AFOSR
Orbital-Dependent Density Functionals for Chemical Catalysis

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Motivations

Modeling catalytic systems with quantum chemical methods is important for understand 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 more affordable and can be 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

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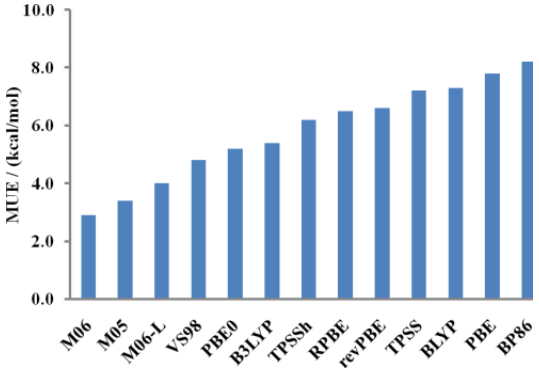
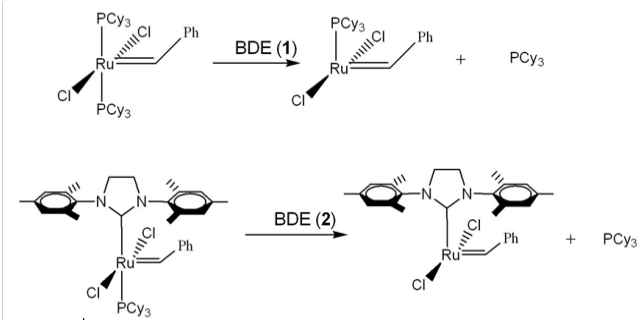
Representative database for catalysis (RDC42):

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.



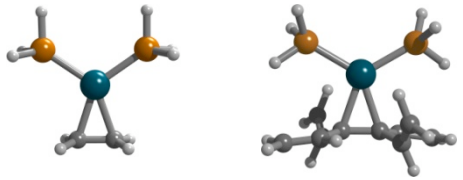
The mean unsigned errors of the Minnesota functionals and other popular functionals for the RDC42 database

Grubbs catalysts for olefin metathesis



	BDE(1)	BDE (2)	difference
B3LYP (gas)	16	14	+2
M06-L (gas)	34	38	-4
experiment (gas)	34	37	-3

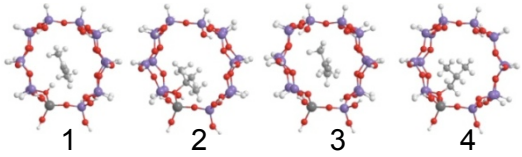
Pd–polyene bond dissociation energies



1 = $Pd(PH_3)_2C_2H_4$ 2 = $Pd(PH_3)_2C_{10}H_{12}$

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



1 2 3 4

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