Motivations
Modeling catalytic systems with quantum chemical methods is important for understanding the detailed mechanisms of catalytic processes, and it is the first step in the rational design of catalysts. Although most catalytic systems are too large to be modeled by reliable wave function theory (WFT), density functional theory (DFT) is a good choice if we have reliable exchange-correlation functionals. In recent years, our group has developed several functionals with broad applicability. We have tested our new Minnesota functionals and other popular functionals against diverse and representative bond energies and barrier heights which are relevant to catalysis to ascertain their performance, as judged for example by the mean unsigned error (MUE) relative to benchmark data. We have also tested the functionals for prototype catalytic systems such as palladium complexes with polyenes, zeolites complexes with isobutene, and Grubbs olefin metathesis catalysts. The results of these methods were compared to experimental values and those from accurate WFT methods including BCCD(T) and CCSD(T)-F12.

Team
Boris Averkiev, Ke Yang, Anant Kulkarni, Jingjing Zheng, Yan Zhao, and Donald G. Truhlar

Representative database for catalysis (RDC42):
- 6 atomization energies of small molecules
- 4 alkyl bond dissociation energies (BDEs)
- 4 bond energies of transition metal dimers
- 4 metal-ligand bond energies of transition metal complexes
- 24 barrier heights for H atom transfer, heavy-atom transfer, nucleophilic substitution, and unimolecular & association reactions.

Pd–polyene bond dissociation energies
1 = Pd(PH₃)₂C₂H₄  2 = Pd(PH₃)₂C₁₀H₁₂

Method | 1 | 2 | MUE
B3LYP  | 10.2 | -1.5 | 10.7
BP86   | 17.2 | 5.9 | 6.5
PBE0   | 18.0 | 8.8 | 5.1
M06    | 13.4 | 11.5 | 2.5
M06-L-D| 17.8 | 14.6 | 1.5
M06-D  | 14.6 | 14.9 | 1.3
Best estimate | 17.6 | 17.3 |

Isobutene adsorption energies in zeolites

Method | 1 | 2 | 3 | 4 | MUE
B3LYP  | -2.5 | -5.5 | -20.7 | -4.8 | 16.6
TPSSh  | -0.9 | 1.8 | -17.7 | 1.6 | 12.1
PBE0   | 2.9 | 4.7 | -15.6 | 4.7 | 9.1
M06    | 13.3 | 16 | -3.9 | 14.4 | 2.6
M06-L  | 14.4 | 15.6 | -2.3 | 13.5 | 2.6
M06-2X | 12.7 | 16.6 | -9.1 | 15.6 | 1.9
Best estimate | 15.1 | 13.9 | -9.8 | 13.9 |

All energies in kcal/mol