

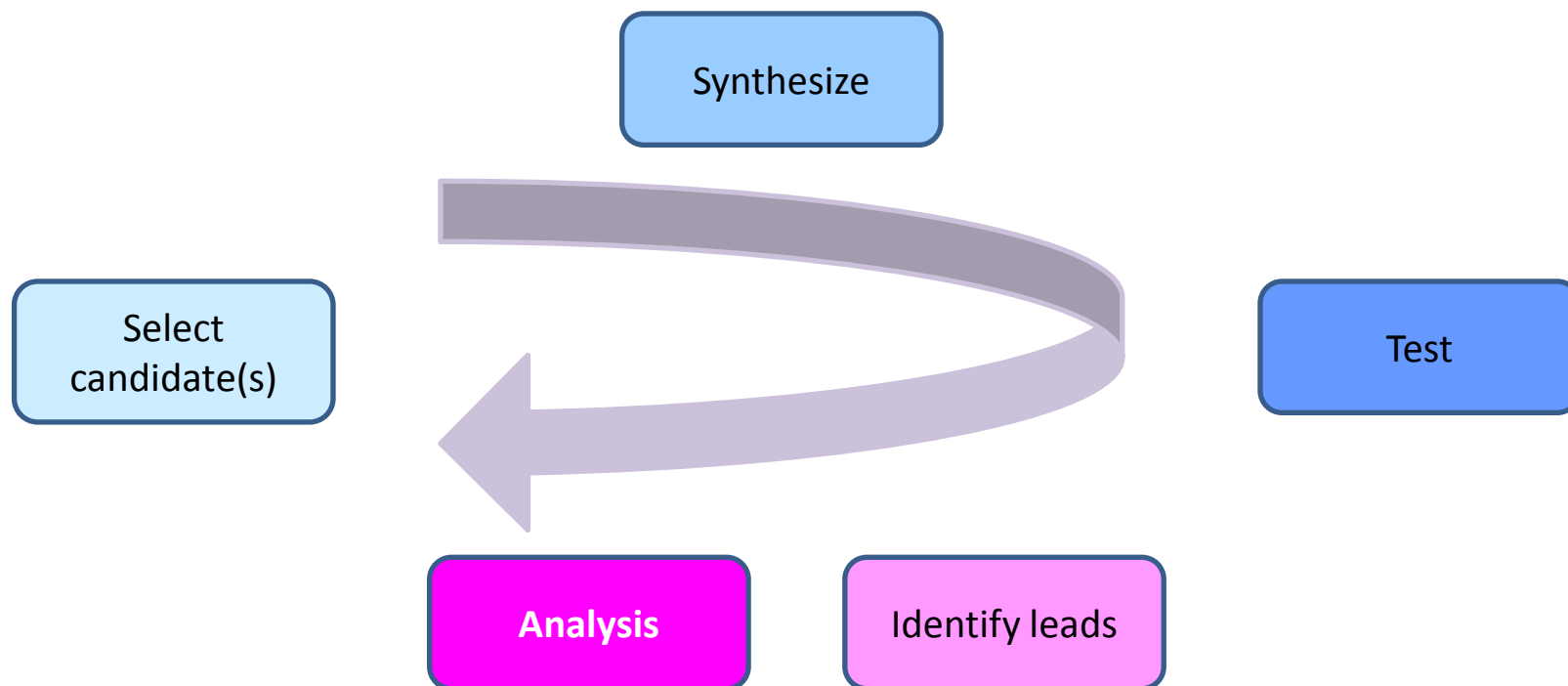
# Materials Science Applications of HPC

George Fitzgerald, Ph.D.  
Accelrys, Inc.

- Need for competitive products, e.g.
  - Lightweight alloys
  - Energy efficiency – batteries, fuel cells, biofuels
  - Pharmaceuticals
  - Cheaper chemical manufacturing
- Increasing regulation and environmental issues
- Raw Material Costs – Oil, Natural Gas, Copper
- Cost of discovering and producing products

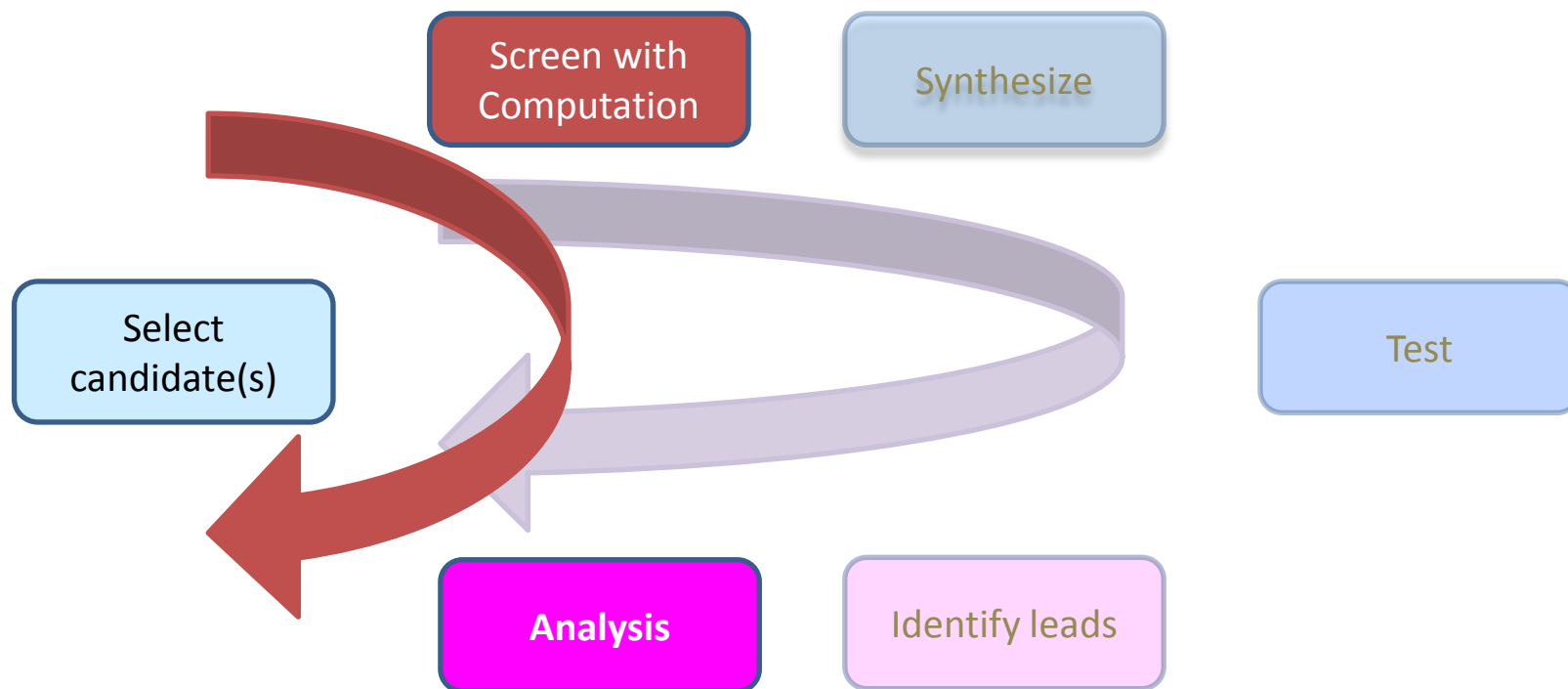
# Why Use Modeling?

- Typical R&D workflow
- Each iteration can take days or months and cost \$\$

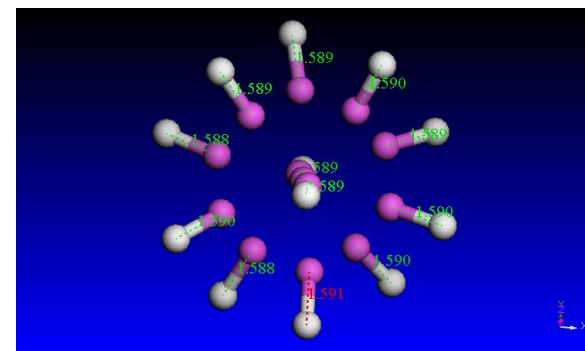
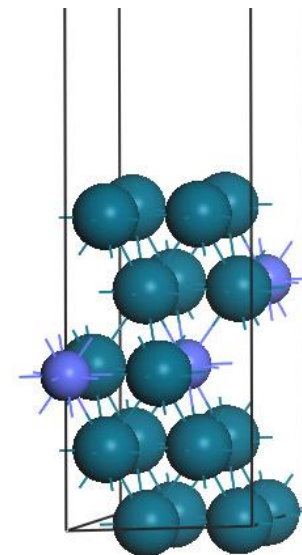


# Why Use Modeling?

- Typical R&D workflow with modeling
- Each iteration takes minutes or days

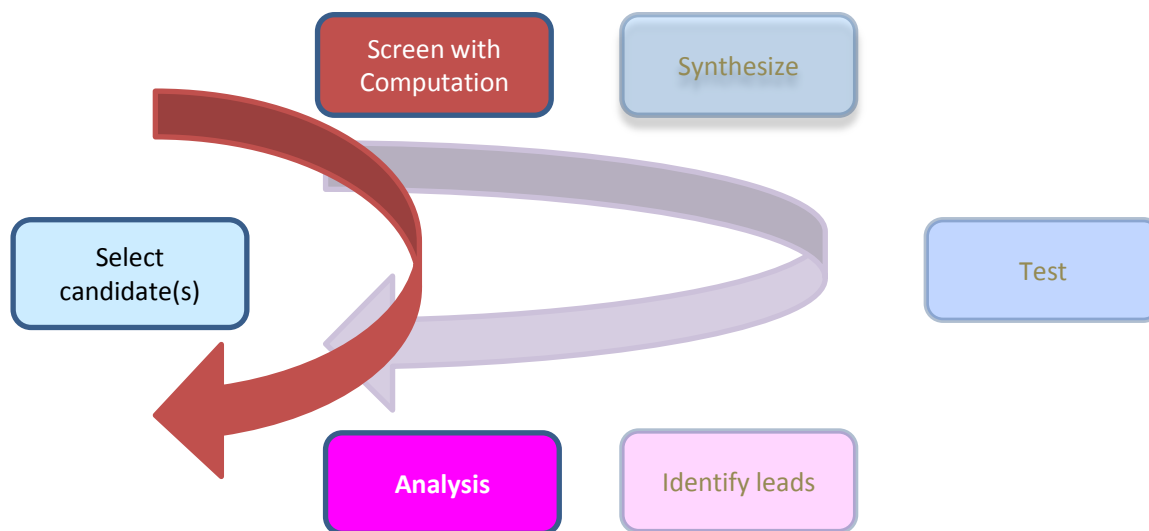


- Calculations can take a long time, e.g.,
  - Polymer shearing
  - Catalyst activity
- There are many materials to screen, e.g.,
  - Supported transition metal catalyst: 260K samples
  - Doped  $\text{Mg}_{13}$  nanocluster for  $\text{H}_2$  storage: 1.6 million samples
- Researchers are under pressure to provide results *fast*
  - Over coffee, over lunch, over night



# Options for Reducing Time to Solution

- Run each calculation on multiple cores
- Run many simultaneous calculations
  - Automation
- Calculate smarter, not harder, i.e., make judicious choices in which calculations to run
- New s/w algorithms



- Aims
  - Linear scaling problem size vs. CPU time and memory
  - Linear scaling # cores vs CPU time
  - SCF Convergence independent of system size
  - Systematically controllable accuracy
  - Plane-wave accuracy in energy & forces

$$\hat{\mathcal{H}}|\Psi\rangle = \mathcal{E}|\Psi\rangle$$

$N$ -body equation

DFT

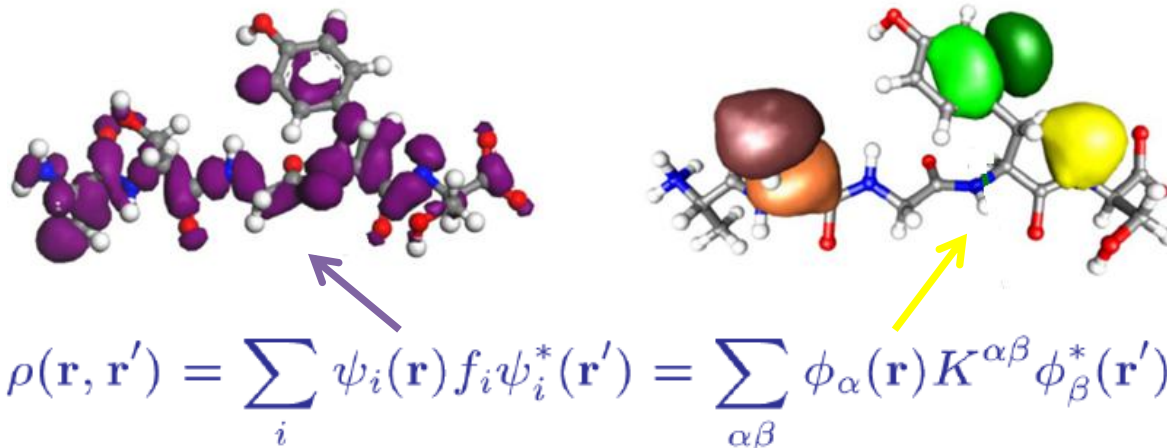
$$\hat{H}_{\text{KS}}\psi_i(\mathbf{r}) = \left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right] \psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

$N$  1-body  
equations

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2, \quad E = E[n(\mathbf{r})]$$

- $\langle \psi_i | \psi_j \rangle = \delta_{ij} \longrightarrow \mathcal{O}(N^3)$  bottleneck

# ONETEP: DFT density matrix formulation

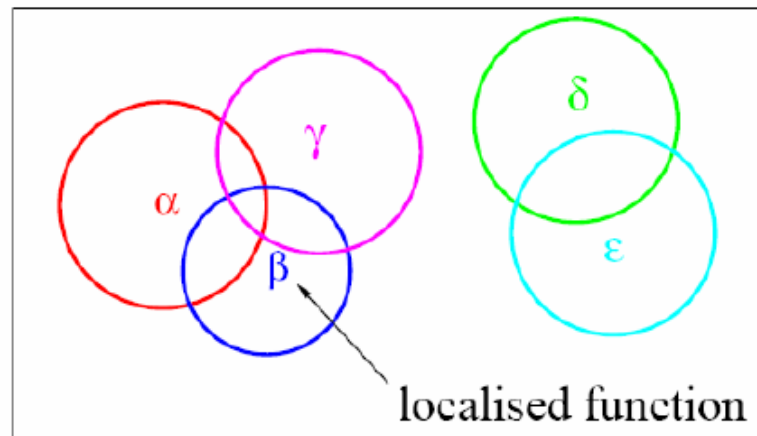


Exploit **short range** of density-matrix

$$\rho(\mathbf{r}, \mathbf{r}') \rightarrow 0 \text{ as } |\mathbf{r} - \mathbf{r}'| \rightarrow \infty$$

By making

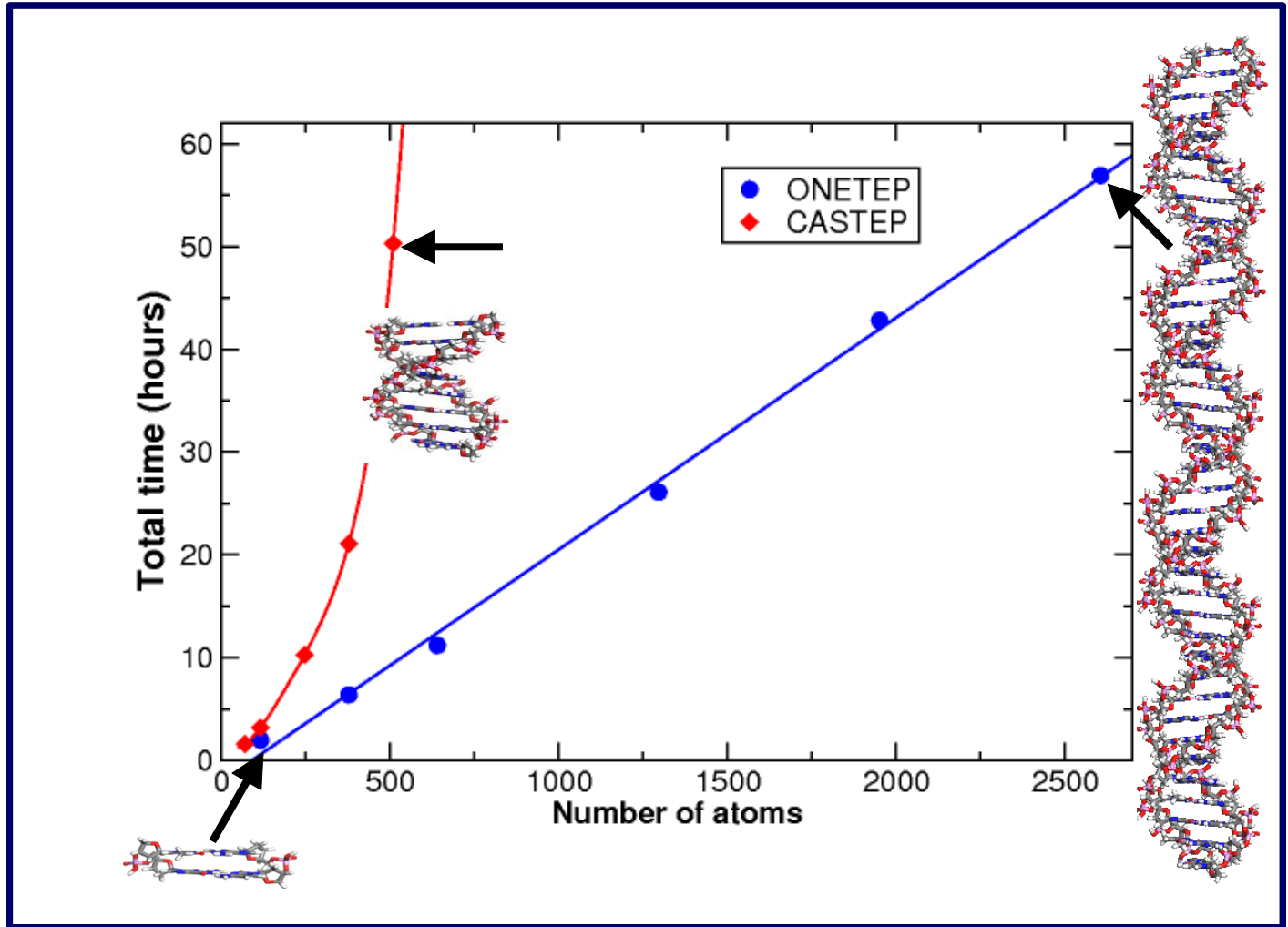
- **K** sparse
- $\{\phi\}$  strictly localised



simulation cell

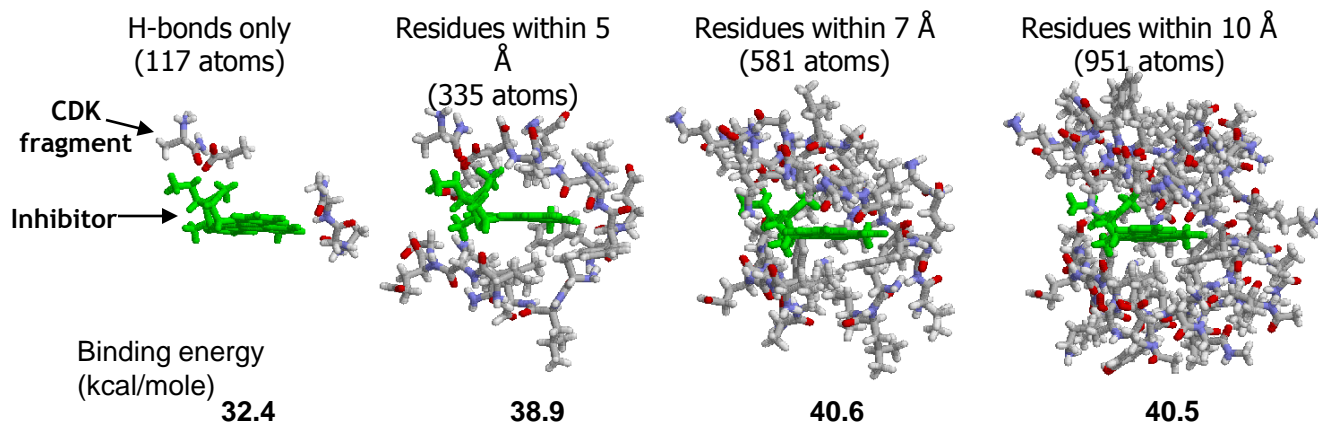
Non-Orthogonal Generalised Wannier Functions (NGWFs)

# Linear Scaling DFT Results



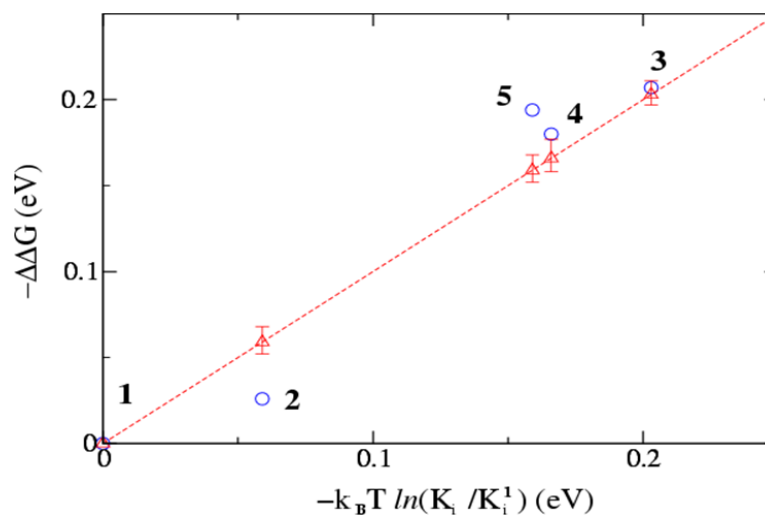
# ONETEP Case Study: Inhibiting CDK proteins

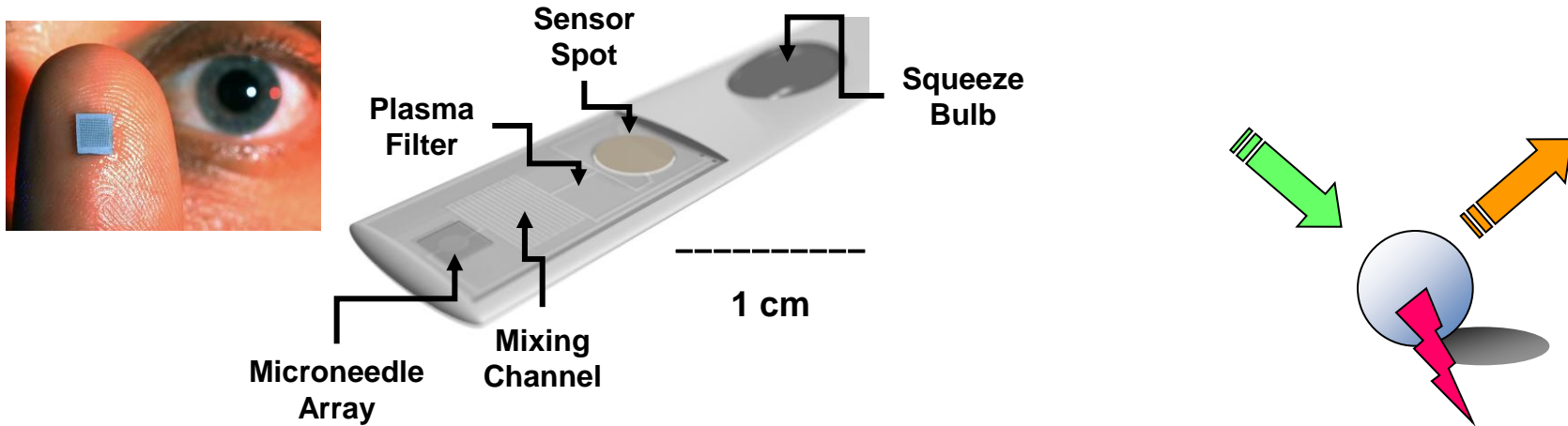
Binding of Inhibitor into protein active site: Convergence with protein fragment size: you need a large fragment to achieve accuracy < 1 kcal/mole



Predicted inhibition of Cyclin Dependent Kinases (CDKs) shows good agreement with experiment

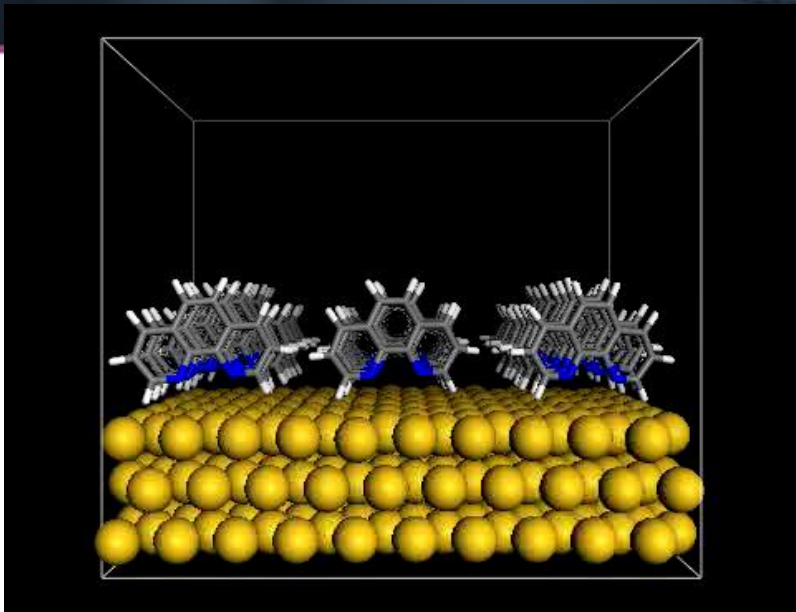
- ONETEP
- △ Experiment



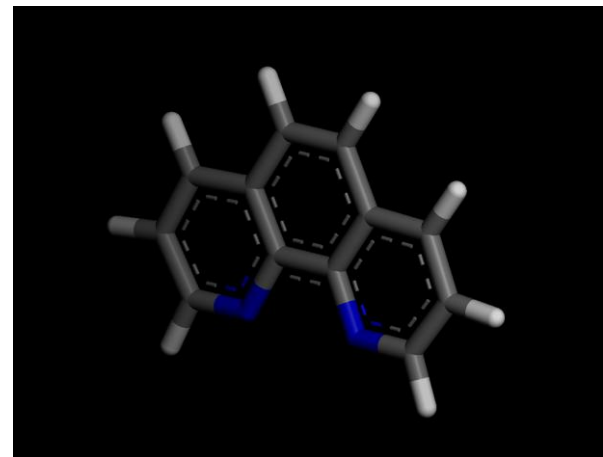
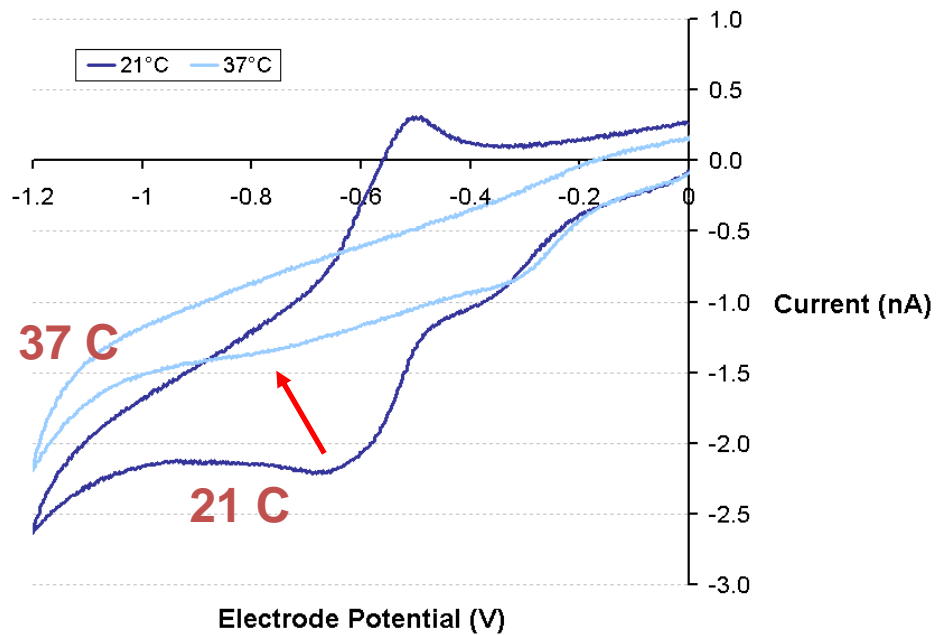
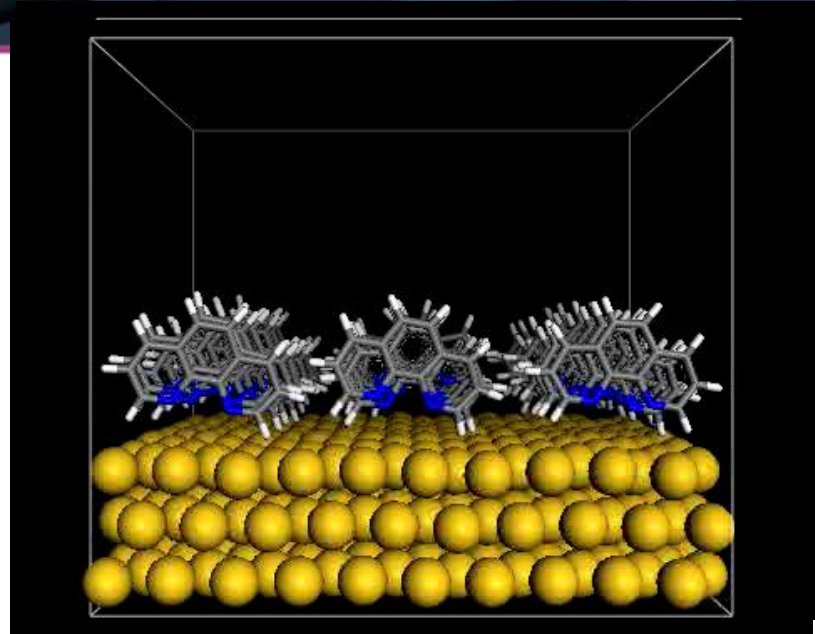


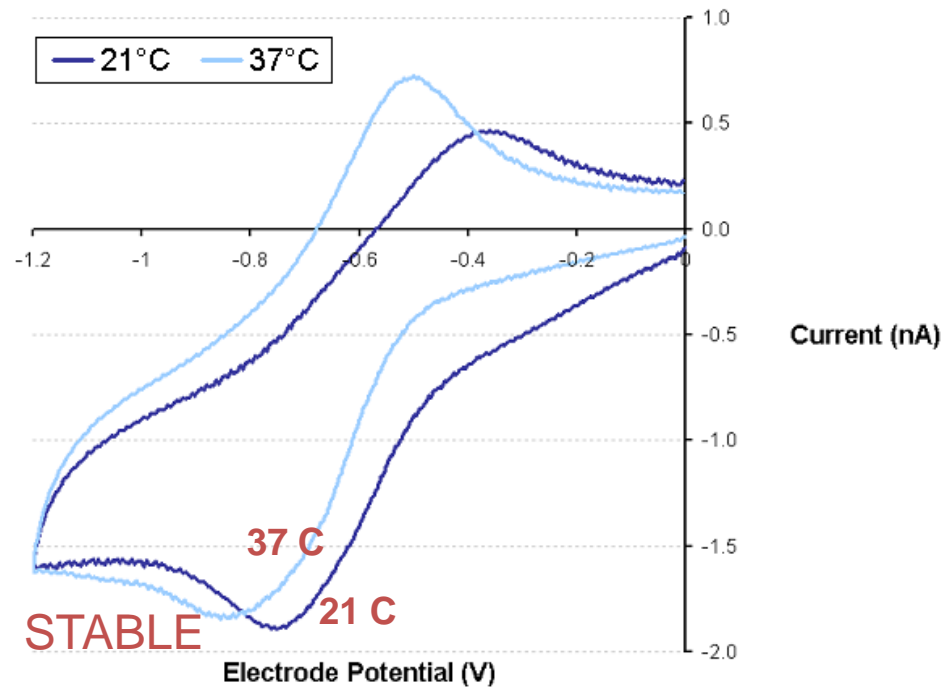
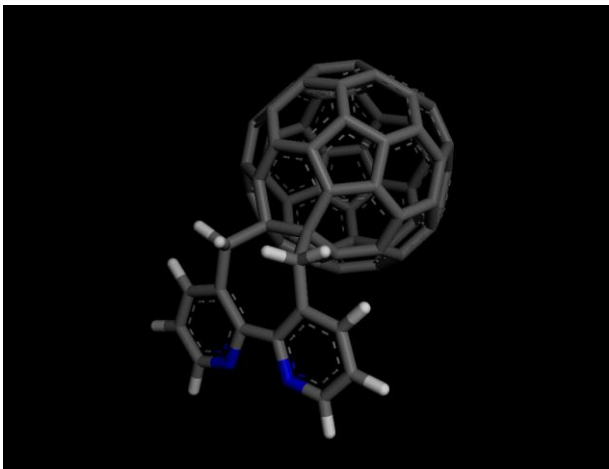
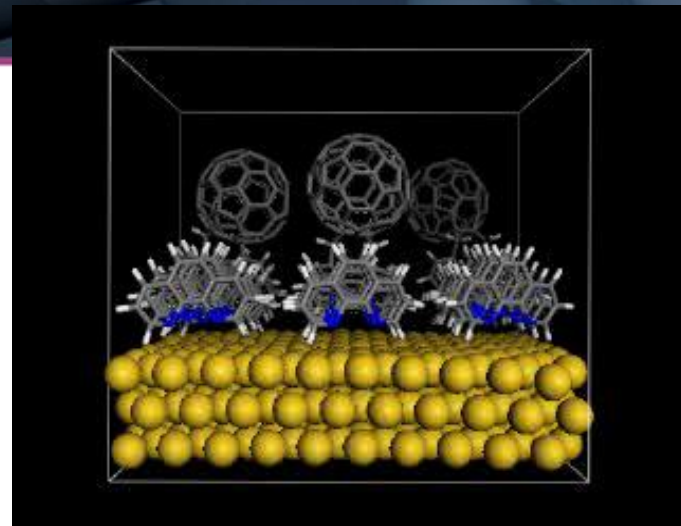
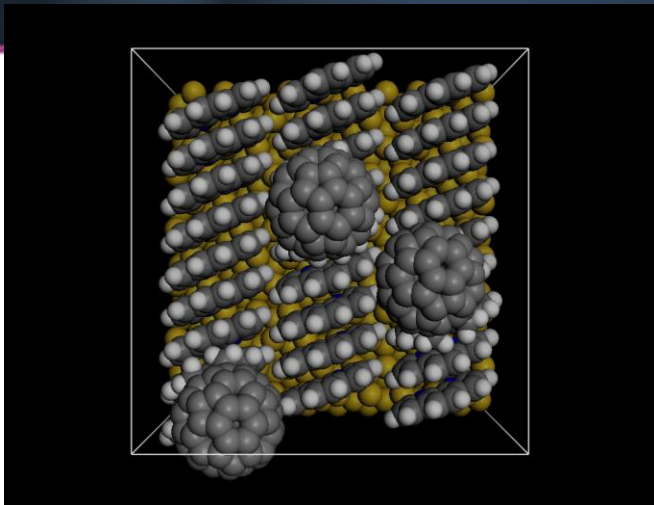
- **For use in point-of-care diagnostics & monitoring**
  - Human & animal trials
  - Clinical applications
- **Incorporates a painless microneedle array for blood collection**

21 C Stable Sensor Surface



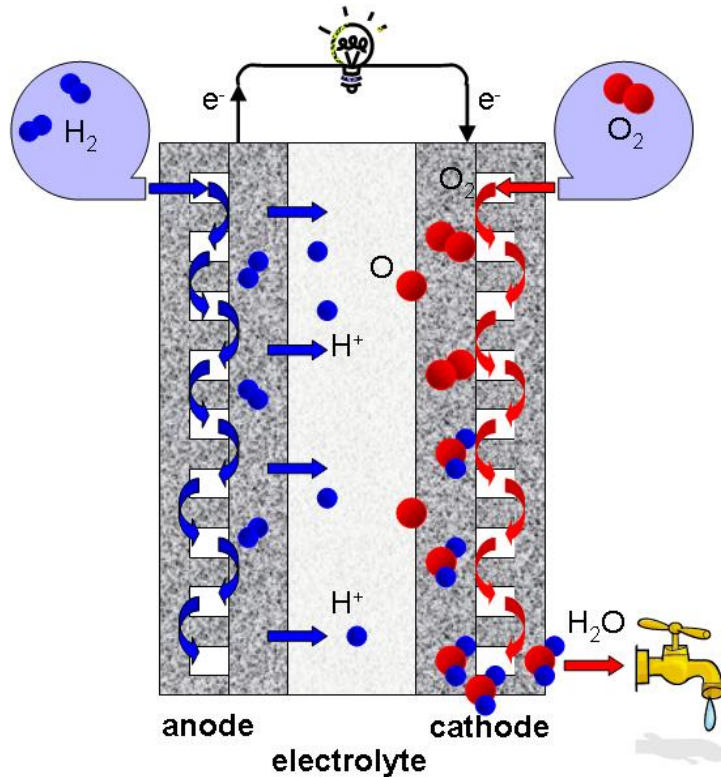
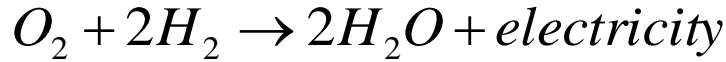
37 C Unstable Sensor Surface



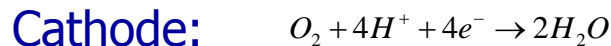
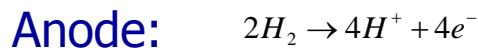


- "The use of modeling solved a problem that had been present for about one year. This work found a solution in less than two weeks."
- "Materials modeling, when used to solve a problem with an existing product, saved over £500k in development costs."

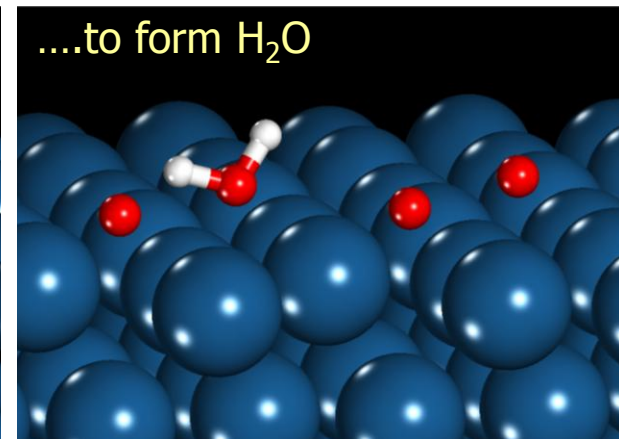
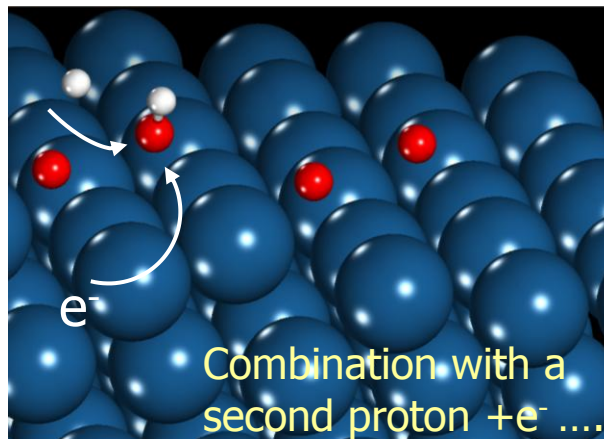
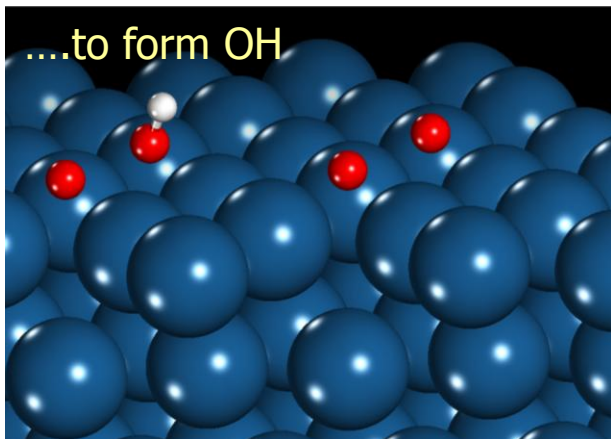
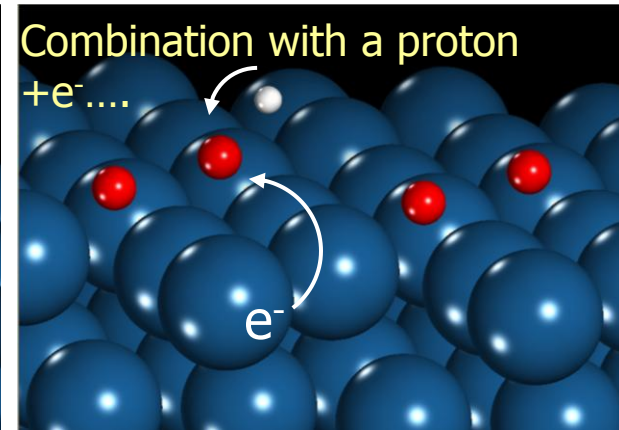
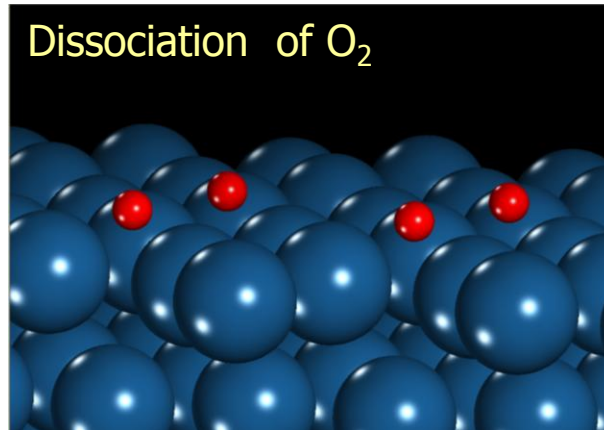
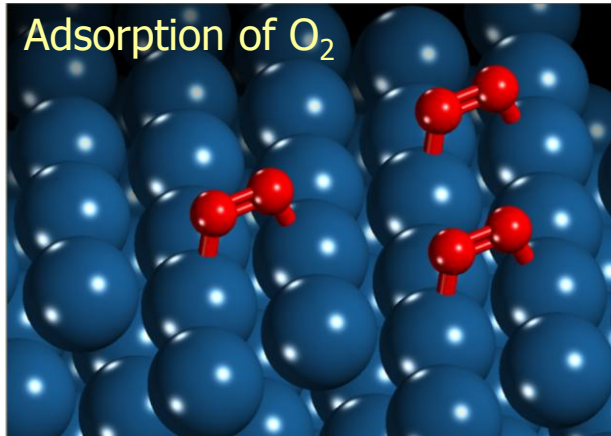
# PEM Fuel Cells Challenges



- **iCatDesign project used combined theory and experiment to find new catalysts for oxygen activation in fuel cells**
  - Johnson Matthey
  - CMR Fuel Cells
  - Accelrys
  - Co-funded by the UK Technology Strategy Board's Collaborative Research and Development programme
- **One challenging step is Oxygen Reduction Reaction (ORR)**
- **Pt is effective catalyst for activating O<sub>2</sub> but too expensive for large-scale application**
  - How can we find catalysts that are just as effective but less expensive?
  - **High-throughput DFT calculations with CASTEP**
- **Published:**
  - Gavartin, et al., *ECS Transactions* **25**, 1335-1344 (2009)

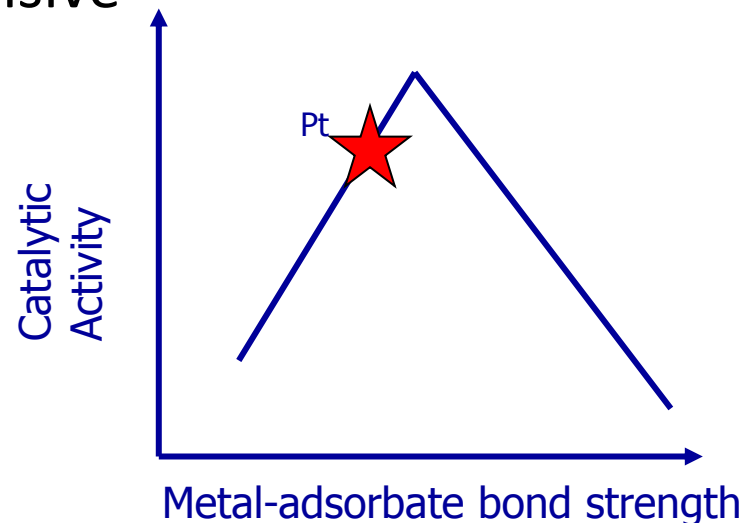


# Dissociative ORR mechanism in PEMFC



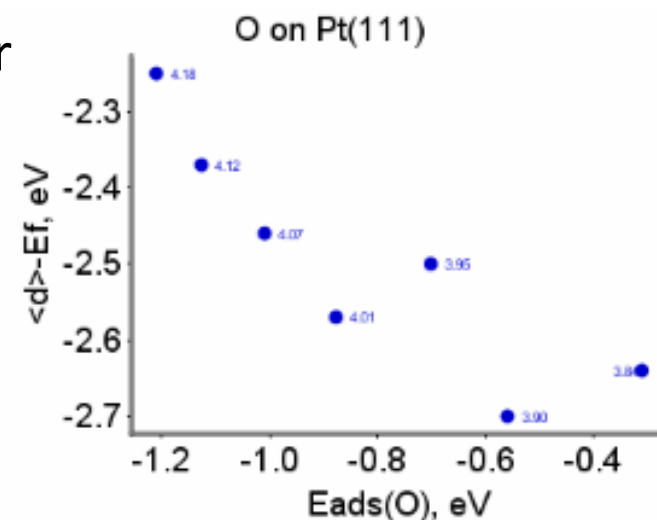
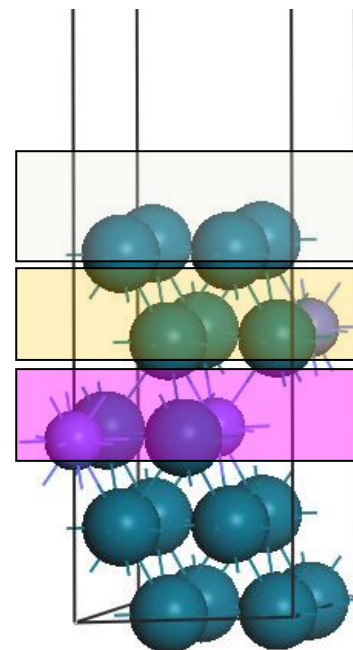
# Ideal Catalyst – Sabatier's Principle

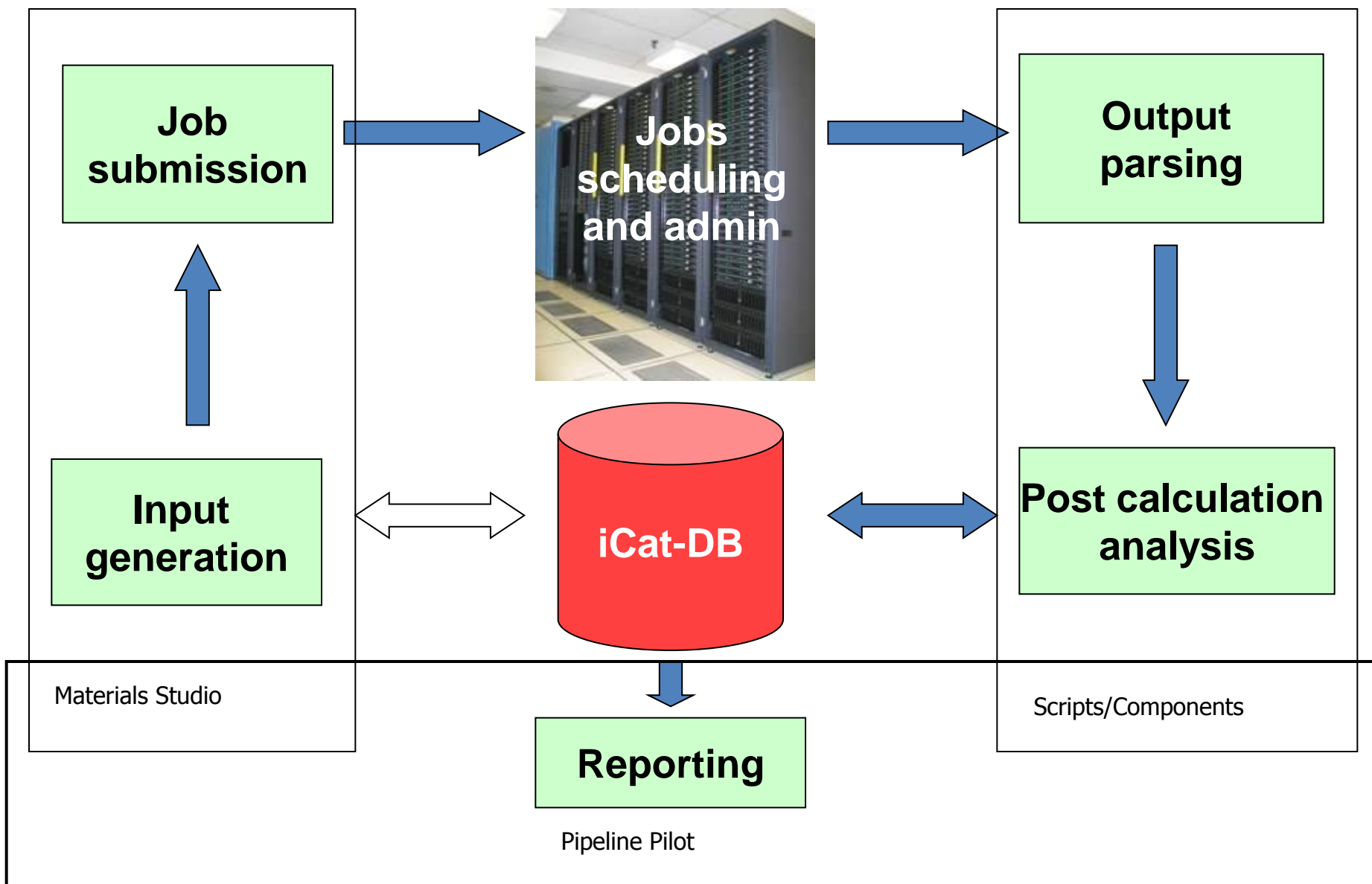
- The optimum catalyst-adsorbate interaction must
  - Not be too weak:
    - Insufficient charge transfer from bond to surface
    - Insufficient weakening of O-O bond
  - Not be too strong
    - Desorption cannot take place
    - Surface becomes poisoned
- Pt is close to optimum, but expensive
  - Other pure metals perform worse
  - What about alloys?



# Reducing Computational Cost

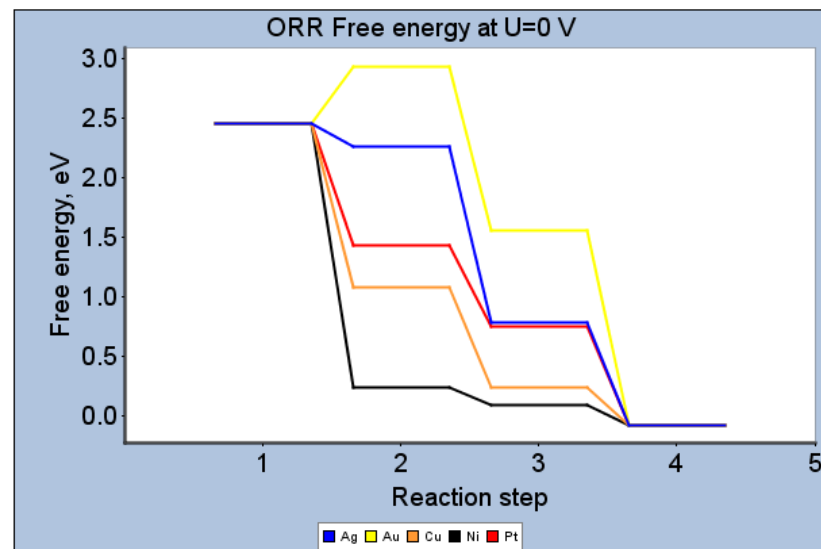
- This work examined alloys of the form  $A_3B$ , e.g.,  $Pt_3Co$
- Use 5 layer model with lowest layers fixed
  - In 3 layer model, there are 220 unique structures
  - For  $2xA$  and  $10xB$  elements  $> 2,000$  calculations
  - Grows factorially with # of dopants
- Need ORR activation for each
  - How can we avoid 2,000 ORR calculations?
- We can estimate activity with  $E_{ads}$
- Furthermore:  $d$ -band center is roughly linear with  $E_{ads}$
- Reduction in computational cost:
  - ORR barrier = expensive
  - $E_{ads}$  calculation = cheaper
  - $d$ -band center = cheapest





- Ability to make sense of 1000s of results is critical
- Database searching, reporting, analysis makes these results useful

U = 0.0 V



## Oxygen Reduction Reaction Steps

- 1:  $2(\text{H}^+ + 1/2\text{O}_2)$
- 2:  $2(\text{H}^+ + \text{e}^-) + \text{O}^*$
- 3:  $(\text{H}^+ + \text{e}^-) + \text{OH}^*$
- 4:  $\text{H}_2\text{O}$

### Parameters used

$E(\text{H}_2\text{O}) = -469.5462120488 \text{ eV}$

$E(\text{H}_2) = -31.89024451841 \text{ eV}$

### Corrections

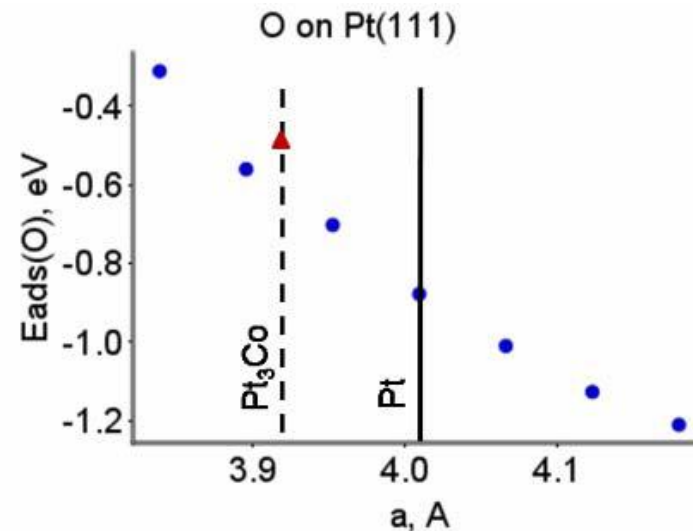
$C_0 = -4. \text{e-}002 \text{ eV}$

$C_1 = -7. \text{e-}002 \text{ eV}$

$C_2 = -3. \text{e-}002 \text{ eV}$

myname1	Eads_OH	Eads_O	G0_U0	G1_U0	G2_U0	G0_U	G1_U	G2_U
Ag	0.89161	2.3071	2.2671	-1.4855	-0.86161	2.2671	-1.4855	-0.86161
Au	1.6680	2.9787	2.9387	-1.3807	-1.6380	2.9387	-1.3807	-1.6380
Cu	0.34972	1.1155	1.0755	-0.83582	-0.31972	1.0755	-0.83582	-0.31972
Ni	0.20330	0.28119	0.24119	-0.14789	-0.17330	0.24119	-0.14789	-0.17330
Pt	0.85709	1.4743	1.4343	-0.68724	-0.82709	1.4343	-0.68724	-0.82709

- Automated screening of 1000s of  $A_3B$  alloys
  - Results in min/hours instead of days/weeks(?)
- Combined experimental/computational data
- Lead mixture identified and forwarded to experimentalist



# High-throughput Quantum Chemistry and Virtual Screening for Lithium Ion Battery Electrolytes

George Fitzgerald<sup>a</sup>

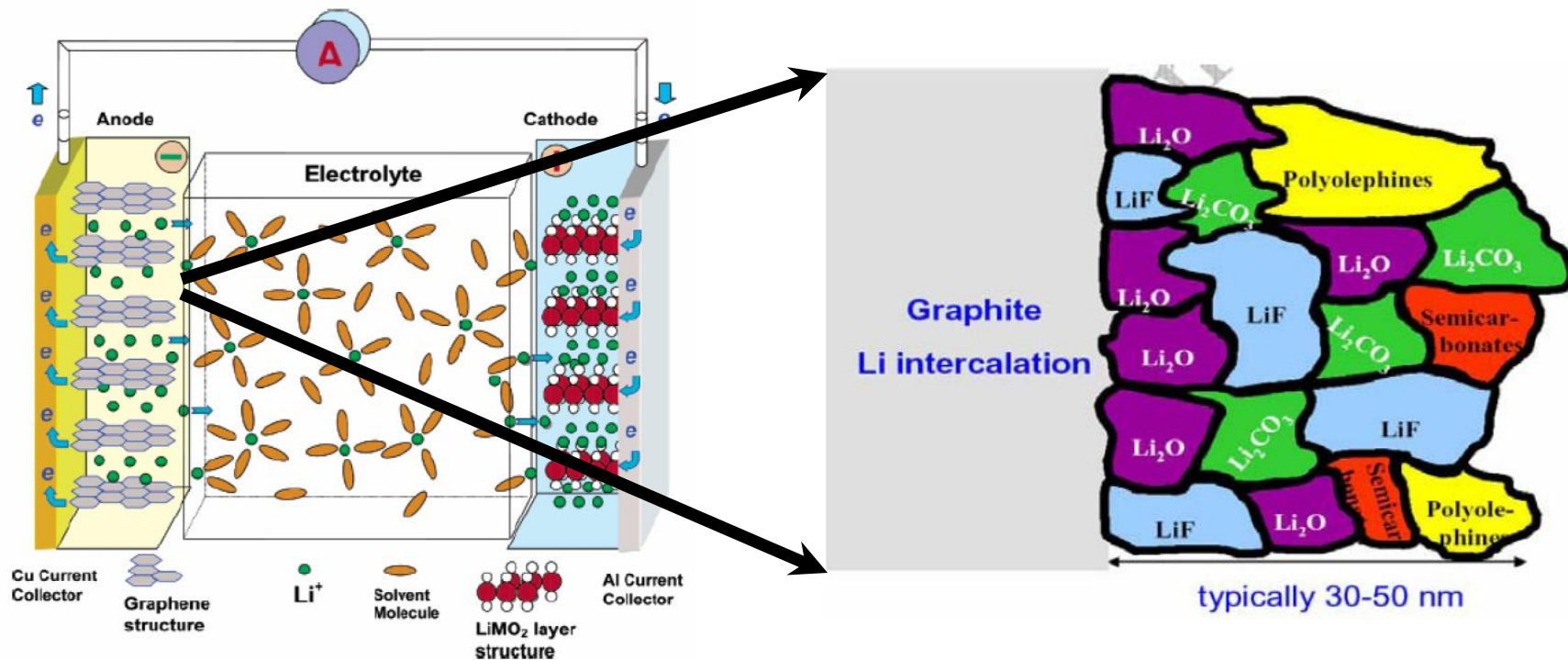
Mathew D. Halls<sup>a</sup>

Ken Tasaki<sup>b</sup>

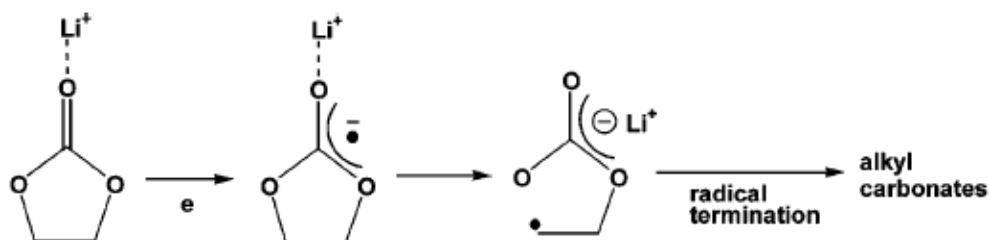
<sup>a</sup> Accelrys, Inc

<sup>b</sup> Mitsubishi Chemical, Inc

# Lithium Ion Batteries and SEI Film Formation



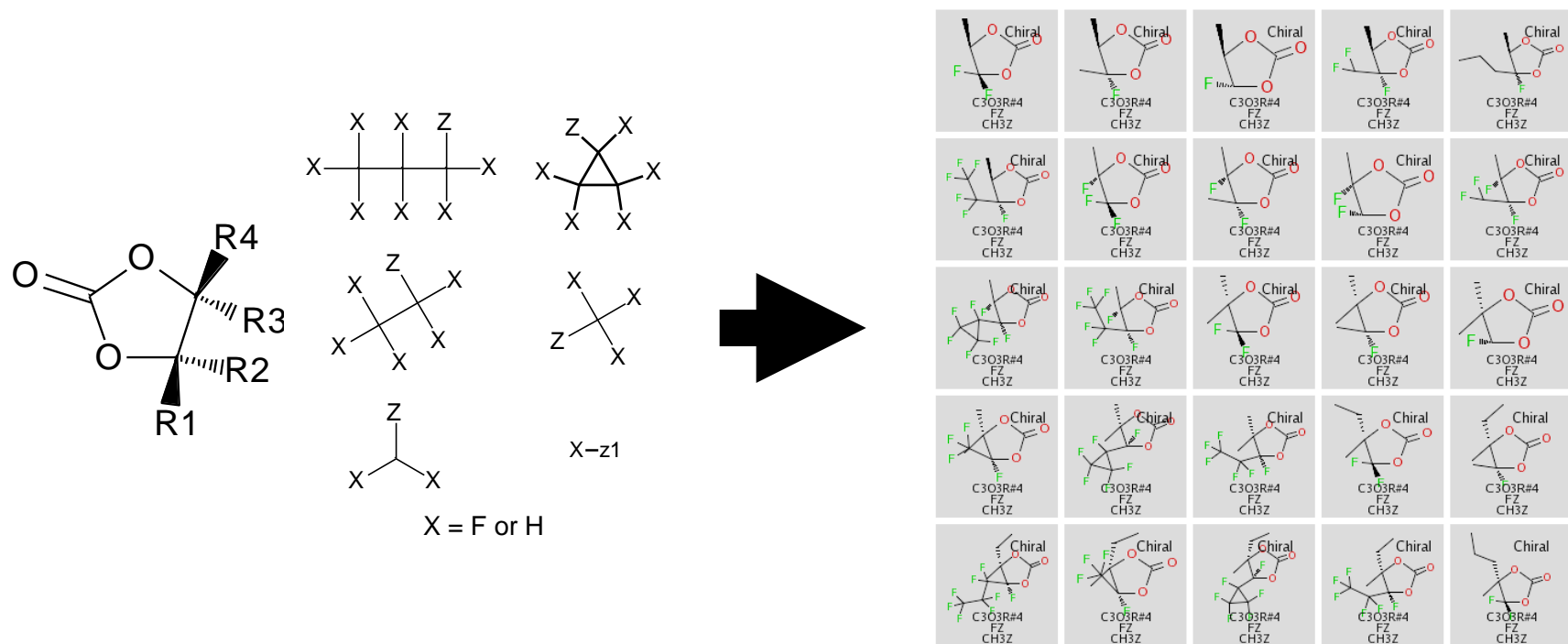
- The electrolyte typically consists of one or more lithium salts dissolved in an aprotic solvent with at least one additional functional additive
- Additives are included in electrolyte formulations to increase the dielectric strength and **enhance electrode stability by *facilitating* the formation of the solid/electrolyte interface (SEI) layer**



## 1 $e^-$ decomposition scheme

- Initiation step leading to anode SEI formation is electron transfer to the SEI forming species
  - Results in decomposition reaction
  - Produces the passivating SEI layer
- Important requirements for electrolyte additives selected to facilitate good SEI formation are:
  - Higher reduction potential than the base solvent
  - Maximal reactivity for a given chemical design space
  - Large dipole moment for interaction with Li

# Anode SEI Additive Structure Library



- Cyclic carbonates, related to ethylene carbonate (EC), are often used as anode SEI additives for use with graphite anodes
- To explore the effect of alkylation or fluorination on EC-based additive properties an R-Group based enumeration scheme was used to generate a EC-based additive structure library (7381 stereochemically unique structures)

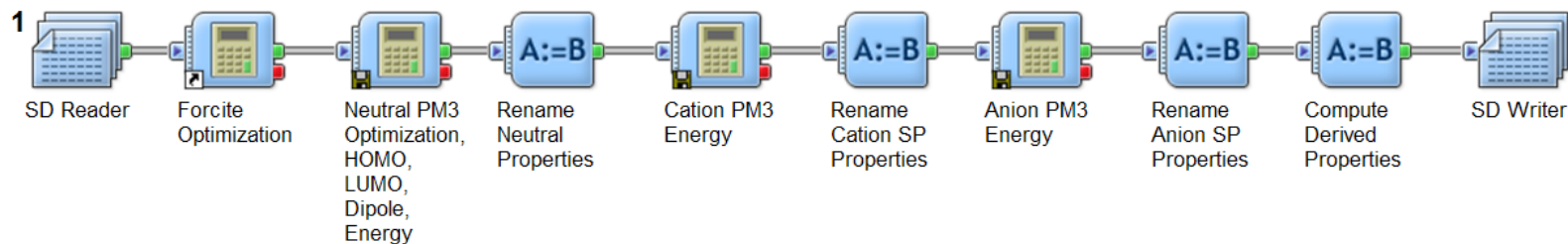
# Anode SEI Additive Descriptors

- Increased reduction potential correlates with a lower LUMO higher  $EA_v$
- Stability or reactivity corresponds to chemical hardness  $\eta$
- Larger dipole moment leads to stronger dipole-cation interactions ( $\mu$ )
- Work by Chung *et al*, has shown that the PM3 is adequate for these systems, 60x faster than DFT
- Workflow automation is needed to process the 7381 structures

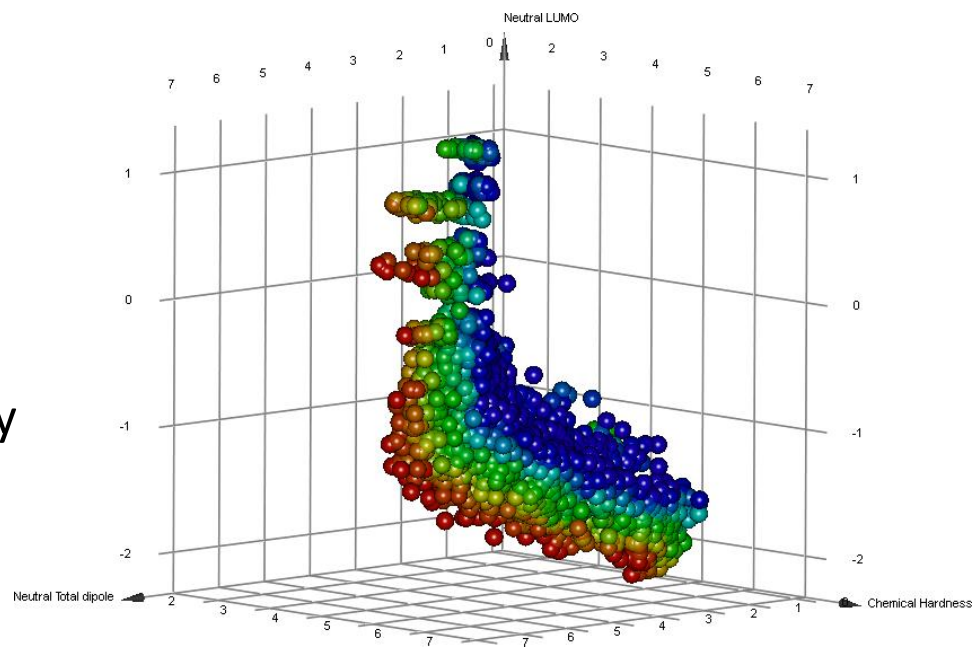
$$E_{\text{LUMO}}, EA_v$$

$$\eta = \frac{IP_v - EA_v}{2}$$

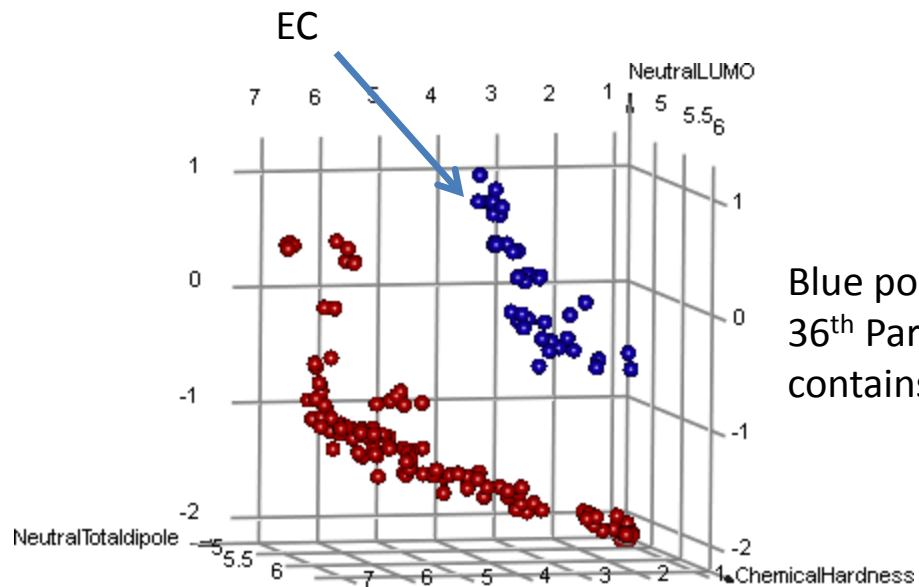
$$\mu$$



- Optimal materials must satisfy a number of objectives
- Multi-objective solutions represent a trade-off between objectives
- One approach is to adopt the “Pareto-optimal” solution
  - Set of solutions such that is not possible to improve one property without making any other property worse
  - This case:
    - Minimize the chemical hardness
    - Maximize the dipole moment and electron affinity



# Comparison of EC with optimum compounds



Blue points represent the 36<sup>th</sup> Pareto surface which contains EC

Red points represent the 1<sup>st</sup> Pareto surface

- High-throughput calculation screened a library of fluoro- and alkyl derivatized ethylene carbonate (EC)
- The effect of fluorination leads to a maximum electron affinity across the library of 4.13 eV, compared to alkylation leading to a maximum value of only 0.43 eV, relative to EC
- The results presented here introduce a new and powerful approach for exploring the property limits of structural motifs for lithium battery electrolyte additives.
- This work has appeared in print as *Journal of Power Sources* 195 (2010) 1472–1478.
- Thanks to HP for computing resources for this project



- HPC is being used by many commercial organizations to solve challenging problems
  - Computation reduces cost, speeds time to solution compared to expt alone
  - HPC necessary to make computation competitive
  - Automation tools make it possible to screen 1000's of compounds, make efficient use of HPC resources
- New s/w algorithms + h/w make it possible to address new problems