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

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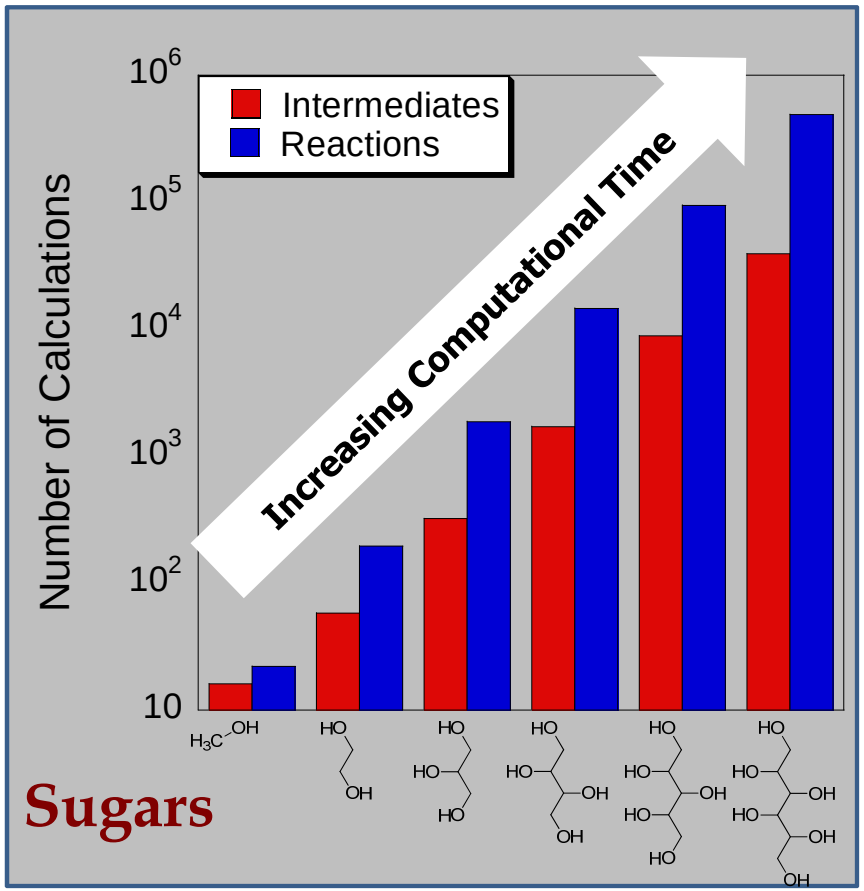
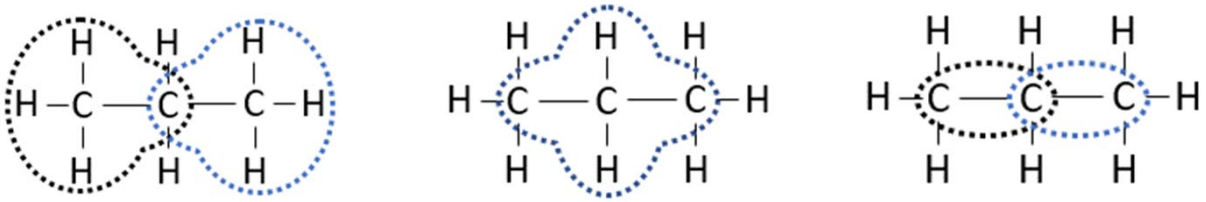
# Modeling Reactions of Large Molecules is Challenging




- 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)

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

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

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

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

GrAdd[3]

$\hat{\sigma}_{C_P} = 0.12 - 0.73\ cal/mol \cdot K$

$\hat{\sigma}_{H} = 4.53\ kcal/mol$

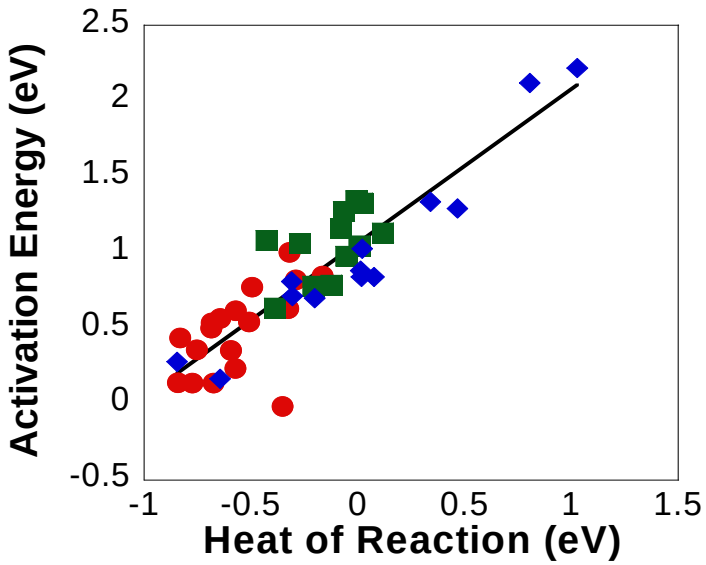
$\hat{\sigma}_{S} = 2.07\ cal/mol \cdot K$

[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*.

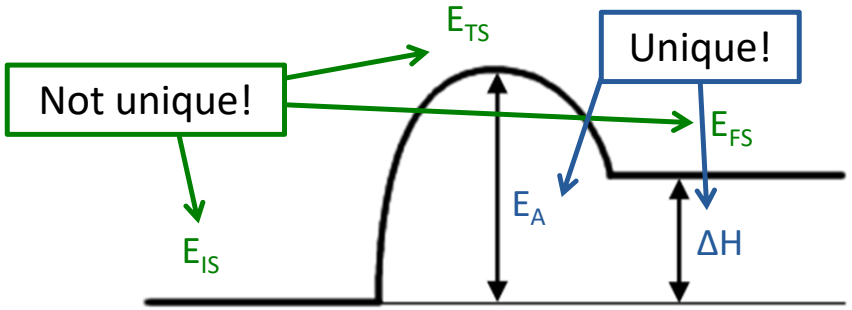
# Brønsted-Evans-Polanyi (BEP) Relationships[1]




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

- 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

C—C
C—H
C—OH
C—O
O—H



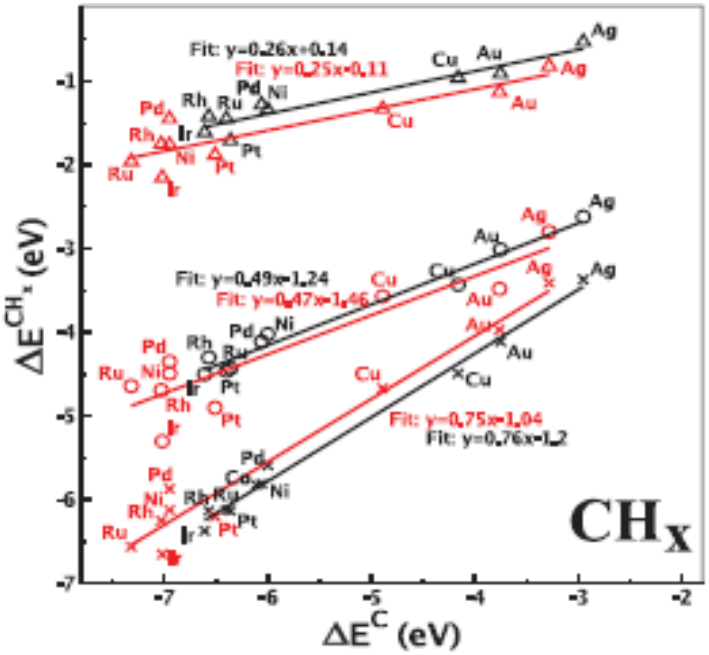

[1] Sutton and Vlachos, *ACS Catal.*, **2**, 1624 (2012)

# 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