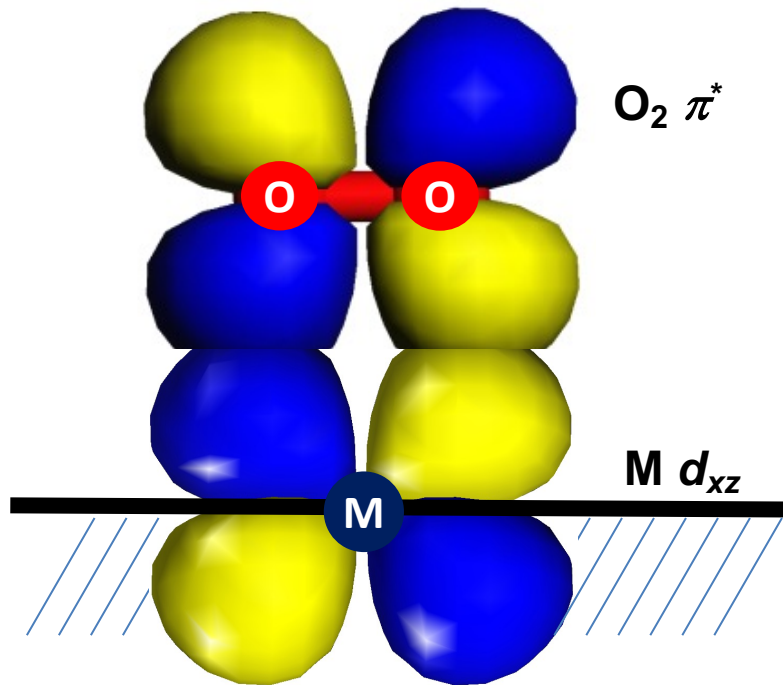
M d_{xz}

O$_2$ π^* and M d_{xz} form a bonding orbital

Occupation lowers energy – O$_2$ has an exothermic adsorption

E(O$_2$) = -9.823 eV
E(Pt(111)) = -315.201 eV
E(O$_2$ on Pt(111)) = -325.624 eV

Adsorption energy = -0.60 eV = 58 kJ/mol

Donation of e$^-$ from M d_{xz} to O$_2$ π^* orbital weakens O—O bond, lowering bond dissociation barrier

(O—O gas 1.23 Å, O—O on Pt(111) 1.37 Å)

Potential energy surface of O$_2$ activation on metals
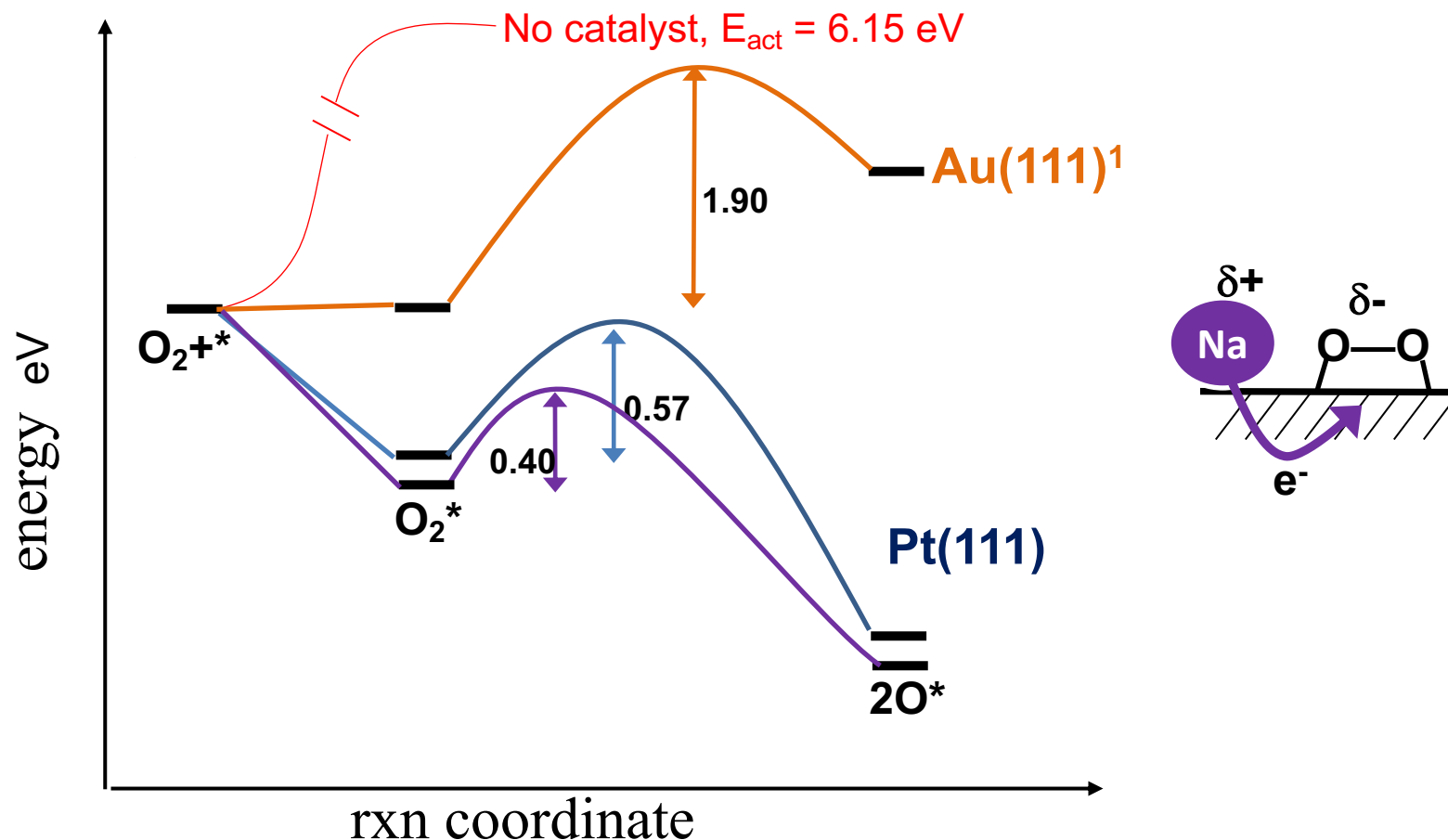
We can connect the O$_2$ dissociation barrier and resultant rate to the extent of electron donation to the O$_2$ π^* orbital

1) Au(111) data from Fajin et al. *Applied Catalysis A: General* 458 (2013) 90

What DFT calculations did I have to run to map out the "potential energy" surface on the last slide?

?

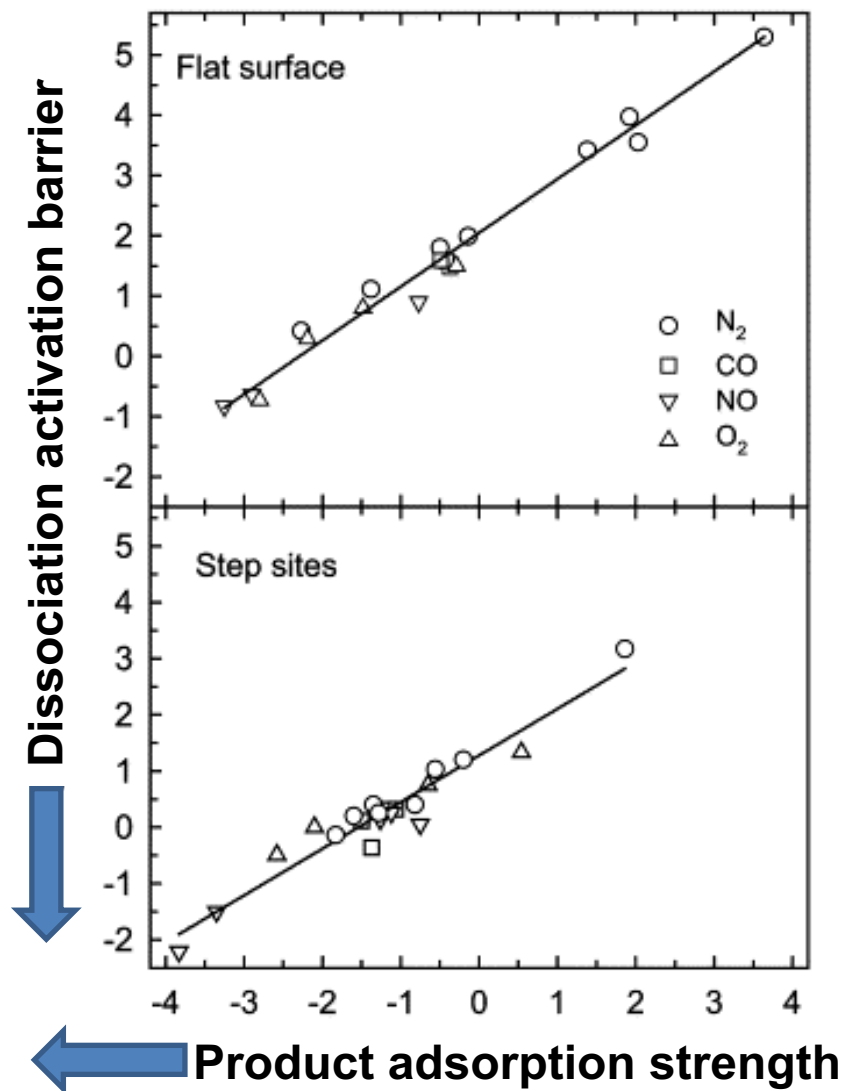# What DFT calculations did I have to run to map out the "potential energy" surface on the last slide?

O2 gas phase

*

O2*

2O* (ie, the product state for O2 molecule dissociating)

A transition state search for the highest energy state as the O-O bond stretched to become 2 O

# Faster O$_2$ activation correlates with stronger O binding

If O$_2$ activates easier (more quickly) than O binds more strongly.

Note same pattern for other diatomics (N$_2$, CO, NO)

1) **Figure from Bligaard et al., *J. Catal.* 224 (2004) 206**

Sabatier's principle: optimal rate occurs with medium binding reaction intermediate

Oxygen reduction reaction (proton oxidation reaction)

$O_2 + H_2 \rightarrow$ **O or OH intermediates** $\rightarrow H_2O$
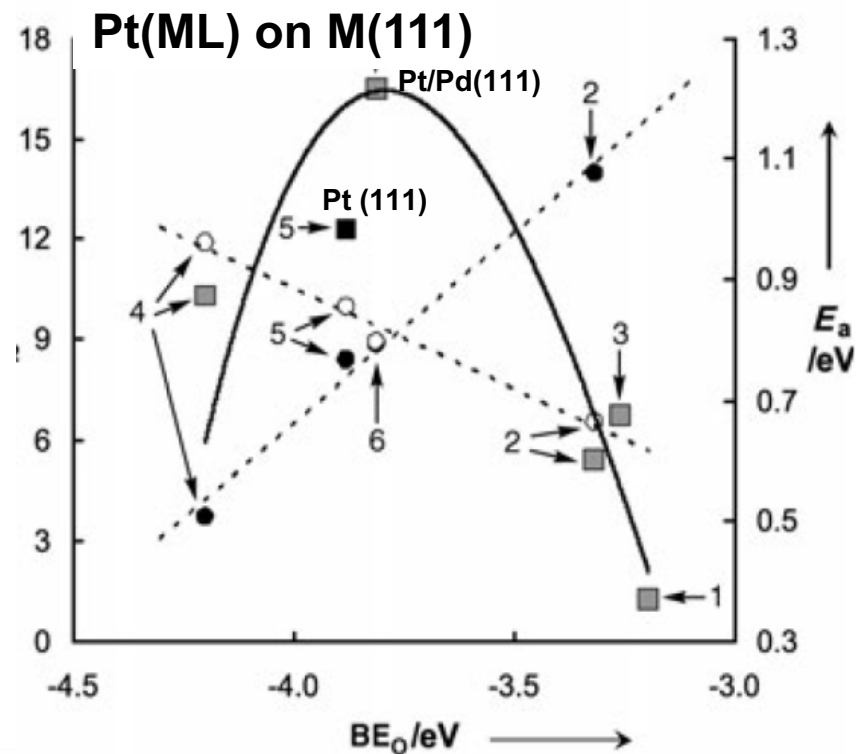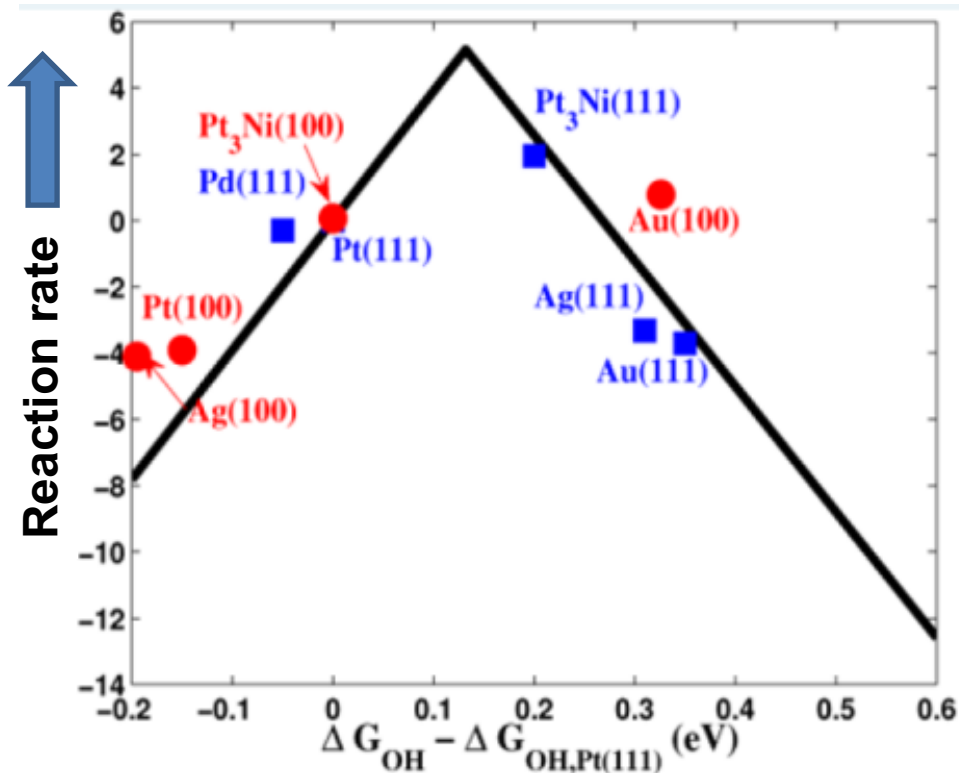
Optimal catalyst has an intermediate binding energy for oxygen

DFT can give us remarkably detailed and accurate insight

Electronic structure nature of
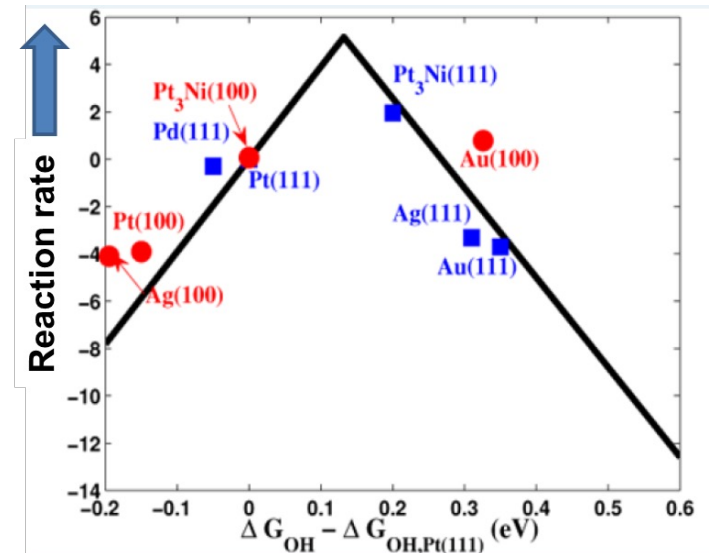
$O_2 \, \pi^*$ - Metal d interaction

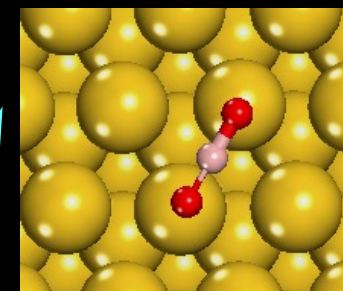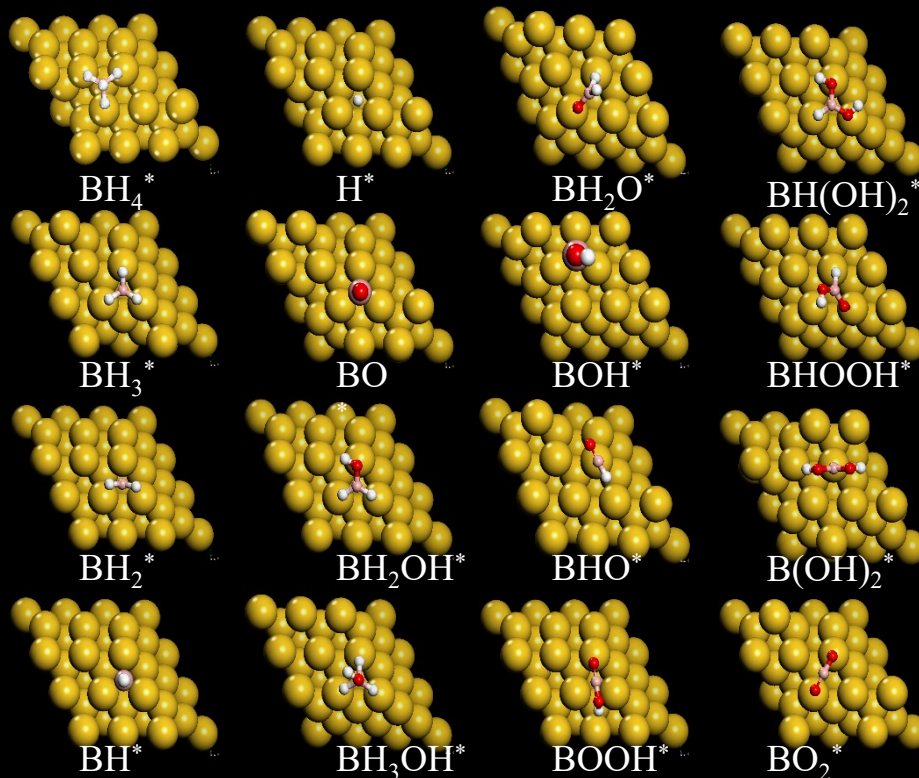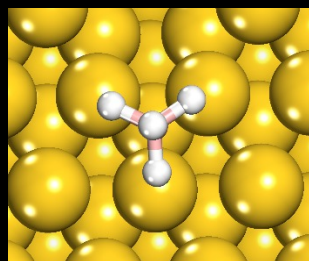
$O_2 \, \pi^*$

$M \, d_{xz}$
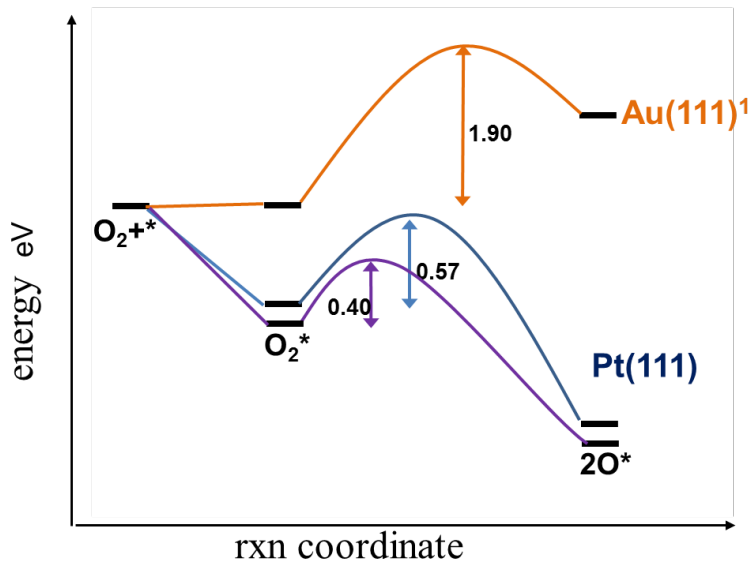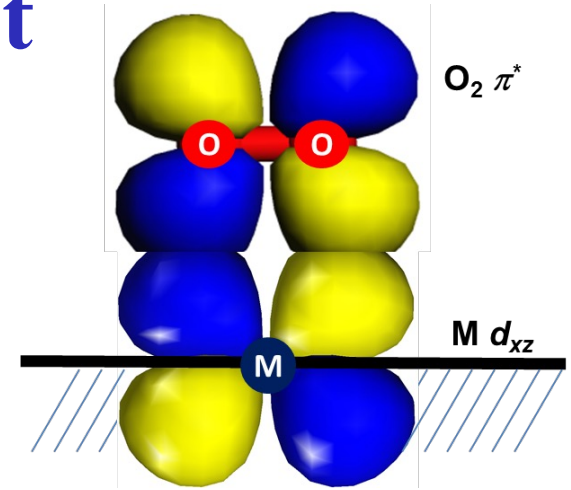
Elementary reaction energetics (activation barriers)

Correlations across reaction steps in a mechanism

Catalyst material optimization

Reaction Intermediates and Adsorption Sites

BH_4^* (+8OH$^-$)

BH_4^*

H^*

BH_2O^*

$BH(OH)_2^*$

BH_3^*

BO

BOH^*

$BHOOH^*$

BH_2^*

BH_2OH^*

BHO^*

$B(OH)_2^*$

BH^*

BH_3OH^*

$BOOH^*$

BO_2^*

BO_2^*
(+6H$_2$O+8e$^-$)

Assumption – all adsorbates can access there most stable configuration

PENNSTATE
1855

Minimum Energy Path over Au(111)