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DFT Studies of Transition Metal Catalysis

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Sandia National Laboratories

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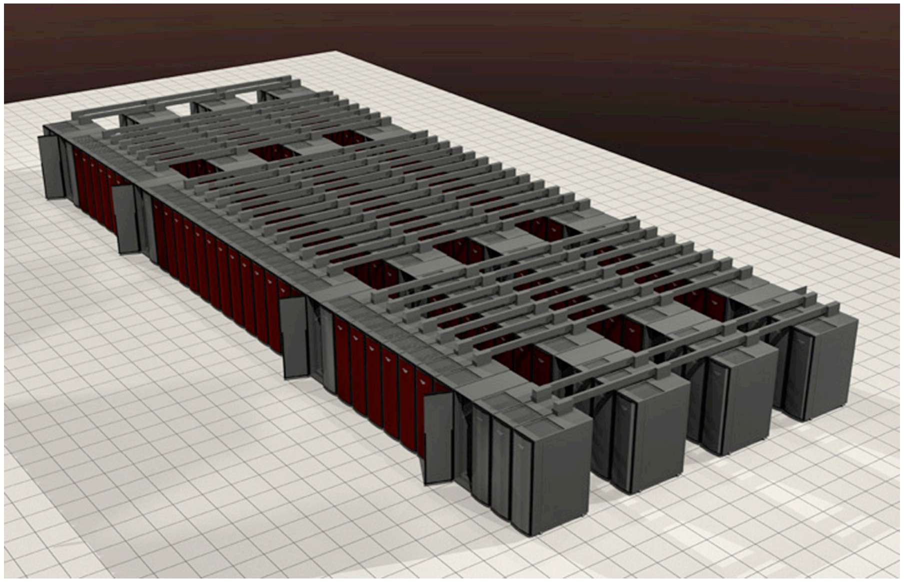
NNSA
National Nuclear Security Administration

Abstract

- My research focuses on developing computational techniques to make density functional theory calculations faster and more accurate, as well as applying these techniques to understand chemical catalysis. I will present a brief overview of my research interests, and will then describe work on the reduction of oxygen by cofacial metalloporphyrins. This study is part of the Sandia Bio Micro Fuel Cell Program, and hopes to focus on a simple system to understand aspects of oxygen reduction in biological and fuel cell systems.

Sandia Computer Science Research Institute

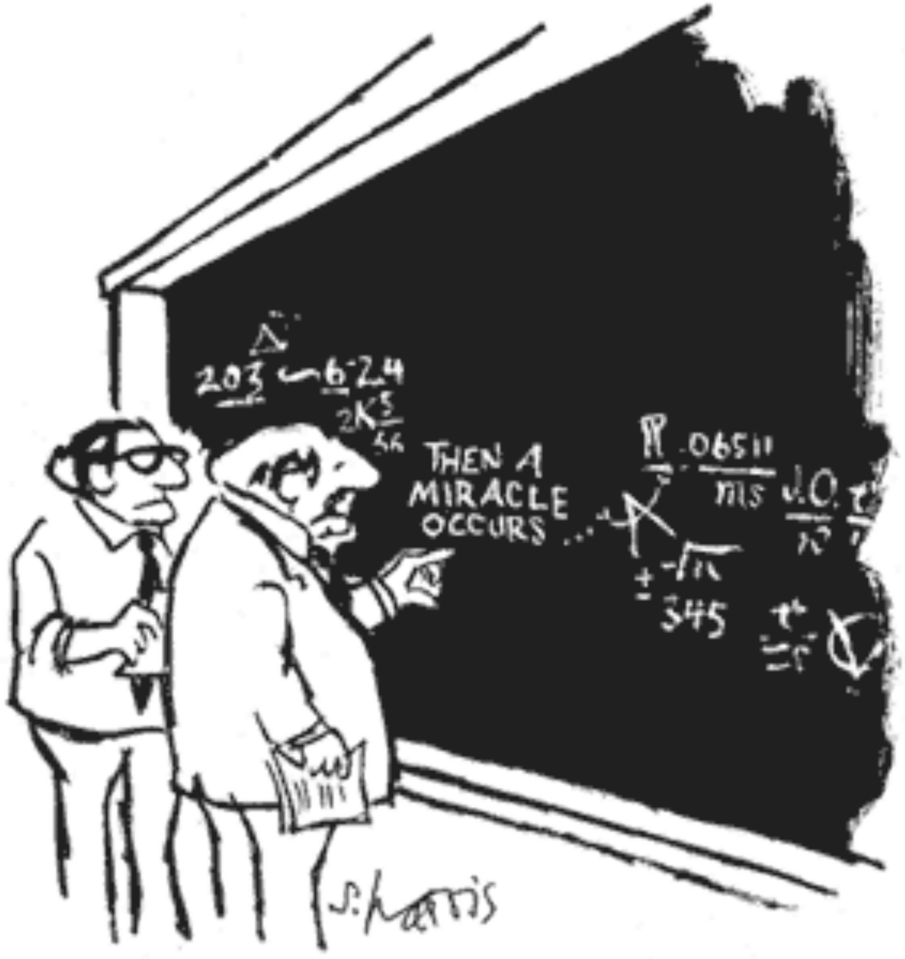


- “Outside the Fence” facility for collaborating with scientists and students
- Vertically integrated:
- Build Red Storm (currently worlds fastest), designed hardware and software
- Design applications to run in a HPC environment
- Integration of math, computer science, computational physics, chemistry, …

Computational Chemistry

- We want to be able to predict chemical behavior without the experiments
  - Enables us to test systems that haven't been synthesized, design new materials
  - Enables us to determine chemistry in regions where experiments are difficult or expensive
- Solutions to the time-independent Schrodinger equation for the electronic wave function
  - Electrons → bonding → chemistry
  - Heats of formation, reaction barriers
  - Optical properties

Density Functional Theory

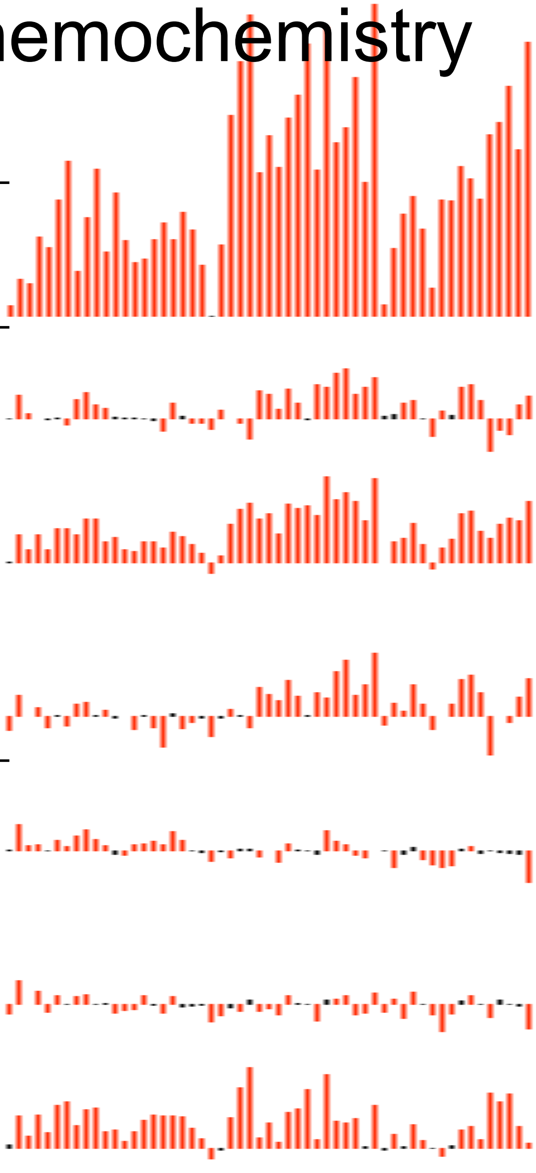


"I THINK YOU SHOULD BE MORE EXPLICIT HERE IN STEP TWO."

- Map electron density onto total energy
  - $E = F[\rho(\mathbf{r})]$
  - Differentiate to find optimal density
- Problem: we don't know the real functional, so we approximate with known systems
- Works well for chemistry (sometimes), but often not for extreme systems
- Sandia cares about extremes

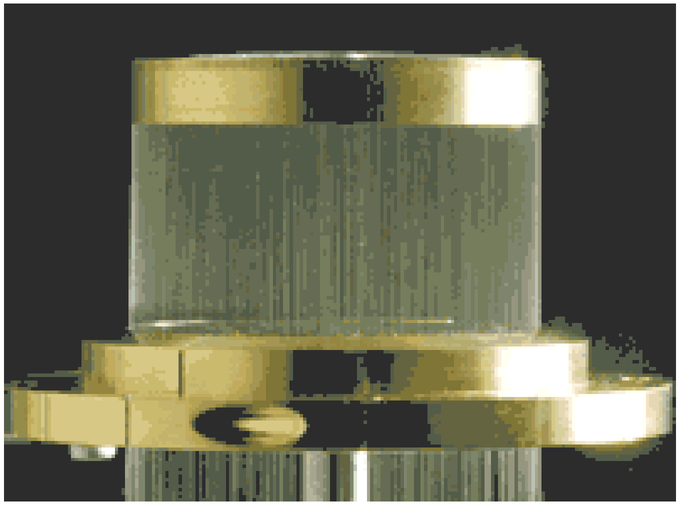
Accuracy of DFT Functionals for Themochemistry

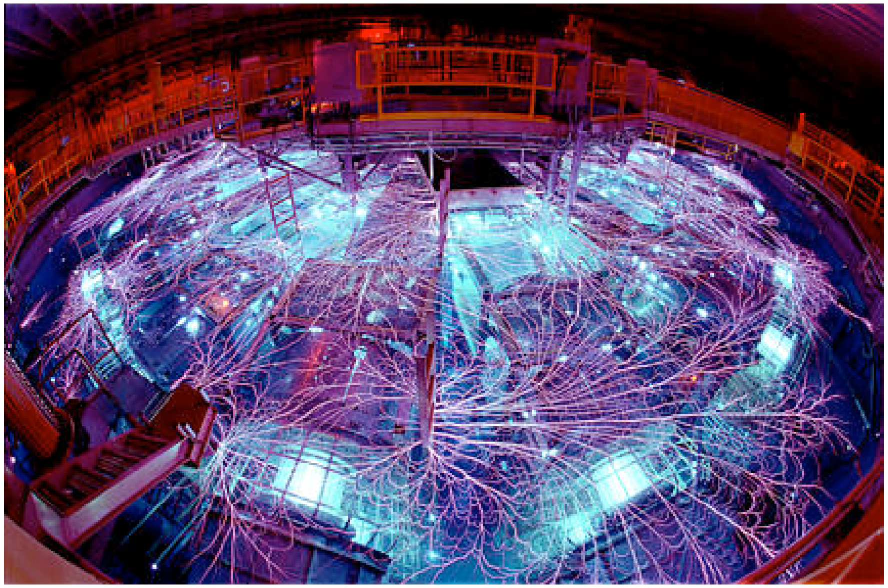
Functional	Year	Avg. Error	Max. Error
SVWN	1980	39.6	93.8
BLYP	1988	4.69	15.3
BP86	1986	10.53	26.1
BPW91	1991	5.20	19.1
B3LYP	1993	2.43	8.42
B3PW91	1993	2.59	7.4
B3P86	1993	7.84	24.6



G2 Thermochemical Test Suite.
From Curtiss *et al.*, J. Chem. Phys., 106, 1063 (1997).

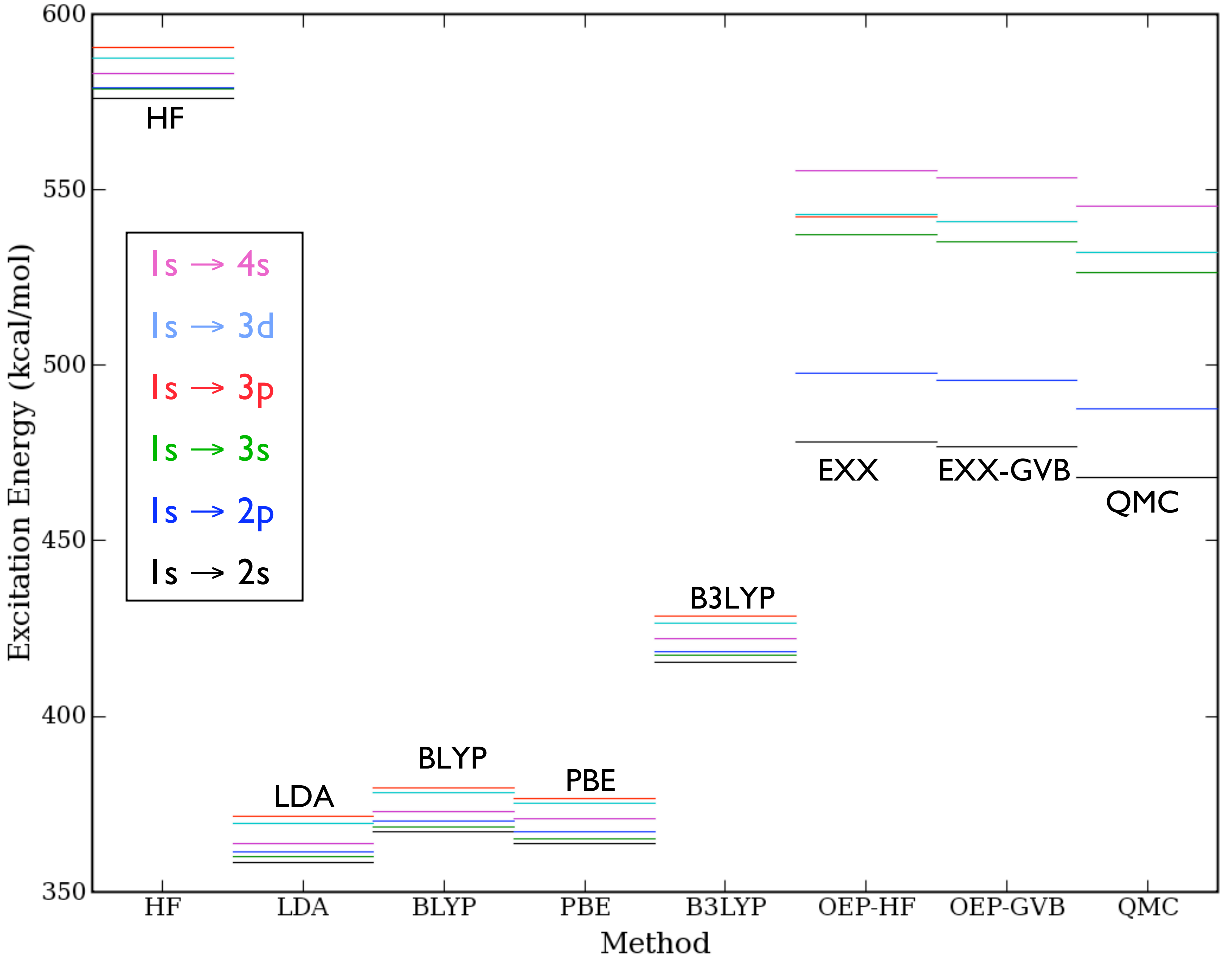
Z Machine: Materials under Shock Conditions





- Sandia Z Machine
  - Facility for studying shock and plasma physics
  - Current drives wires to crush test samples
  - Use DFT to analyze results and design new experiments
- Experimental probes are optical
  - DFT underestimates band gap
  - Leads to overestimate of optical properties

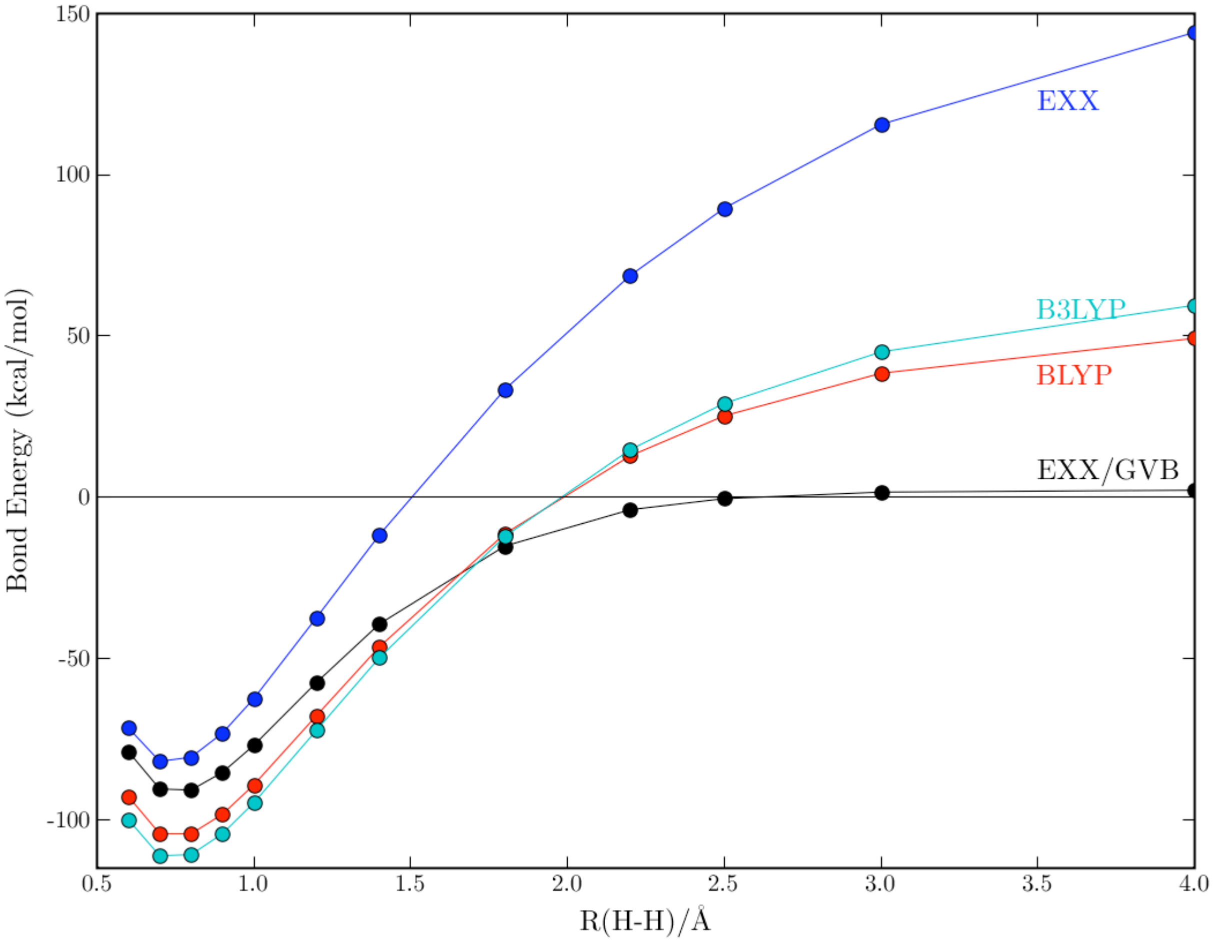
DFT with Accurate Band Gaps



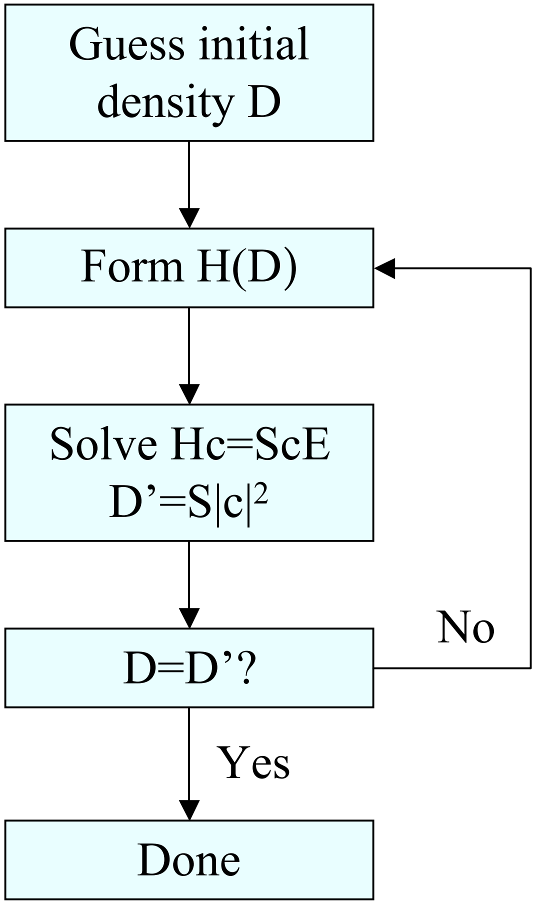
- Optimized effective potential method
- We use exact exchange will some amount of the orbital-dependent correlation to accurately reproduce excited state behavior

Dissociation of a Chemical Bond: H_2

- Putting in correlation has the added effect of making bonds dissociate correctly, fixing another well-known failing of DFT



Improved DFT Performance



Guess initial density D

Form H(D)

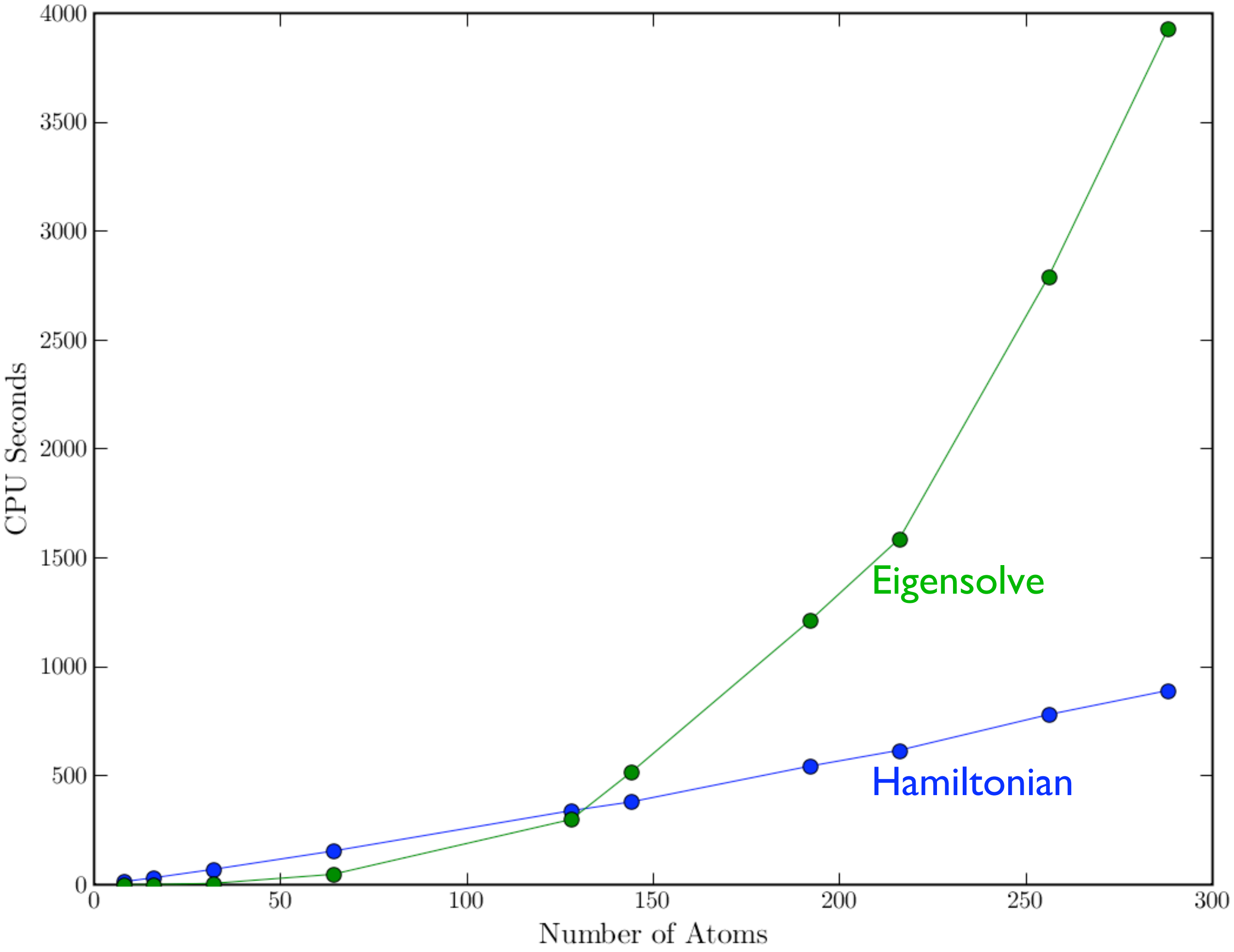
Solve Hc=ScE $D'=S|c|^2$

D=D'?

No

Yes

Done



- N^3 eigensolve prevents large simulations
- Form D from H directly without eigensolve

Modeling Catalyst Behavior

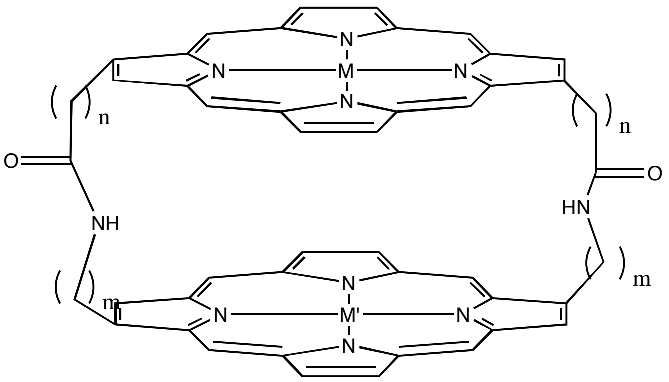
Sandia's Bio Micro Fuel Cell Program

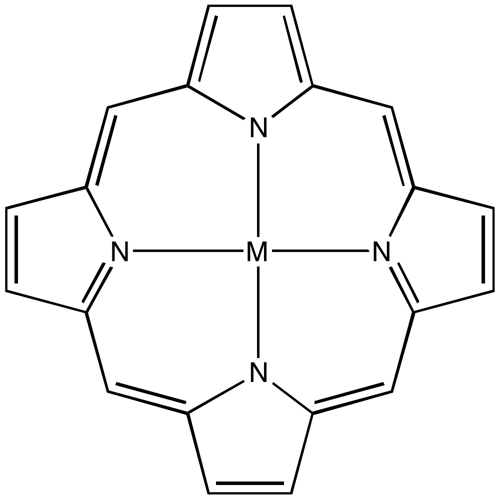
- Project at Sandia to use **glucose** instead of hydrogen or methanol to power PEM fuel cell.
- Harvest glucose from living plants.
- Use enzymes (glucose oxidase and laccase) instead of Pt electrodes for catalysis
- *Bioinspired* catalysis: Can we extract a small portion of an enzyme and use this as an electrocatalyst?
- If so, how much/what to extract?

Laccase and Oxygen Reduction

- Goal: Improve the oxygen reduction catalyst in the biofuel cell.
  - Reduce amount of precious metals
  - Reduce overpotential and poisoning
- Laccase and Cyctochrome C Oxidase both reduce oxygen
  - 4 e-: $O_2 \rightarrow 2\ H_2O$ (fungal)
  - 2 e-: $O_2 \rightarrow H_2O_2$ (tree)
- Use modeling to understand how enzymes select between 2e and 4e pathways to build the preference for 4e processes into our catalysts

Anson-Collman Face-to-Face Porphyrins





- Cofacial porphyrins with varying spacing
- Spacing changed preference for 2e vs 4e oxygen reduction
  - Co_2FTF_4 (n=m=1, M=M’=Co) best for 4e reduction
  - Co_2FTF_3 (0,1), Co2FTF5 (1,2) show only 2e reductions
  - Monoporphyrin had high activity for 2e process, but low lifetime
- Can we use DFT to understand this chemistry?
- If we understand it, can we generalize to enzymes?

Methods

- Use high quality computational modeling to understand difference between 4e and 2e reductions in FTF4
- Quantum chemistry - Density functional theory
  - Hybrid gradient-corrected functional (B3LYP)
  - Gaussian basis set (6-31G**, LACVP on Co)
- Poisson-Boltzmann solvation method to represent water
- Jaguar program suite

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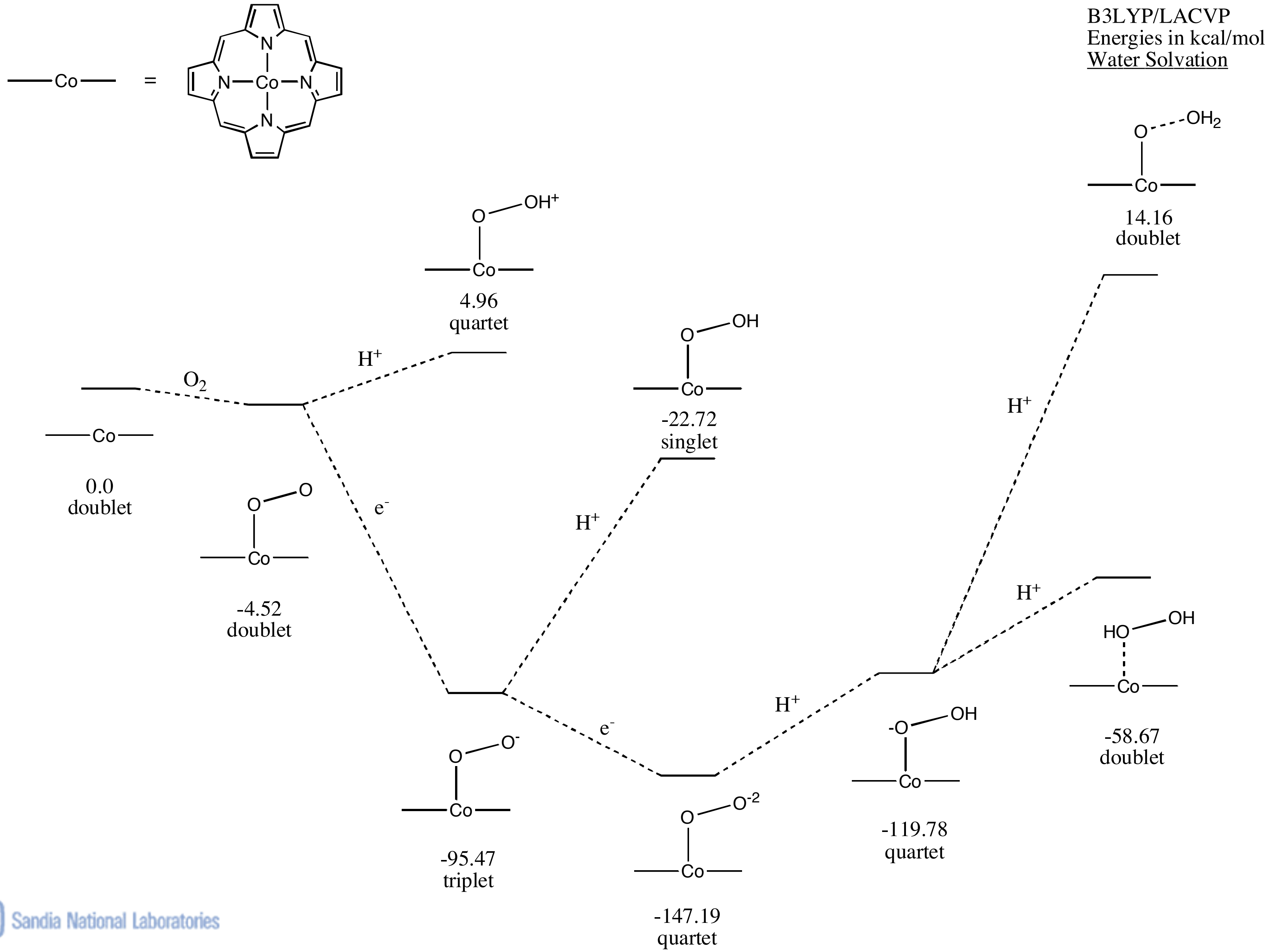
Monoporphyrin Chemistry (Solution)

B3LYP/LACVP
Energies in kcal/mol
Water Solvation

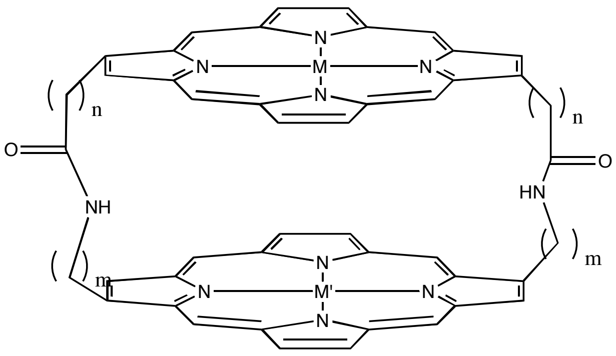


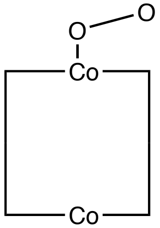
Monoporphyrin Results

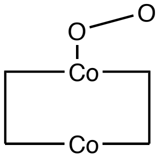
- Correctly conclude that 2e process results from monoporphyrin
- Experimental results shows that lifetime of monoporphyrin is very short
  - Can we look at a potentially caustic intermediate and show that it can dissociate?
  - Maybe HOOH is caustic enough…
- Don't currently know how to evaluate the cost of H^+/e^- in computing the enthalpy of formation
  - Currently approximate:
    - $\Delta H_f(e^-) = 0$ Open circuit voltage
    - $\Delta H_f(H_2) = 0$ Neutral pH
  - Need to use voltage, pH to adjust these values
    - Nice to be able to compute critical voltage, pH
    - $H_2 \rightarrow 2\ H^+ + 2\ e^-$

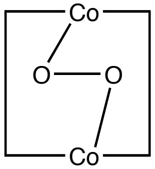
Ways to Bind O_2 to FTFs

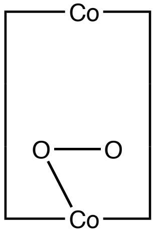
- *Outside* binding should lead to chemistry similar to the monoporphyrins
- *Inside* binding could lead to different chemistry
- The rings in *close FTFs* are too close to allow inside binding
- The rings in *far FTFs* are too far away to allow inside binding
- There may be an ideal spacing that allows good inside binding. The fact that FTF4 shows markedly different chemistry suggests that this may be that ideal distance



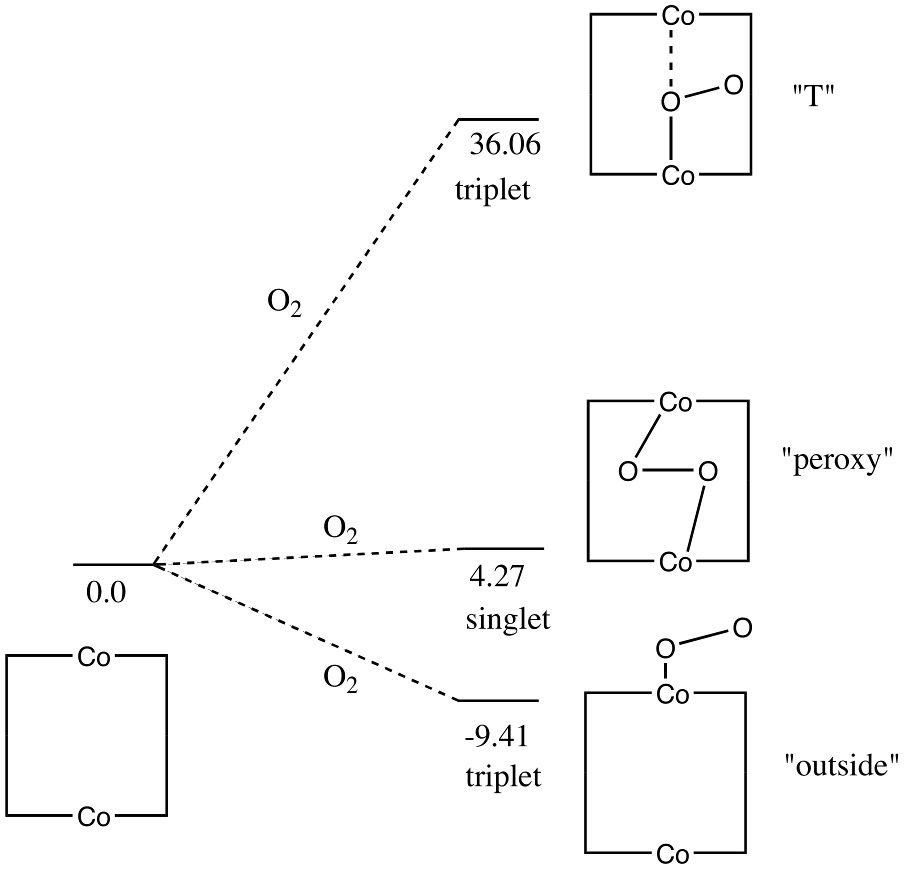








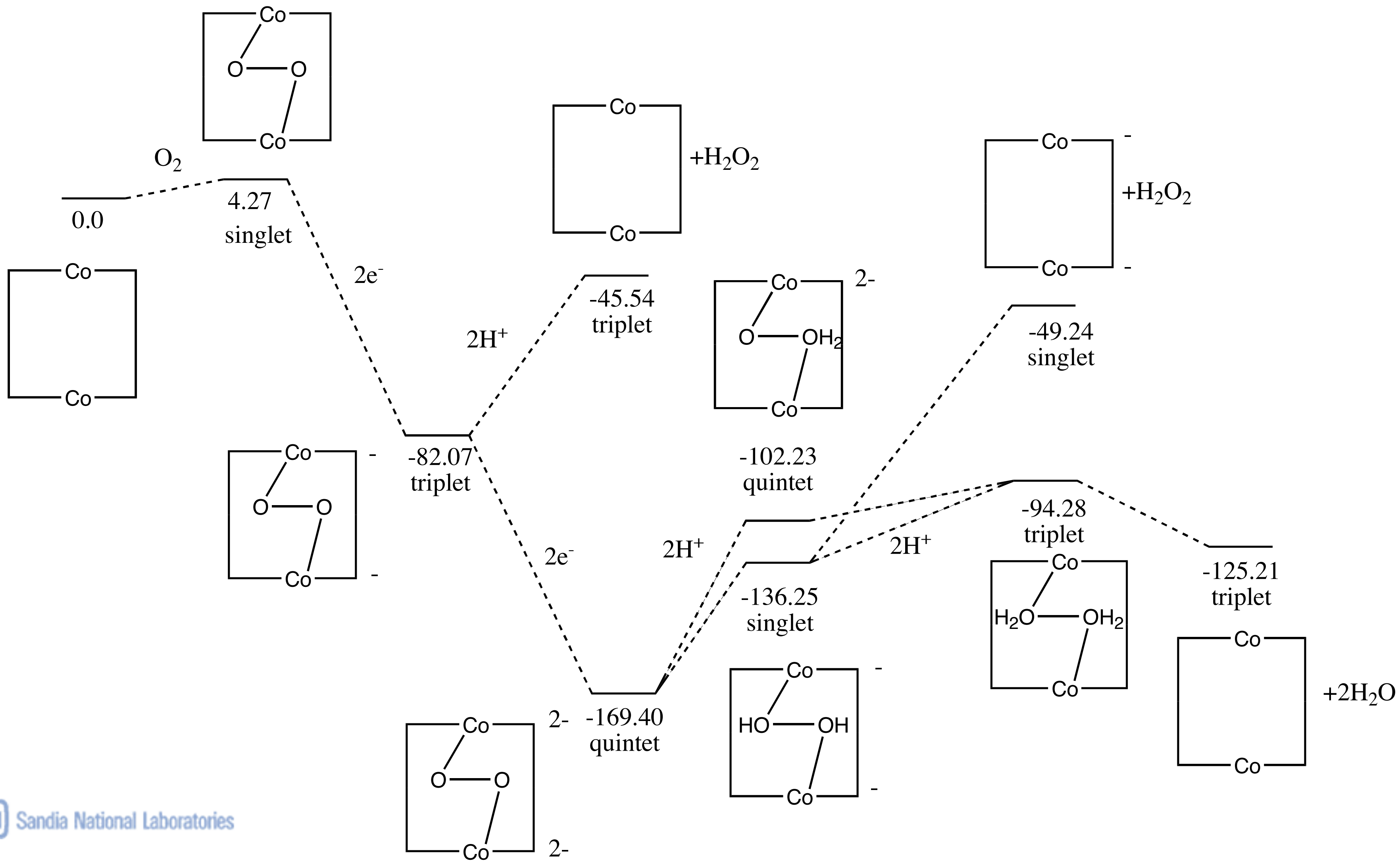
FTF4 O_2 Binding



B3LYP/LACVP
Water Solvent
Energy in kcal/mol

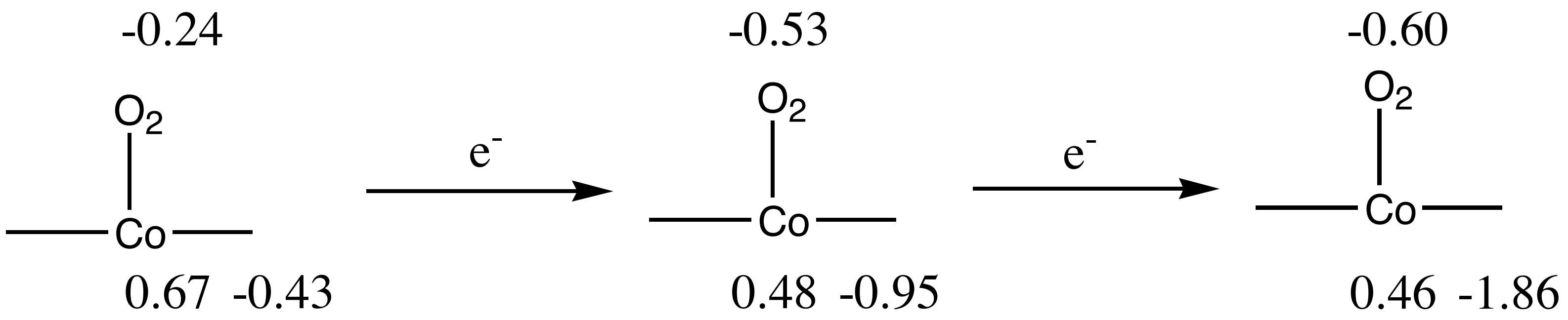
FTF4 O_2 Reductions

B3LYP/LACVP
Water Solvent
Energy in kcal/mol



Conclusions: Why Porphyrins Work

- Porphyrins can store charge without affecting substrate chemistry



- FTF4 can complex O_2 throughout reduction to keep H_2O_2 from dissociating after 2e reduction