# Integrated Tools for Computational Chemical Dynamics

- **Develop powerful simulation methods and incorporate them into a user-friendly high-throughput integrated software suite for chemical dynamics**

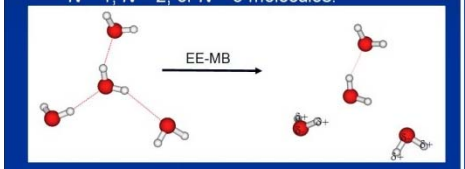
New Models (Methods) → Modules → Integrated Tools

# Development of new methods for the calculation of potential energy surface

## 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.




3. Calculate the total energy of the system using

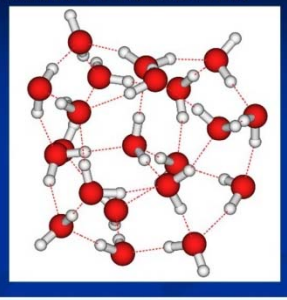
$$E_{\mathrm{EE-PA}} = \sum_{i<j}^{N} E_{ij} - (N-2)\sum_{i}^{N} E_i$$

or

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

where $E_i$, $E_{ij}$, and $E_{ijk}$ are the energies of the embedded monomers dimers and trimer from step 2.

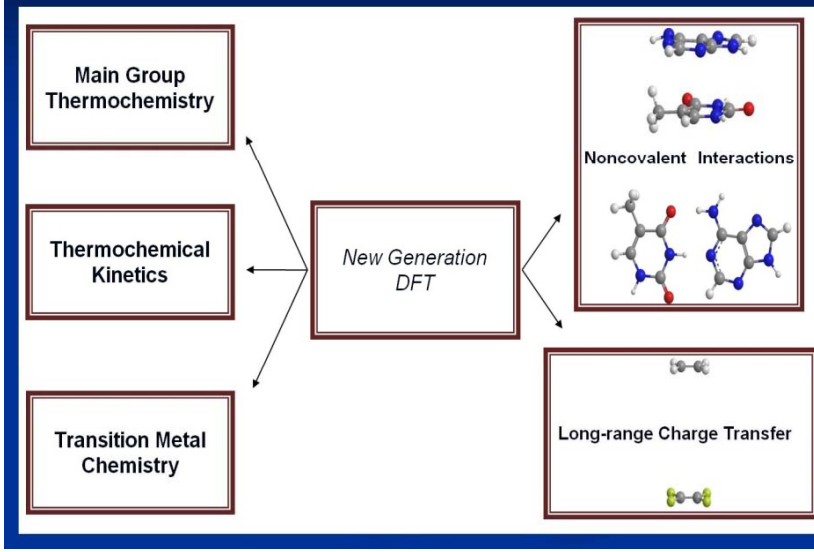
Results for water 21-mer



| Method | $E_{bind}$ | %ΔE | Time (hr) |
|---|---|---|---|
| Full Cluster | 203.64 | | 688 |
| EE-PA | 206.61 | 1.46 | 8 |
| EE-3B | 204.02 | 0.18 | 55 |

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

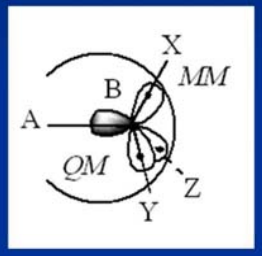
## Next Generation of Density Functional Theory




## QM/MM

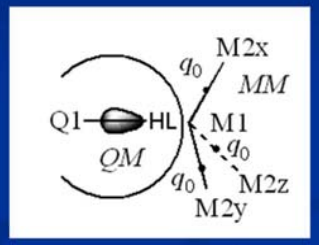
Combining QM & MM in real space — two approaches

**Quantum boundary**




*Examples:*
LSCF, GHO, Pseudobond

**Classical boundary**

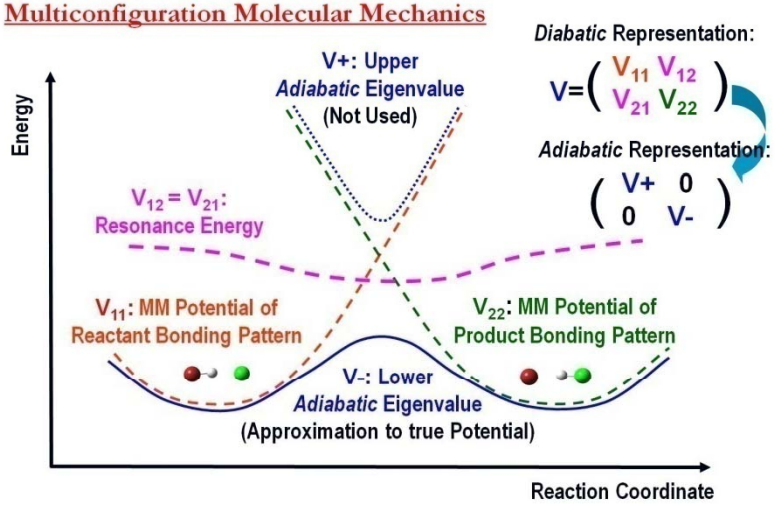



*Examples:*
ONIOM, RCD

In CHARMM and CHARMMRATE.

General QMMM program available in Web

## Multiconfiguration Molecular Mechanics



# Development of new simulation methods

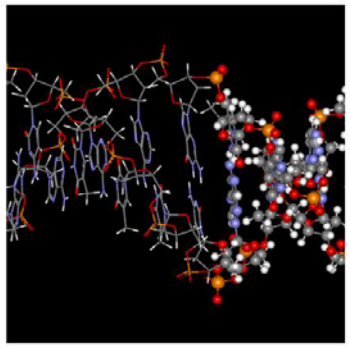
## Adaptive Partitioning in Multilevel and Multiscale Simulations

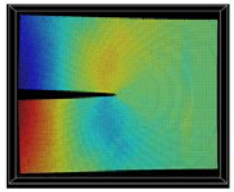
We have developed an algorithm that enables the use of multilevel and multiscale simulation methods for systems where the **active region** is **not localized** and atoms enter and leave the active region during the simulation.

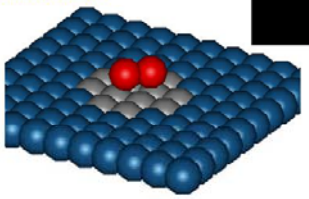
Examples include:

- Ligand exchange in solution
- Crack propagation in a material
- Diffusion and reaction on nanoparticles

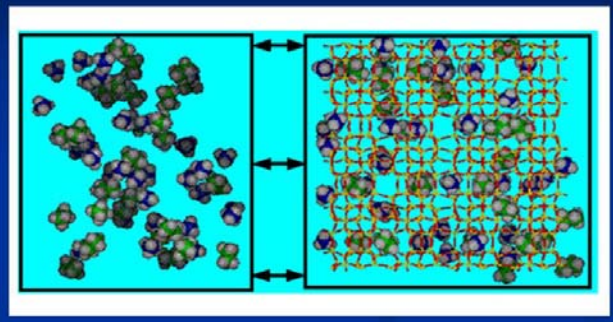
⇒ **Can study larger systems over longer time scales without loss of accuracy!**







## Grand Canonical Monte Carlo (GCMC) Module for Simulations of Heterogeneous Catalysis

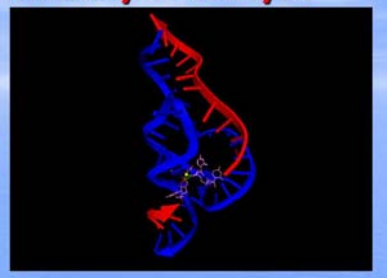


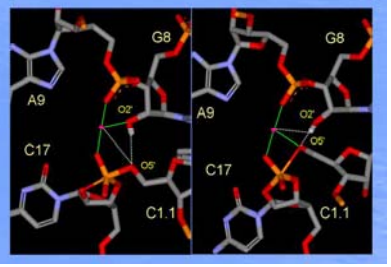
A Grand Canonical Monte Carlo (GCMC) module for the simulation of adsorption isotherms in heterogeneous catalysts has been written and validated. This MC module was written in a general way such that it may be seamlessly integrated into a larger simulation software suite. The purpose of the integration is to facilitate the use of various QM, MM, QM/MM, and/or semi-empirical energy routines to compute the configuration energies that are used in a MC simulation.

# Applications and Validations

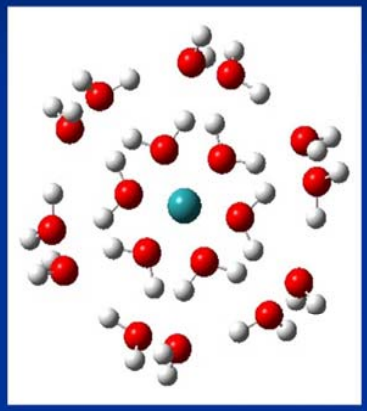
## Molecular dynamics simulation reveals insight into the role of $Mg^{2+}$ in hammerhead ribozyme catalysis

- RNA catalysis is an important heterogeneous catalytic process that spans large spatial domains and long time scales.
- An understanding of mechanism requires the use of multi-scale quantum models combined with molecular simulation.
- The very recent full-length hammerhead ribozyme (*Cell*, 2006) is an archetype system to study RNA catalysis.
- Computational resources from the Grand-Challenge have been utilized to perform molecular dynamics simulations including QM/MM simulations of the fully solvated system.
- The simulation results provide detailed insight into the role of catalytic $Mg^{2+}$ ion cofactors that are consistent with available experimental data.



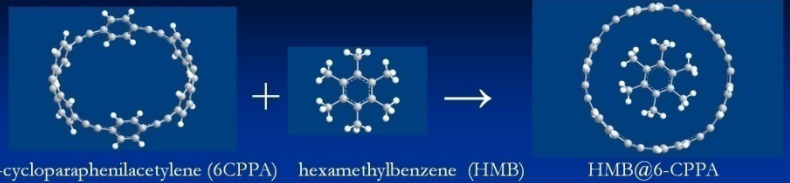



## Solvation Effects and Computational Electrochemistry



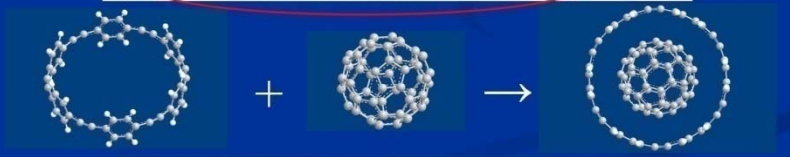
We have developed implicit solvation models for ions and neutral molecules in water and nonaqueous media. We showed how these can be combined with DFT and up to 18 explicit waters to predict the standard reduction potential of ions in solution.

## Suprachemistry in a Hydrocarbon Nanoring



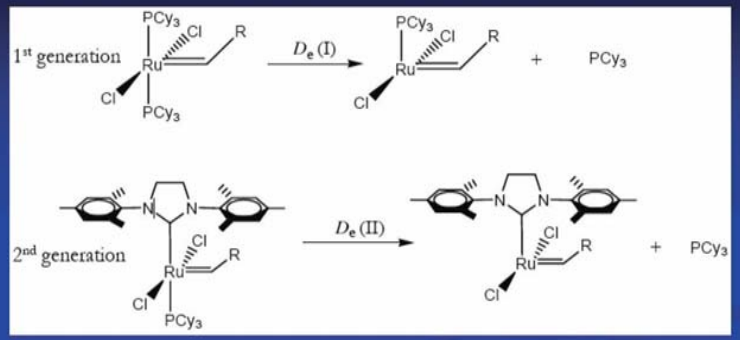
6-cycloparaphenilacetylene (6CPPA) hexamethylbenzene (HMB) HMB@6-CPPA

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



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

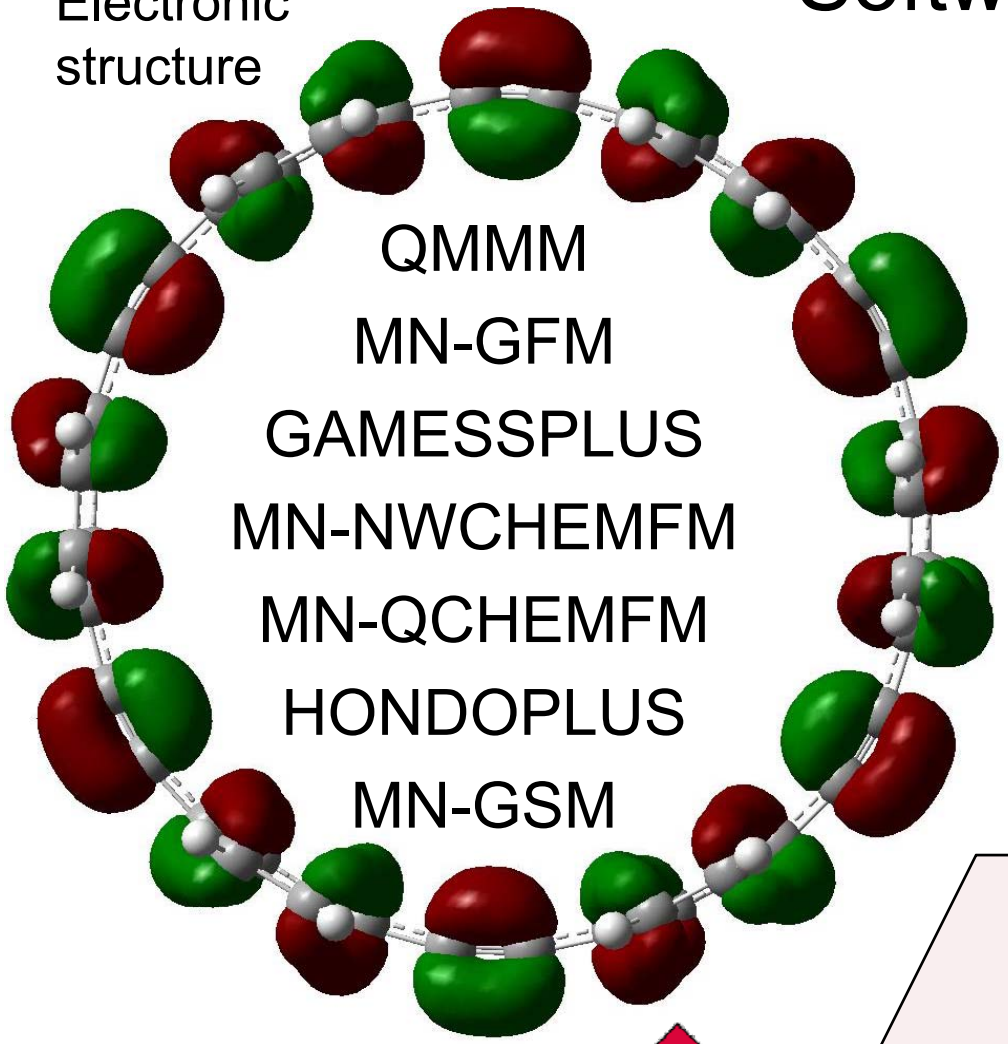
## Metathesis: 'Grubbs type' catalysts




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

# Software

Electronic structure



QMMM

MN-GFM

GAMESSPLUS

MN-NWCHEMFM

MN-QCHEMFM

HONDOPLUS

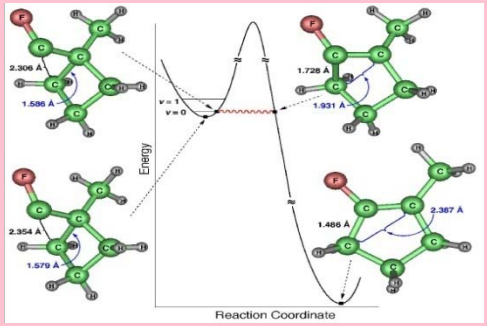
MN-GSM

Dynamics

ANT

GCMC

POLYRATE




Interfaces

GaussRate

JaguarRate

NWChemRate

# Electronic Structure Software

**QMMM 1.3**: QMMM is a computer program for combining quantum mechanics (QM) and molecular mechanics (MM).

**MN-GFM 3.0**: MN-GFM is a module incorporating Minnesota DFT functionals into GAUSSIAN 03.

**MN-GSM 6.2**: MN-GSM is a module incorporating the SMx solvation models and other enhancements into GAUSSIAN 03.

**MN-NWCHEMFM 2.0**:MN-NWCHEMFM is a module incorporating Minnesota DFT functionals into NWChem 5.0.

**MN-QCHEMFM 1.0**: MN-QCHEMFM is a module incorporating Minnesota DFT functionals into Q-CHEM.

**GAMESSPLUS 4.8**: GAMESSPLUS is a module incorporating the SMx solvation models and other enhancements into GAMESS.

**HONDOPLUS 5.1**: HONDOPLUS is a computer program incorporating the SMx solvation models and other photochemical diabatic states into HONDO.

# Dynamics Software

**ANT 07**: ANT is a molecular dynamics program for performing classical and semiclassical trajectory simulations for adiabatic and nonadiabatic processes.
**GCMC**: GCMC is a Grand Canonical Monte Carlo (GCMC) module for the simulation of adsorption isotherms in heterogeneous catalysts.
**POLYRATE 9.6**: POLYRATE is a computer program for the calculation of chemical reaction rates of polyatomic species.

# Interfaces Software

**GaussRate 9.5**: GaussRate is a computer program interfacing POLYRATE and GAUSSIAN for direct dynamics calculations.
**JaguarRate**: JaguarRate is a computer program interfacing POLYRATE and JAGUAR for direct dynamics calculations.
**NWChemRate**: NWChemRate is a computer program interfacing POLYRATE and NWChem for direct dynamics calculations.