Theory, Applications, and Tools for Multiscale Kinetic Modeling: Parameterizing Large Models

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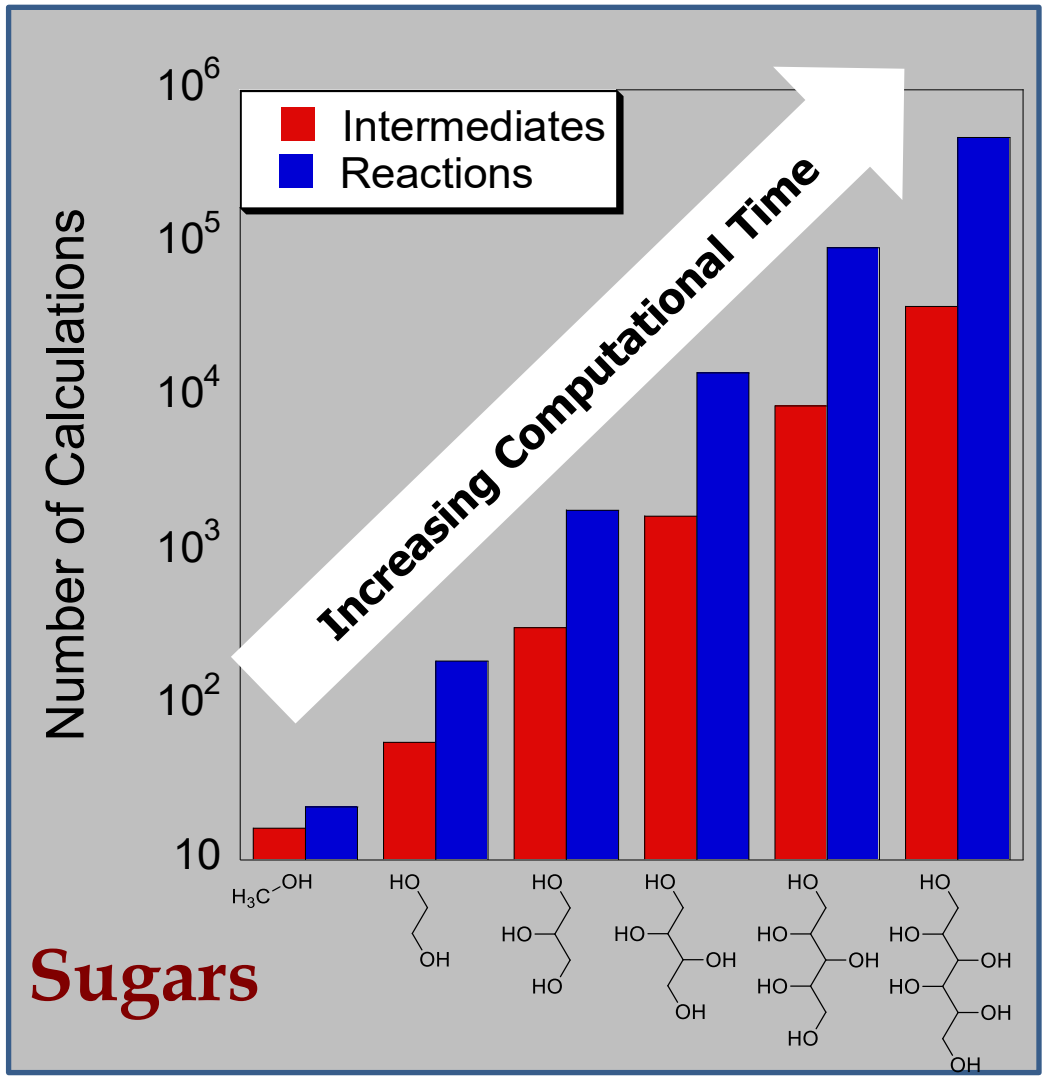
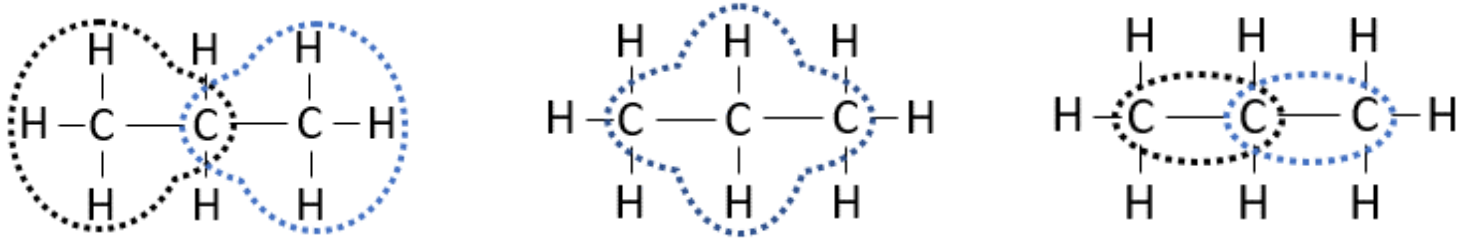
Modeling Reactions of Large Molecules is Challenging



- Combinatorial explosion in number of calculations for first-principles (DFT) calculations
- Semi-empirical methods can potentially parametrize relevant species and reactions instantaneously
- Major advances in systematic development of semi-empirical methods and understanding of errors

Method: Group Additivity[1,2]



Propane (C_p, H, S) = 2 x **C(C)(H)$_3$** + 1 x **C(C)$_2$(H)** + 2 x **CC**

Training Molecules \ Groups													
	2	0	0	0	0	1	0	0	0	0	1	0	0
	1	0	2	0	0	0	0	0	0	0	0	0	0
	2	0	0	0	1	0	0	0	0	0	1	0	0
	0	0	0	0	2	0	0	0	0	1	0	0	2
	0	0	0	2	0	0	0	0	2	0	0	1	0
	0	0	2	2	0	0	1	0	0	1	0	2	2
	1	1	0	0	0	0	0	0	1	0	0	1	0
	0	1	0	0	0	0	0	0	2	1	0	0	0
	2	2	2	0	0	0	2	0	0	0	1	1	0
	2	0	0	0	0	0	1	0	0	0	1	0	0
	2	1	0	0	0	0	0	0	1	0	2	0	0
	0	0	0	1	0	0	0	0	0	1	0	0	1

Thermodynmic Property (Group) = Thermodynamic Property (Molecule)

$$\mathbf{X}_{T[m\times g]} \bullet \beta_{[g\times 1]} = Y_{T[m\times 1]}$$

$$\beta_{[g\times 1]} = \mathbf{X}^{+}_{T[m\times g]} \cdot Y_{T[m\times 1]}$$

$$\beta_{[g\times 1]} = \left(\mathbf{X}'_{T[g\times m]} \cdot \mathbf{X}_{T[m\times g]}\right)^{-1} \cdot \mathbf{X}'_{T[g\times m]} \cdot Y_{T[m\times 1]}$$

$$\hat{\sigma} = \sqrt{\frac{\sum\left(\mathbf{X}_{T[m\times g]} \cdot \beta_{[g\times 1]} - Y_{T[m\times 1]}\right)^2}{m-g}}$$

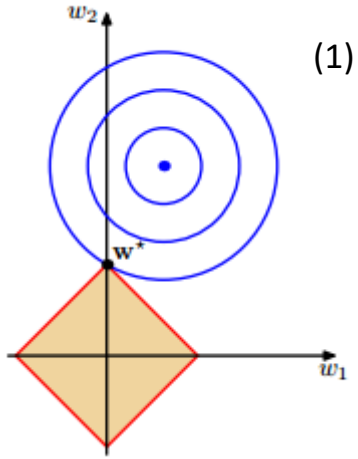
$$\hat{\sigma}_{C_P} = 0.12 - 0.73\ cal/mol\cdot K$$
$$\hat{\sigma}_{H} = 4.53\ kcal/mol$$
$$\hat{\sigma}_{S} = 2.07\ cal/mol\cdot K$$

GrAdd[3]

[1] Benson, S. W. *et al.* (1969), *Chemical Reviews*
[2] Kua, J. and Goddard, W. A. (1998), *J. Phys. Chem. B*
[3] https://github.com/VlachosGroup/PythonGroupAdditivity
Gu et al. (2018), *Reaction Chemistry & Engineering*.

Method: Machine Learning

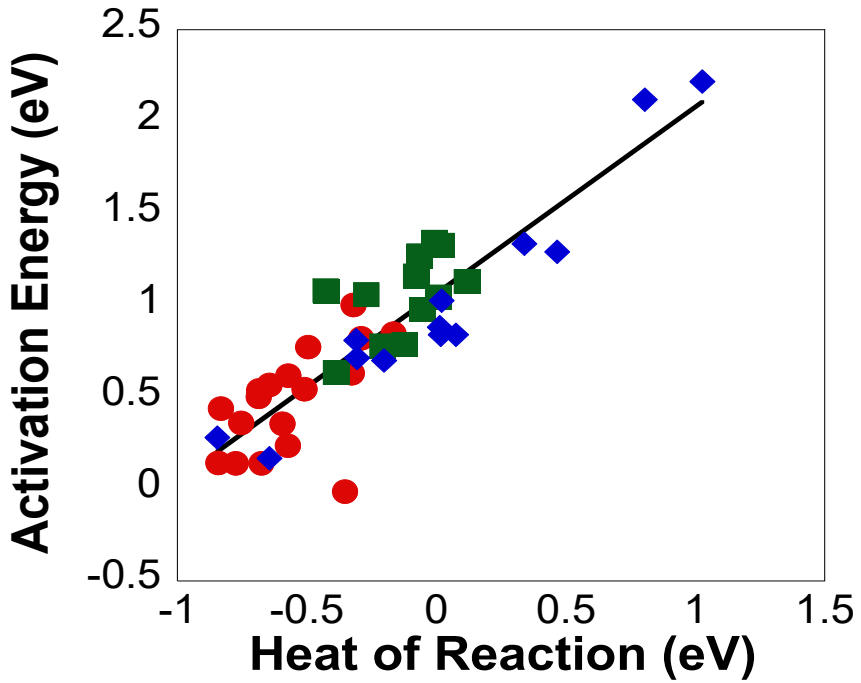
- Increasingly popular approach
- Not limited to a single scheme as group additivity
  - Groups may not be necessary
  - Groups, if used, are not limited to a single scheme
  - Not limited to linear relationships
  - More complex relationships can be explored
- Can achieve better fit with training data
- Can lose some of the physics



(1)

(1) Gu, G. H.; Plechac, P.; Vlachos, *React. Chem. Eng.* **2018**, *3* (4), 454–466.

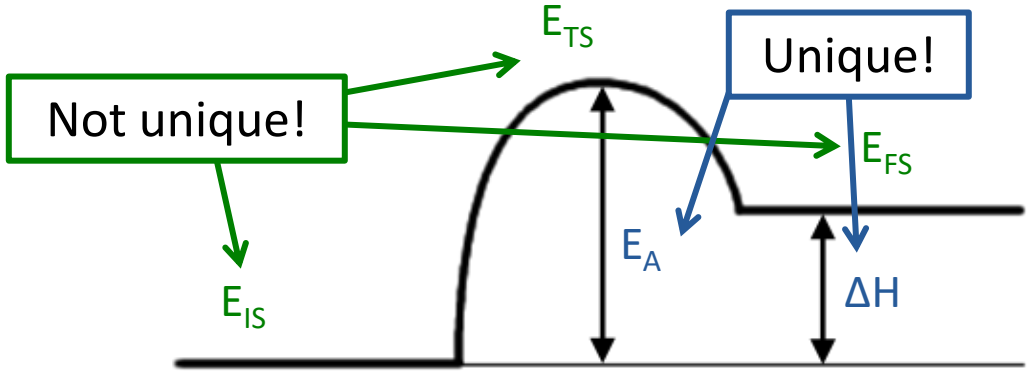
Brønsted-Evans-Polanyi (BEP) Relationships[1]



- BEP relationships can be used as they enable the prediction of reaction barriers from the heat of reactions for an entire homologous series of reactions
- BEPs for common homologous series are available

$$\Delta E_{a,i} = \omega \Delta H_{rxn,i} + \Delta E_0$$

C—C
C—H
C—OH
C—O
O—H

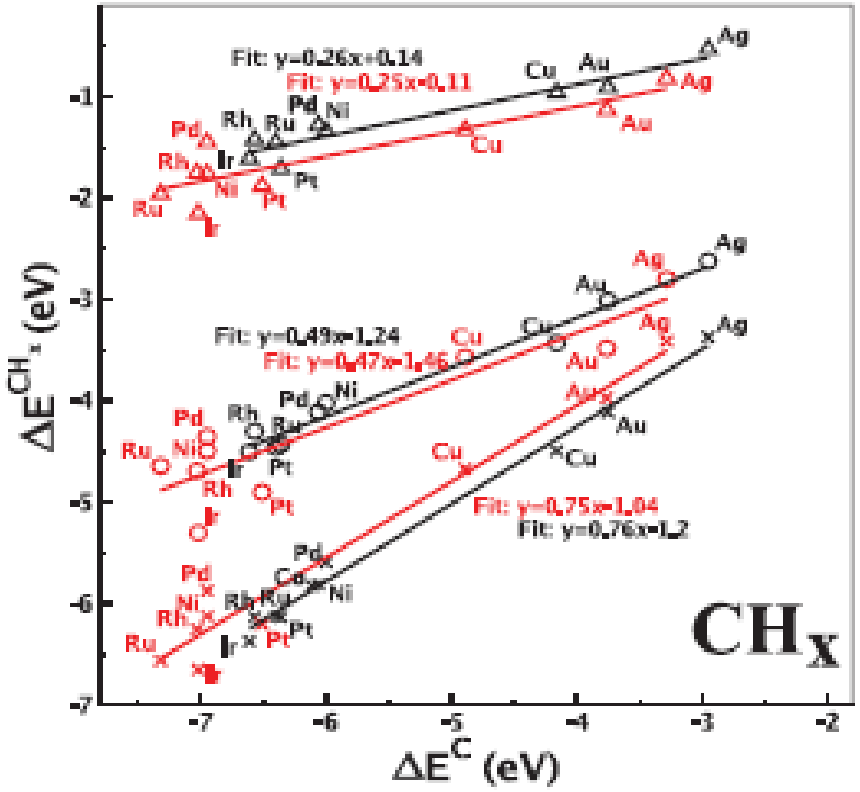


[1] Sutton and Vlachos, *ACS Catal.*, **2**, 1624 (2012)

Linear Scaling Relationships (LSRs) for Metal Cats

$$Q^{AH_x} = \gamma Q^A + \beta, \quad \gamma = \frac{x_{max} - x}{x_{max}}$$

Simple/Small Molecules:
CHx, NHx, OHx, SHx,…



- They work well when AHx binds on catalysts with the same binding mode, e.g., bridge binding
- **Impact**: By computing Q_A on a new catalyst, e.g., bimetallic, you can compute Q_{AHx}, so one saves some comps

- Polyatomic/Multidentate Adsorption: Extended LSR

$$Q_{i,new} = Q_{i,ref} + \sum_{j=1}^{n} \gamma_{i,j} \left(Q_{new}^{ref\ species,\ j} - Q_{ref}^{ref\ species,\ j} \right)$$

[1,2] Jones, G. *et al.* (2008) 'Using scaling relations to understand trends in the catalytic activity of transition metals', *Journal of Physics Condensed Matter* Abild-Pedersen et al. *PRL* **99,** (2007)

Summary of Semi-empirical Methods

- Group additivity estimates species thermochemistry for large molecules and mechanisms
  - Once the groups have been identified via graph theory and the values estimated, these can be used for any mechanism on the same catalyst
  - Reaction thermochemistry is estimated from species thermochemistry
- Extended linear scaling relations can be used to estimate species thermochemistry on a new catalyst from a reference catalyst
- BEPs or transition state scalings can be used to estimate reaction barriers from thermochemistry
  - BEP is applied to the entire homologous series; a few DFT data to estimate and information is then transferable to all reactions of the same family
  - Tacitly assumed that the BEP holds among catalysts for the same chemistry
- These relations are linear; machine learning can be used to improve accuracy, identify descriptors, e.g., groups in GA, and capture nonlinear effects