Thermochemical Kinetics, Environmental Dynamics, Planetary and Earth Sciences, Catalysis, and Combustion Modeling: Next-Generation Density functionals and New Methods for Calculating Potential Energy Functions in the Truhlar Group

Predicting the rates of chemical processes and studying the roles of quantum effects on reaction rates, kinetic isotope effects, and state-selective chemistry. Developing new methods for obtaining, representing, and using potential energy functions for studying the properties of gas-phase and condensed-phase systems important in the environment, in combustion, in catalysis, and in planetary science.

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Variational Transition State Theory with Multidimensional Tunneling (VTST/MT)

- VTST/MT is used to calculate rate constants for chemical reactions

- First find the saddle point (red dot), which is the highest energy point on the minimum energy path (blue line) that connects reactants and products

- Data from the path calculation is used to optimize the location of the dividing surface between reactants and products, then calculate multidimensional tunneling and the rate constant

- The required data can be calculated "on the fly" with high levels of theory. This method is called direct dynamics.
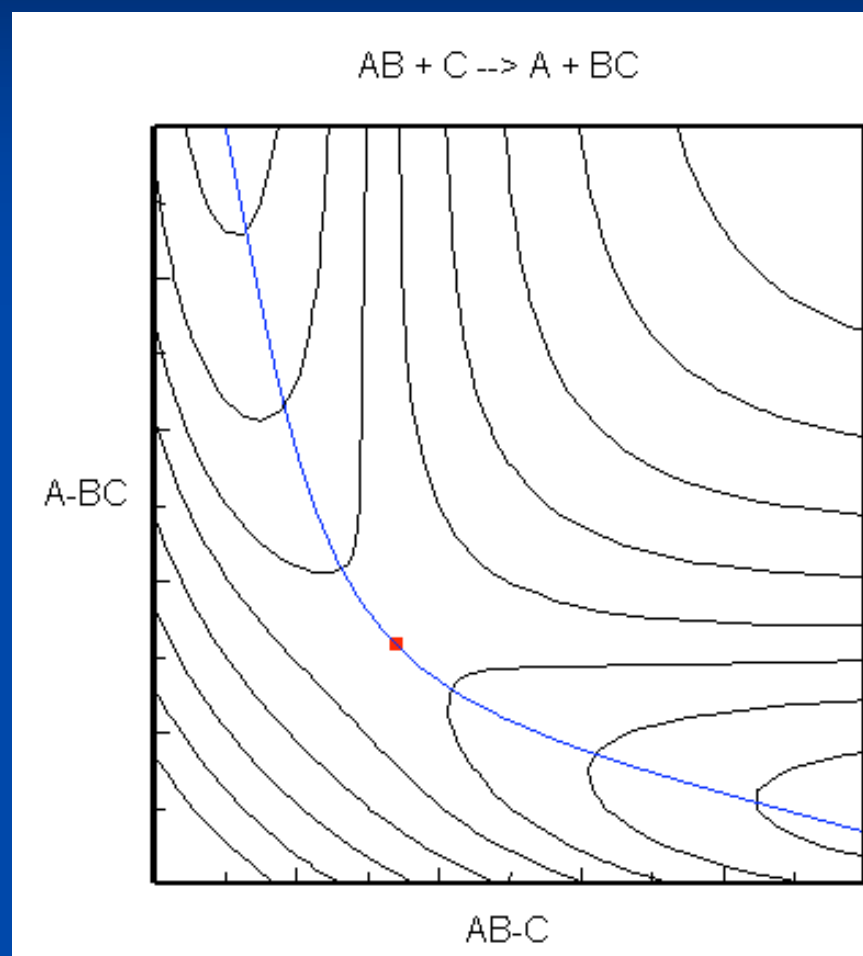
Potential energy surface for a system of atom B being transferred from group A to group C

Applications of VTST/MT

Real world problems can be calculated using direct dynamics. These calculations have been carried out using GAUSSRATE, which interfaces *Gaussian 03* with POLYRATE, our dynamics code.

1. $CH_4 + OH \rightarrow CH_3 + H_2O$
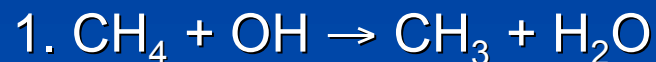
- Methane is an important global warning gas, and the $^{12}C/^{13}C$ kinetic isotope effect is difficult to measure but is needed for atmospheric modeling. This effect has been calculated and a temperature dependence has been found.

2. $H_2O_2 + H \rightarrow OH + H_2O$ and $H_2O_2 + H \rightarrow HOO + H_2$

- These hydrogen peroxide reactions are important for combustion modeling. VTST/MT calculations are helping resolve the experimental uncertainty of the rates associated with these reactions.

3. $H_2S + OH \rightarrow SH + H_2O$

- Hydrogen sulfide is a vital participant in the sulfur cycle and is primarily oxidized by OH. VTST/MT calculations yield insight into how this reaction occurs.

Benchmark Suites for Thermochemical Kinetics

🟢 Introduction

In theoretical chemistry a database is a collection of the best available data of various chemical properties. The data can be obtained experimentally and/or theoretically. Databases are very useful in assessing the performance of new theoretical methods.

🟢 Thermochemistry and Thermochemical Kinetics Databases Developed in the Truhlar Group

- <u>Database/3</u>: Ionization Potentials, Electronic Affinities, Barrier Heights, Atomization Energies
- <u>NHTBH38/04</u>: Non-Hydrogen Transfer Reaction Barrier Heights

🟢 Features of the Full Database

- Larger number of data (computationally demanding)
- Diverse

🟢 Purposes of the Present Work

Reduce full database to small representative database without loosing its diversity
— *more computationally efficient*

Benchmark Suites for Thermochemical Kinetics

Full Database

Database/3

Database/3 contains 44 BHs of HT reactions. It can be reduced to its representative subset HTBH6 only with 6 BHs.

NHTBH38/4

NHTBH38/04 includes 38 BHs for HAT, NS, and UA reactions. The three representative subsets of NHTBH38/04 contain 6 BHs for each of them.

This database includes 3 symmetric and 1 asymmetric HT reactions between methyl, methane, ethynyl, ethyne, and hydrogen. K6 means 5 BHs and 1 reaction energy.

Representative Database

HTBH6

+

HATBH6

+

NSBH6

+

UABH6

HCBH5 & HCK6

Features:
- **Computationally efficient**
- **Diverse**

$=$ **DBH24**

Abbreviations:
BH: Barrier Height
D: Diverse
HAT: Heavy-Atom Transfer
HC: Hydrocarbon
HT: Hydrogen Transfer
K: Kinetics
NS: Nucleophilic Substitution
UA: Unimolecular and Association

QM/MM
Combining QM & MM in real space — two approaches
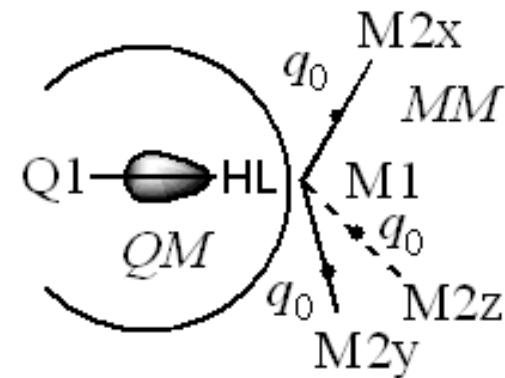
Quantum boundary   **Classical boundary**
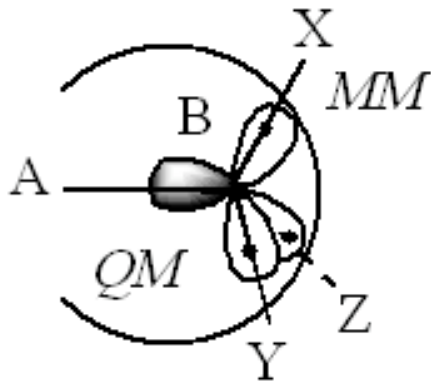
Examples:
LSCF, GHO, Pseudobond

Examples:
ONIOM, RCD

In CHARMM and CHARMMRATE.

**General QMMM program
available in Web
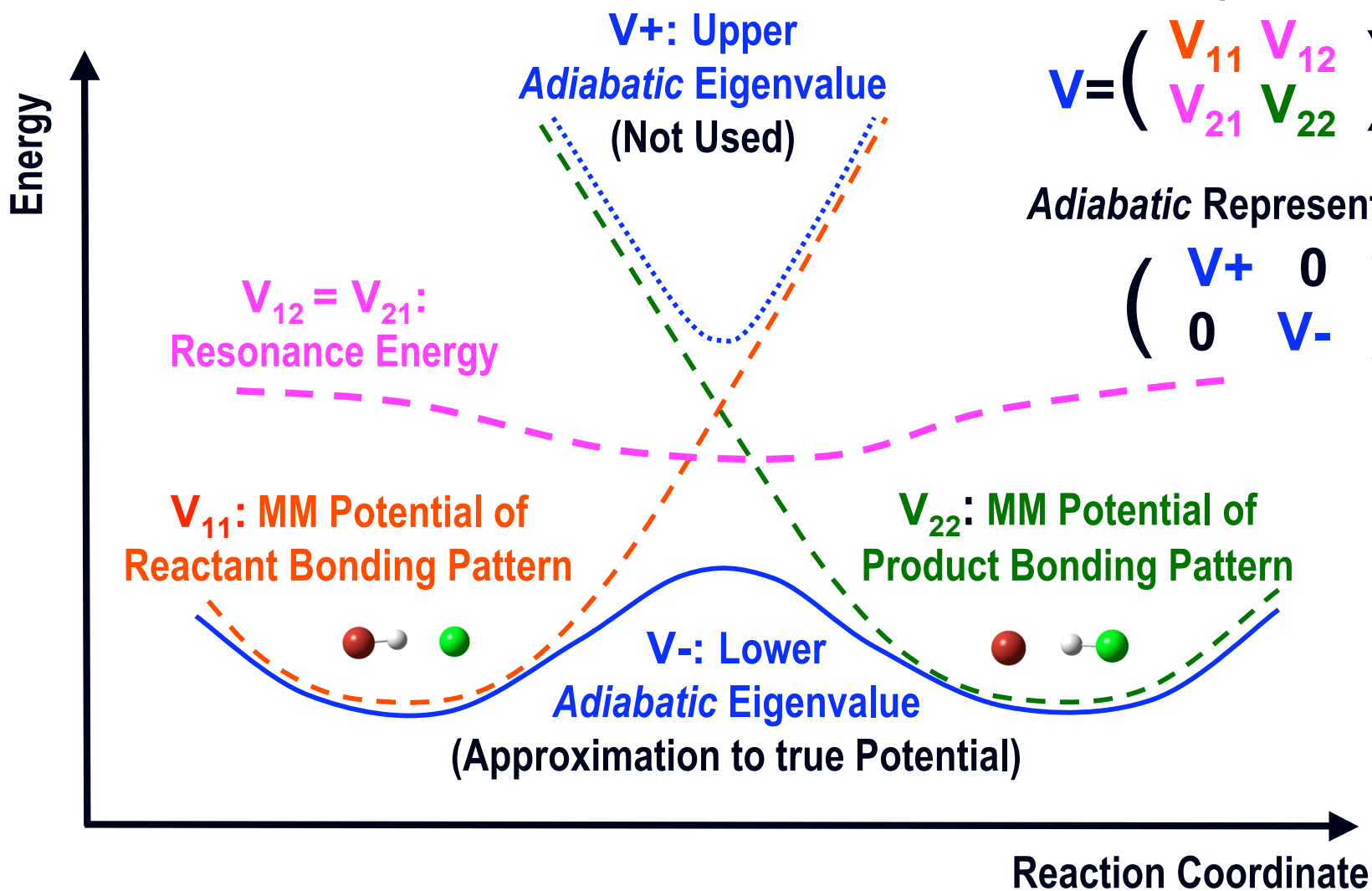(collaboration with Hai Lin,
Univ. of Colorado, Denver)**

MCMM
Combining QM & MM in configuration state space (not real space)

- **Standard molecular mechanics (MM) fails to describe reactions.**

- **Multi-configuration molecular mechanics (MCMM) is an extension of standard MM to treat reactions.**

Bonding pattern of reactant   *Resonance*   Bonding pattern of product

- **MCMM represents a reactive system at any a given geometry through multiple (usually two: reactant and product) interacting MM configurations.**

- **MCMM shares the same basic idea with**
    - **resonance theory (Pauling, organic chemistry)**
    - **semiempirical valence-bond theory**
    - **ab initio multi-configuration self-consistent field theory**

MCMM Representation

V+: Upper *Adiabatic* **Eigenvalue** (Not Used)

Diabatic Representation:

$$V = \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix}$$

Adiabatic Representation:

$$\begin{pmatrix} V+ & 0 \\ 0 & V- \end{pmatrix}$$

$V_{12} = V_{21}$: Resonance Energy

V_{11}: MM Potential of Reactant Bonding Pattern

V_{22}: MM Potential of Product Bonding Pattern

V-: Lower *Adiabatic* **Eigenvalue** (Approximation to true Potential)

Energy

Reaction Coordinate

MCMM Based on QM/MM

- **Use QM/MM as the high-level electronic-structure method.**

- **Examples**

(1) OH + Propane

(2) OH + Camphor

mechanical embedding

electronic embedding
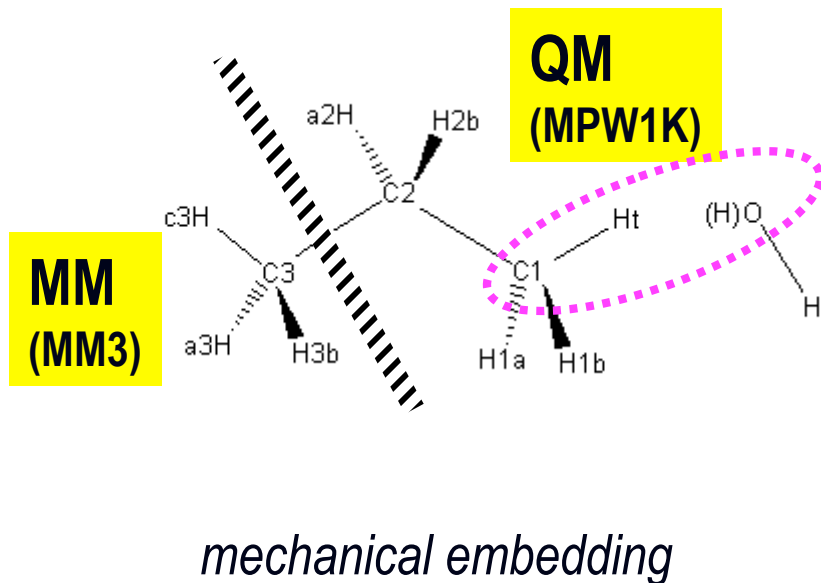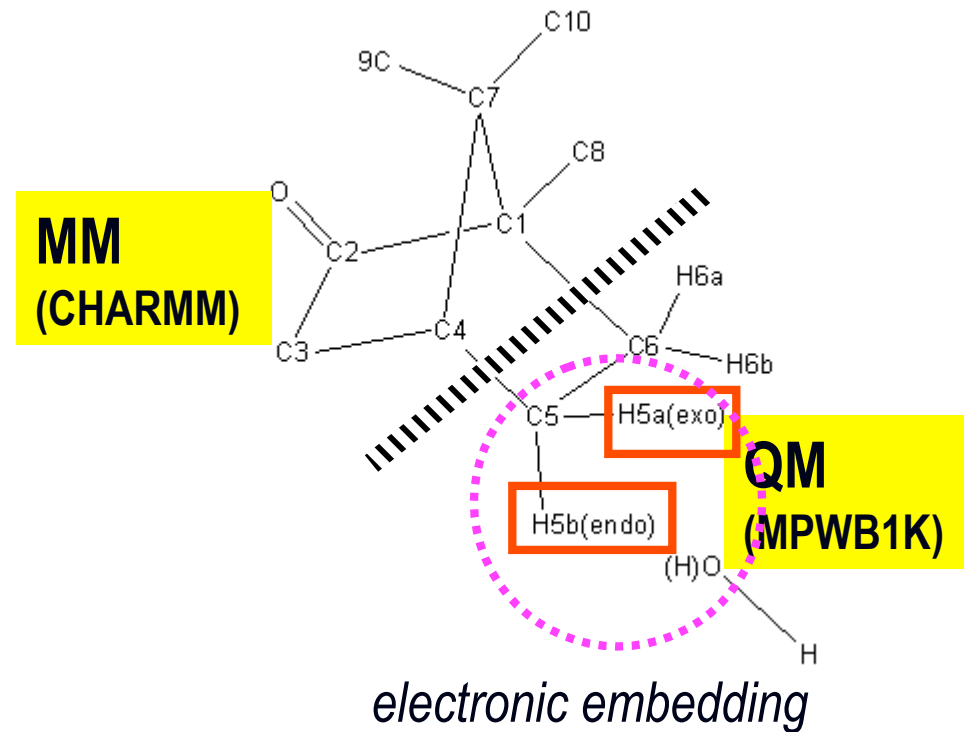
7 QM Hessians (converge rates to 2%)

Diffusion of Water in Silica

- Silica (SiO_2) is found in nature in several forms, including quartz and opal. In fact, 35 crystalline forms have been identified. It is the major component of sand.

- Silica is used as:
  - Support in liquid chromatography
  - Industrial catalyst
  - Catalytic support

- Silicate melts containing water play an important role in magmatic flow in the Earth's crust.

Aim: Better understanding of the diffusion process of water in silica

$$Si\text{-}O\text{-}Si + H_2O \leftrightarrow 2(SiOH)$$

Advantages of Computer Simulations:

- Can study processes at high temperatures and pressures, under electromagnetic fields, etc.
- QM calculations can provide accurate information about structural, dynamic, and electronic properties of hydrogenated silicates.
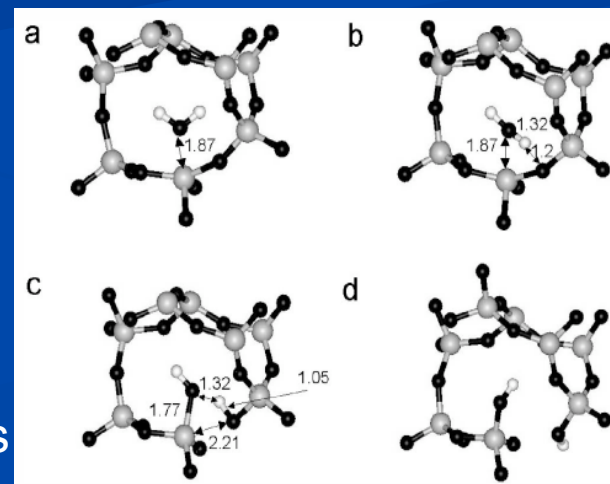
Stages of the $Si\text{-}O\text{-}Si + H_2O \leftrightarrow 2(SiOH)$ reaction (PRL, **2002**, *88*, 55508)

See separate research highlight for kinetics studies involving enzymes and nanoparticles..

Electrostatically Embedded Many-Body Expansion (EE-MB)

EE-MB Method

1. Break up the cluster of N molecules into all possible monomers, dimers, and trimers.
2. Embed each monomer, dimer, or trimer in a field of point charges representing the other $N-1$, $N-2$, or $N-3$ molecules.
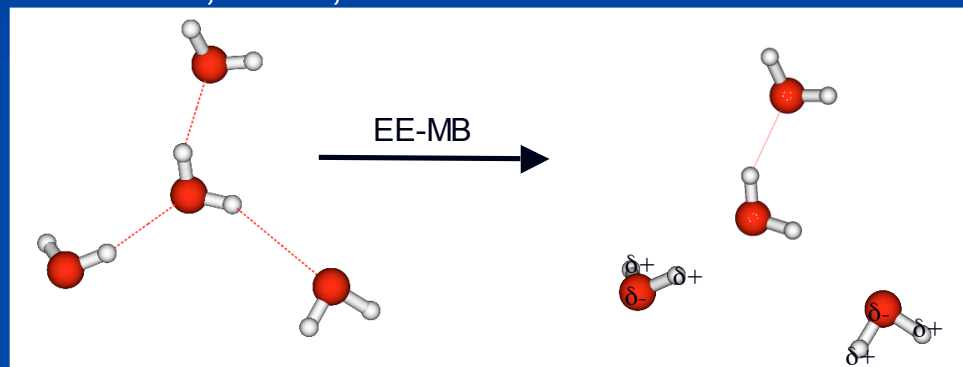
EE-MB

3. Calculate the total energy of the system using

$$E_{EE-PA} = \sum_{i<j}^{N} E_{ij} - (N-2)\sum_{i}^{N} E_i$$

$$E_{EE-3B} = \sum_{i<j<k}^{N} E_{ijk} - (N-3)\sum_{i<j}^{N} E_{ij} - \frac{(N-3)(N-2)}{2}\sum_{i}^{N} E_i$$

where E_i, E_{ij}, and E_{ijk} are the energies of the embedded monomers dimers and trimer from

Results for water 21-mer
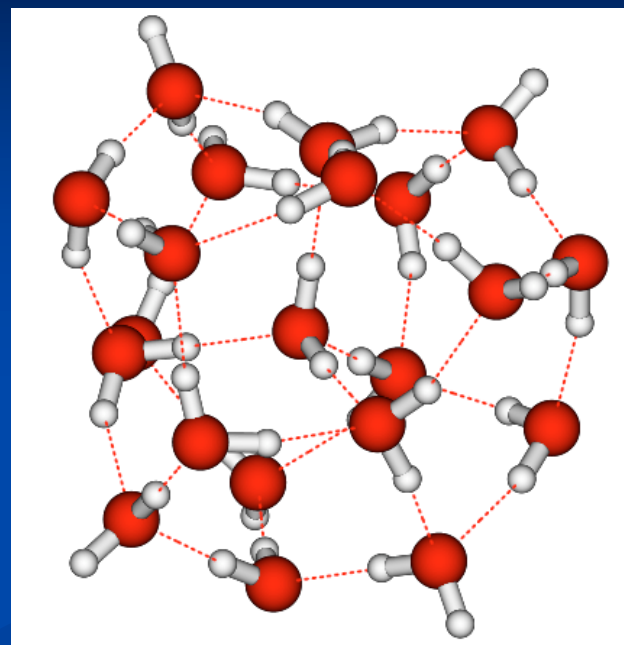
Method	E_{bind}	ΔE
Full Cluster	203.64	
EE-PA	206.61	2.97
EE-3B	204.02	0.38

All calculations use the MP2 level of theory with the aug-cc-pVTZ basis set on O and the cc-pVTZ basis set on H
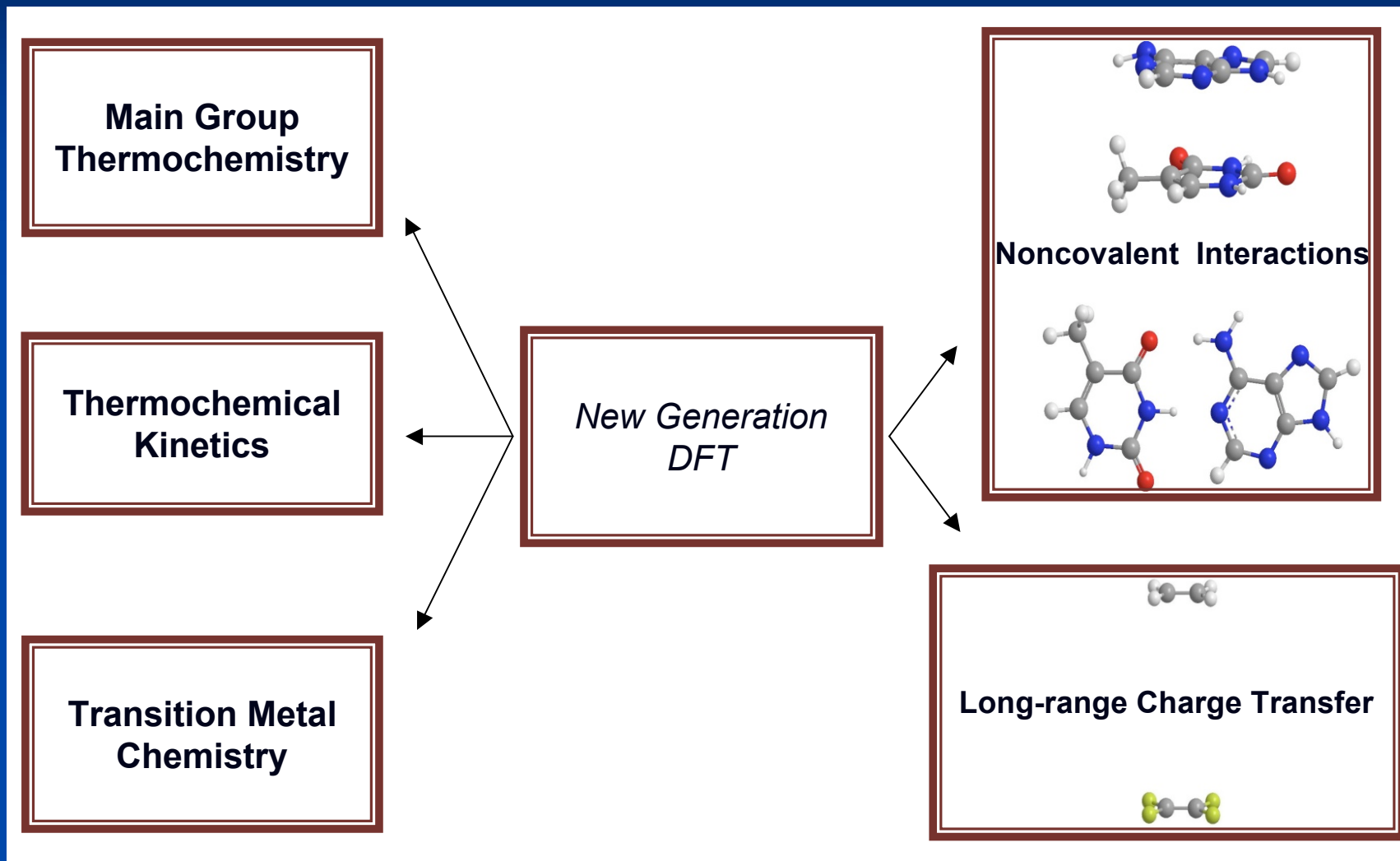
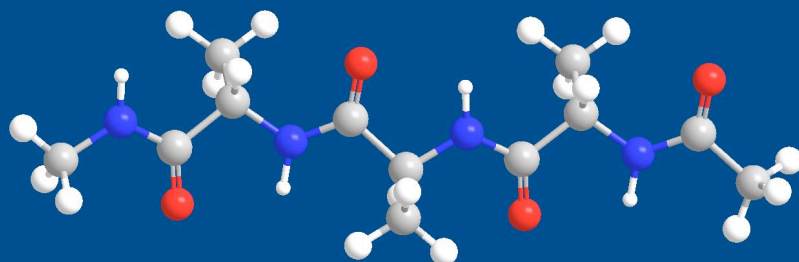New Accurate and Transferable DFT Methods for the Study of Water and Ice
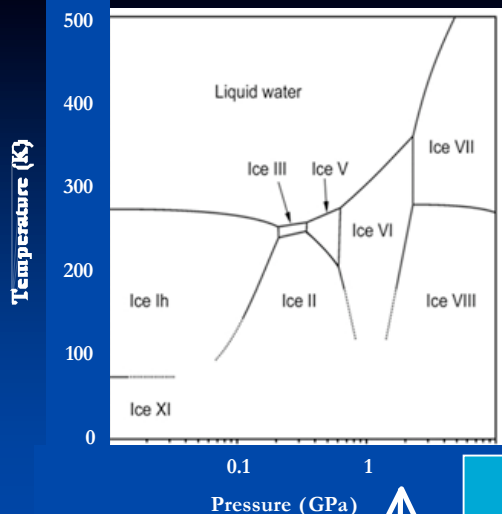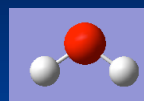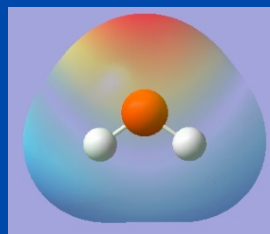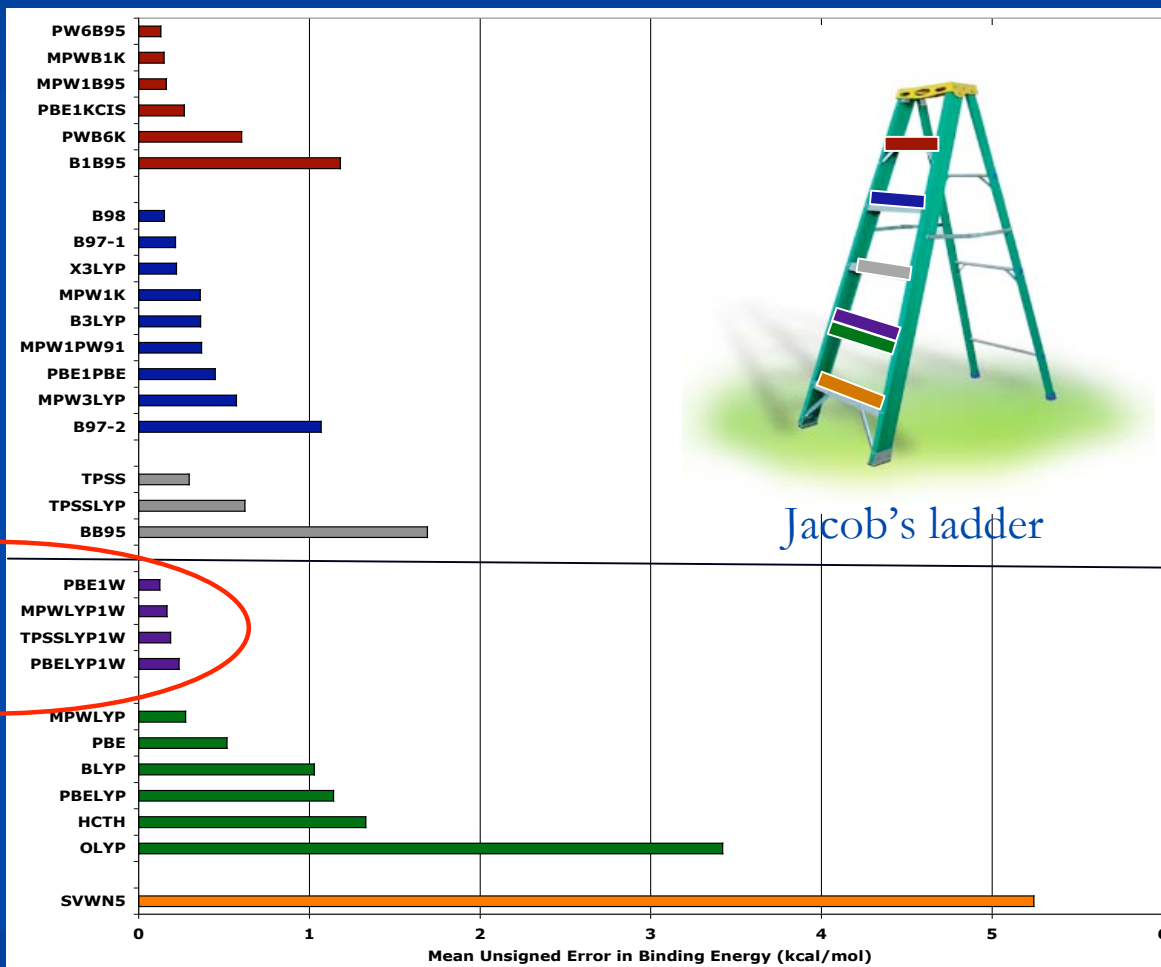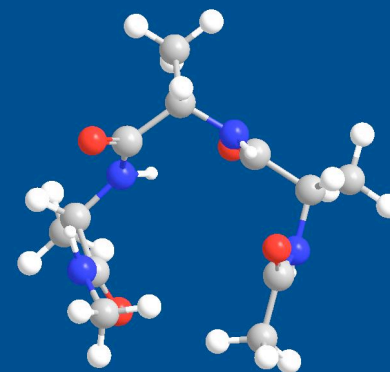
Next Generation of Density Functional Theory

Conformational energy of alanine tetrapeptide

Linear (L)　　　　　　　　　　　　　　　　　　Globular (G)

	Method	E(L) − E(G) (kcal/mol)
Best estimate [a]	RI-MP2/CBS [a]	3.6
Old DFT	B3LYP	-0.4
	PBE0	0.4
	TPSSh	0.3
New DFT	M06-2X	2.4

[a] R. A. DiStasio, Y. Jung, M. Head-Gordon, J. Chem. Theory Comput. **1**, 862 (2005).
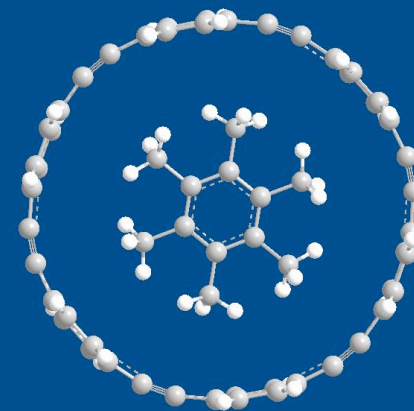
Carbon nanoring - I
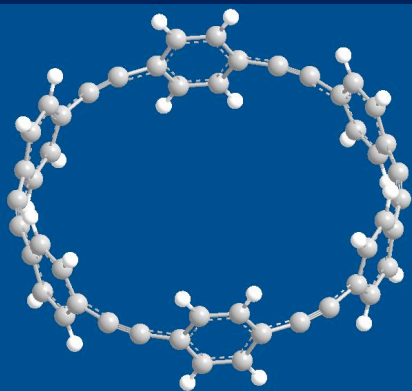
6-cycloparaphenilacetylene
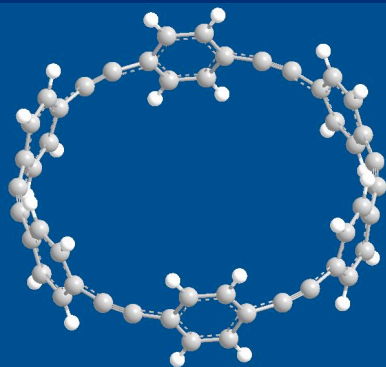(6-CPPA)

+
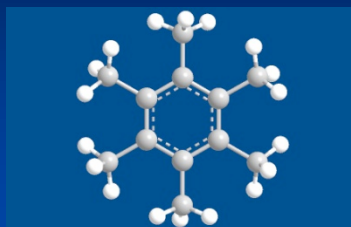
hexamethylbenzene
(HMB)

→

HMB@6-CPPA

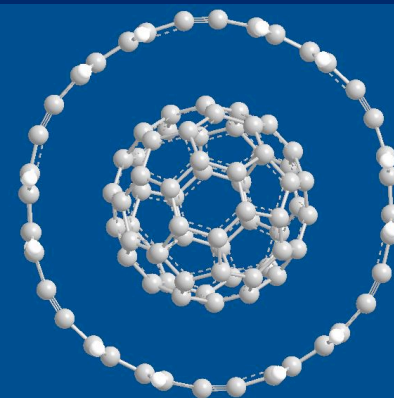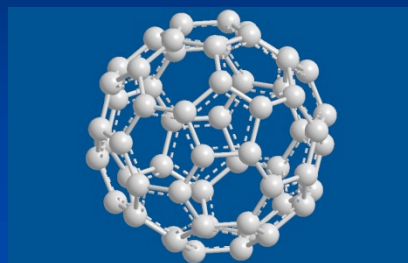| Method	Binding Energy (kcal/mol)
Best estimate [a]	14 ~ 19
B3LYP/6-31+G(d,p)	-5.46
M06-2X/6-31+G(d,p)	14.7

[a] I. G. Guesta, T. B. Pedersen, H. Koch, and A. Sanchez de Meras, ChemPhysChem, **7**, 2503 (2006)
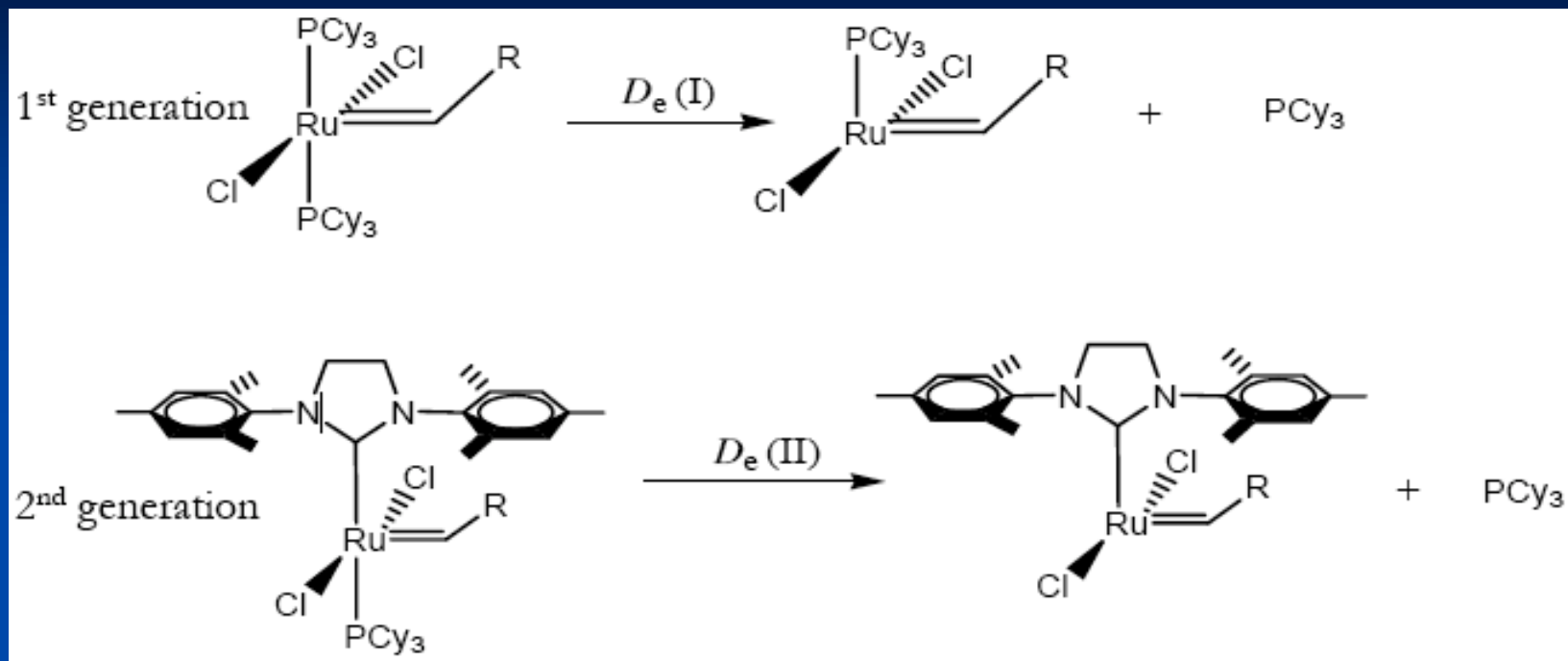
Carbon nanoring - II

6-cycloparaphenilacetylene
(6-CPPA)

C60

C60@6-CPPA

Method	Binding Energy (kcal/mol)
M06-2X/6-31+G(d,p)	24.9

Metathesis: 'Grubbs type' catalysts

	$D_e(II) - D_e(I)$ (kcal/mol)
experiment	+4
Density functionals in literature	-2 to -1
New Minnesota functional	+4

Why do these two pre-catalysts have different dissociation energies? Medium-range correlation energy