

Advances in New Density Functionals for Computational Chemical Dynamics

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Oct. 18, 2007

Outline

■ Why?

- Shortcomings and Limitations of Popular Functionals

■ How?

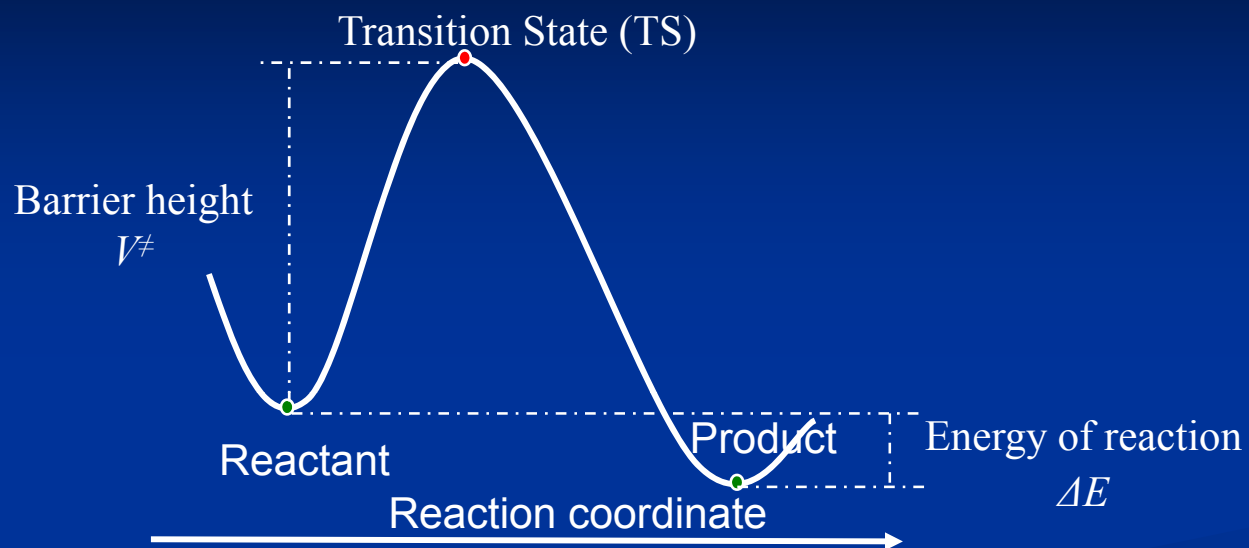
- Constraints and Parametrizations

■ What?

- Performance for Databases
- Performance for Difficult cases

■ Future Plans

Calculating Potential Energy Surfaces for Computational Chemical Dynamics



Increasing Chemical Accuracy ↑

Wave Function Theory

Density Functional Theory

Semi-Empirical Molecular Orbital Methods

Molecular Mechanics

↓ Decreasing Computational Costs

Shortcomings of Popular Functionals

- Schreiner, Peter R. **Relative Energy Computations with Approximate Density Functional Theory - Caveat** *Angewandte Chemie, International Edition* (2007), 46(23), 4217-4219.
- Grimme, Stefan; Steinmetz, M; Korth, M. **Stereoelectronic Substituent Effects in Saturated Main Group Molecules: Severe Problems of Current Kohn-Sham Density Functional Theory.** *Journal of Chemical Theory and Computation* (2007), 45(27), 4460-4464
- Schreiner, Peter R.; Fokin, Andrey A.; Pascal, Robert A., Jr.; De Meijere, Armin. **Many Density Functional Theory Approaches Fail To Give Reliable Large Hydrocarbon Isomer Energy Differences.** *Organic Letters* (2006), 8(17), 3635-3638.
- Wodrich, Matthew D.; Corminboeuf, Clemence; Schleyer, Paul von Rague. **Systematic Errors in Computed Alkane Energies Using B3LYP and Other Popular DFT Functionals.** *Organic Letters* (2006), 8(17), 3631-3634
- Check, Catherine E.; Gilbert, Thomas M. **Progressive Systematic Underestimation of Reaction Energies by the B3LYP Model as the Number of C-C Bonds Increases: why Organic Chemists Should Use Multiple DFT Models for Calculations Involving Polycarbon Hydrocarbons.** *Journal of Organic Chemistry* (2005), 70(24), 9828-9834.
- Izgorodina, Ekaterina I.; Coote, Michelle L.; Radom, Leo. **Trends in R-X Bond Dissociation Energies (R = Me, Et, i-Pr, t-Bu; X = H, CH₃, OCH₃, OH, F): A Surprising Shortcoming of Density Functional Theory.** *Journal of Physical Chemistry A* (2005), 109(33), 7558-7566.

Popular Density Functionals

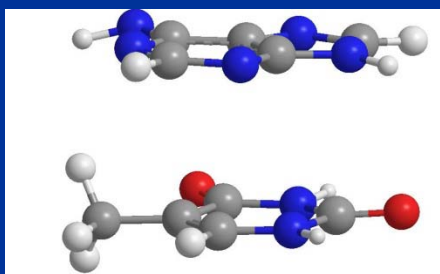
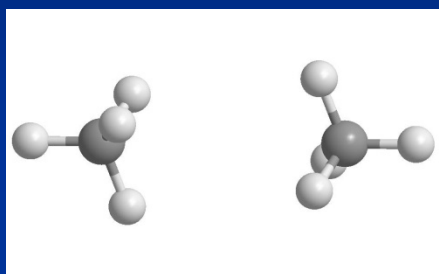
B3LYP 1994

PBEh (PBE0) 1999

TPSSH 2003

Limitations of the Popular Functionals:

I. Noncovalent Interaction



Stacked adenine...thymine

Binding energies (kcal/mol)

Method	$(\text{CH}_4)_2$	Stacked A...T
Best Estimate ^a	0.5	12.2
B3LYP	-0.4	-1.5
PBEh	0.0	2.3
TPSSh	-0.2	-0.0

^a P. Jurecka, J. Sponer, J. Cerny, and P. Hobza, *Phys. Chem. Chem. Phys.* **8**, 1985 (2006).

Limitations of the Popular Functionals:

II. Barrier Heights

Barrier Heights (kcal/mol)

Method	X^*	$\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$	$\text{Cl}^- + \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 + \text{Cl}^-$
Best Estimate ^a		9.6	3.1
B3LYP	20	4.3	-0.5
PBEh	25	5.8	0.9
TPSSh	10	1.3	-3.1

^a B. J. Lynch, P. L. Fast, M. Harris, and D. G. Truhlar, *J. Phys. Chem. A* **104**, 4811 (2000);
Y. Zhao, N. González-García, and D. G. Truhlar, *J. Phys. Chem. A* **109**, 2012 (2005).

* X : percentage of Hartree-Fock exchange in each functional.

Limitations of the Popular Functionals:

III. Transition Metal Chemistry

Bond Dissociation Energies (kcal/mol)

Method	X^*	$V_2 \rightarrow 2V$	$CuF \rightarrow Cu + F$
Best Estimate ^a		64.2	102.5
B3LYP	20	27.0	93.1
PBEh	25	7.6	92.5
TPSSh	10	39.6	95.9

^a F. Furche and J. P. Perdew, J. Chem. Phys. **124**, 044103 (2006).

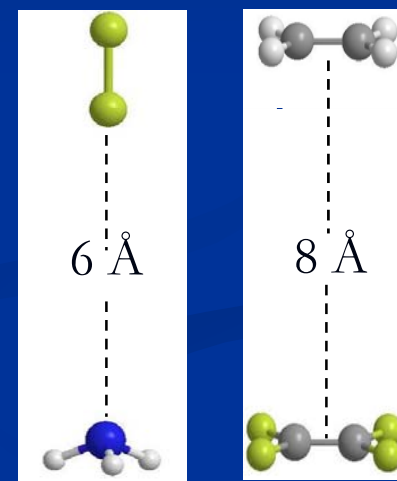
* X : percentage of Hartree-Fock exchange in each functional.

Limitations of the Popular Functionals:

IV. Long-range Charge Transfer

Charge Transfer Excitation Energies (eV) via TDDFT

Method	X	$\text{NH}_3 \cdots \text{F}_2$	$\text{C}_2\text{H}_4 \cdots \text{C}_2\text{F}_4$
Best Estimate ^a		9.5	12.6
B3LYP	20	2.2	7.0
PBEh	25	2.8	7.4
TPSSh	10	1.5	6.4



^a Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A* **110**, 13126 (2006);
Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, and K. Hirao, *J. Chem. Phys.* **121**, 8425 (2004).

How do we develop new functionals?



Functional Developers



Blind Men

Exact Functional



Elephant

Constraints and Parametrization

Functional	Constraints			Training Sets			
	UEG	SCorF	HF	TC	BH	NC	TM
M06-L	√	√	0	√	√	√	√
M06	√	√	Opt	√	√	√	√
M06-2X	√	√	2X	√	√	√	
M06-HF	√	√	Full	√	√	√	

UEG: uniform electron gas limit

SCorF: self-correlation free

HF: Hartree-Fock exchange

TC: main-group thermochemistry

BH: barrier heights

NC: noncovalent interactions

TM: transition metal chemistry

Tested Functionals



BLYP
B3LYP
B98

Axel D. Becke



BMK

Jan Martin



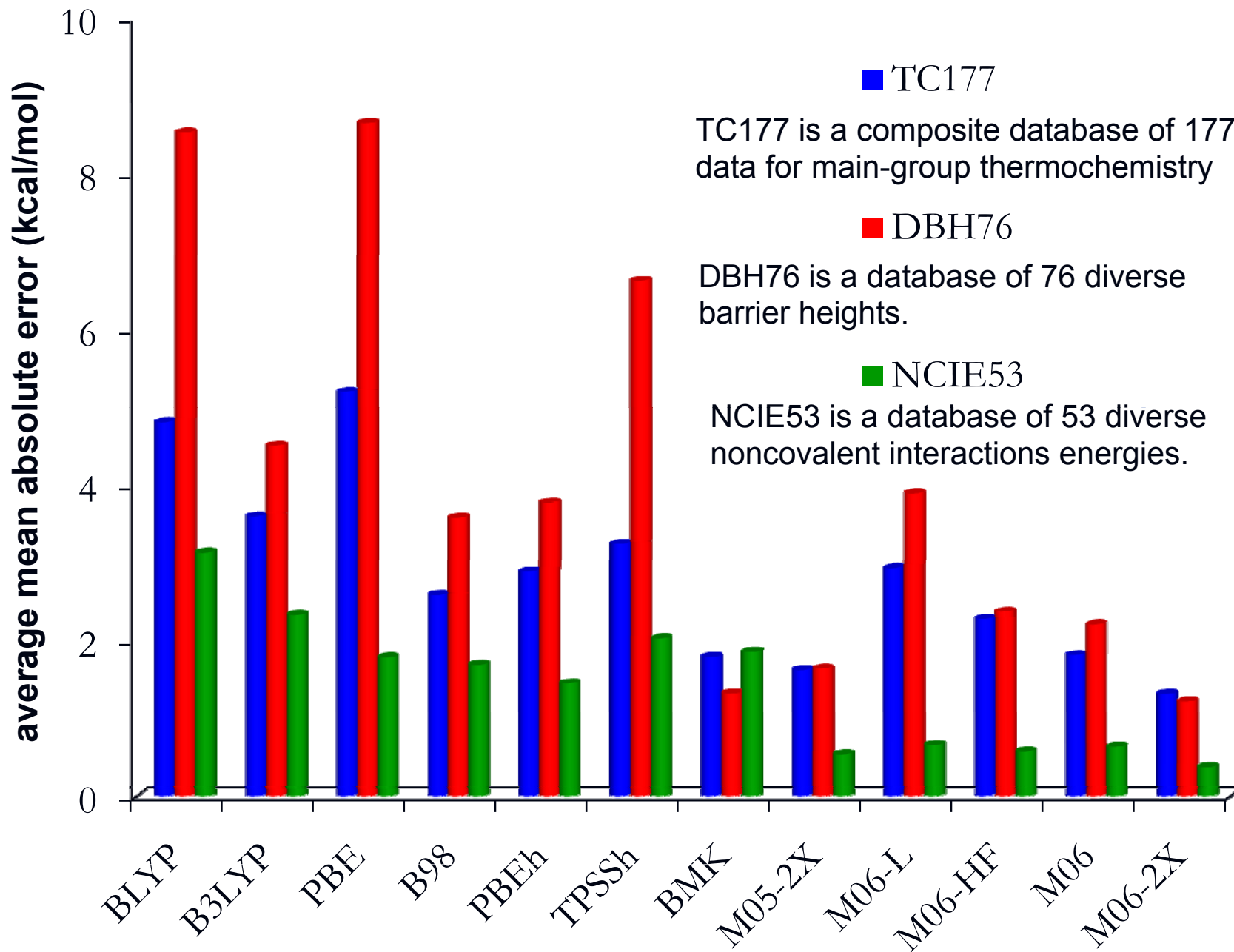
PBE
PBEh
TPSSh

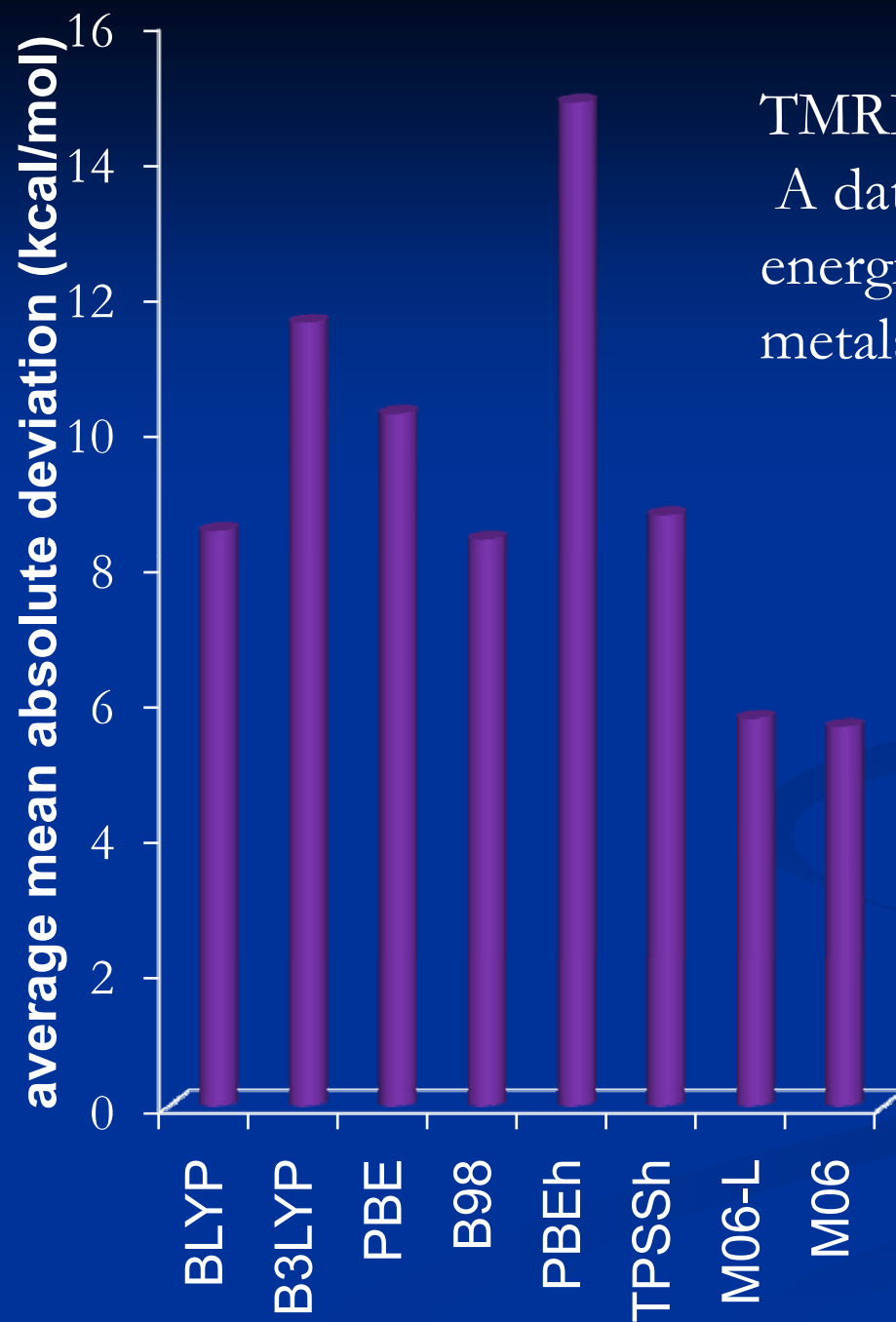
John P. Perdew



M05-2X
M06 suite

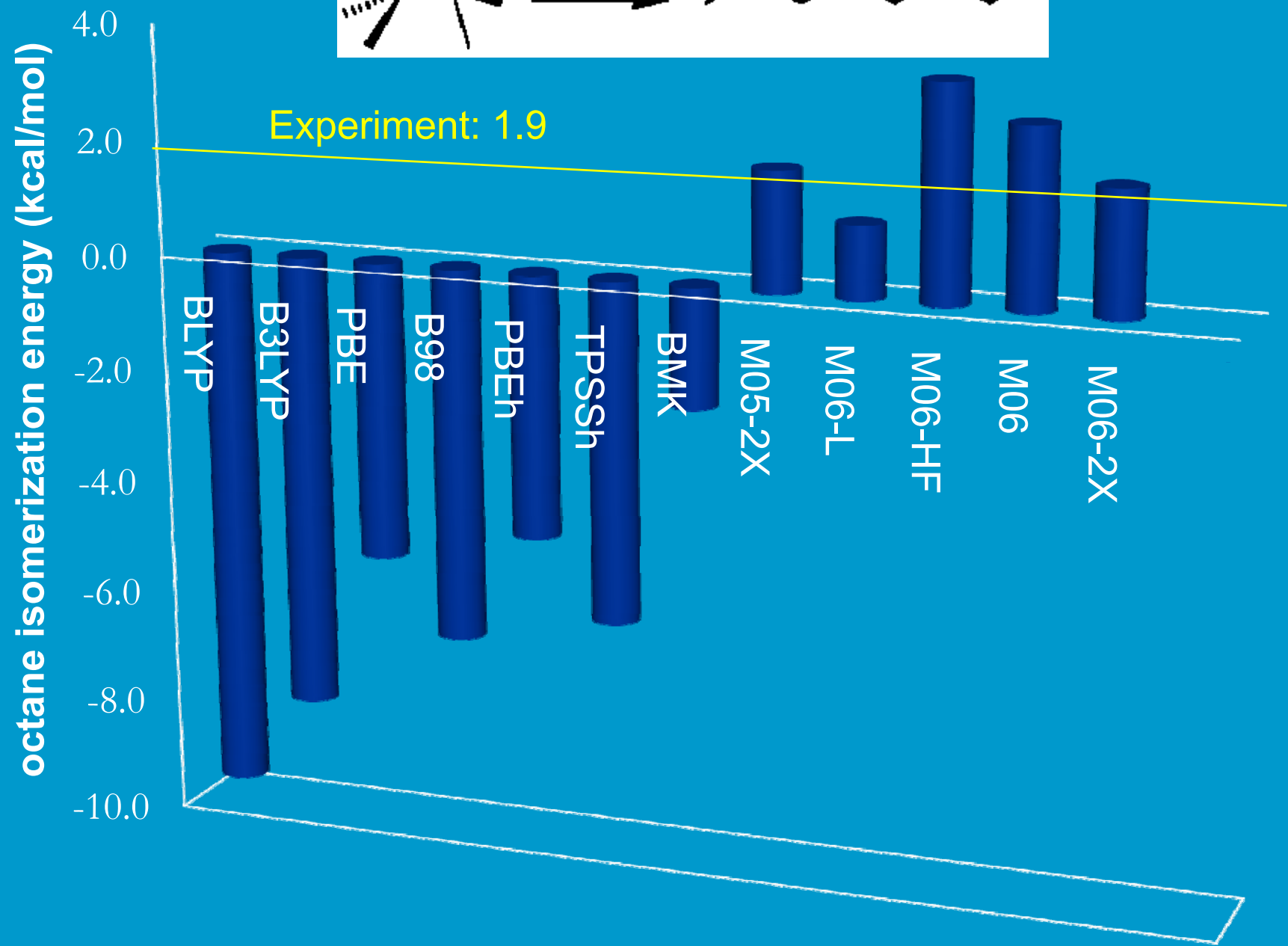
Don Truhlar

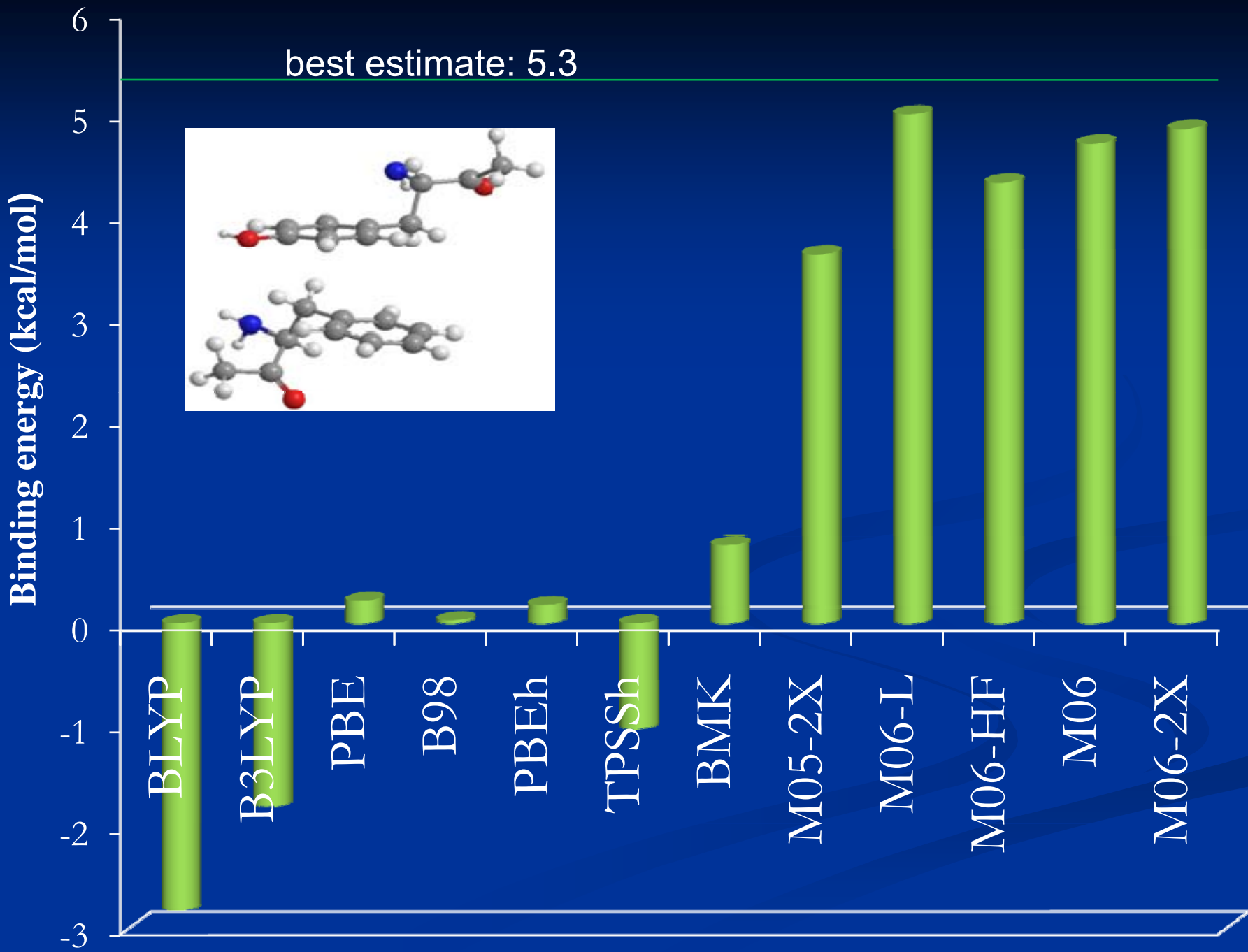


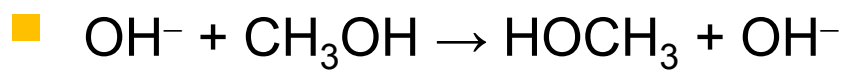
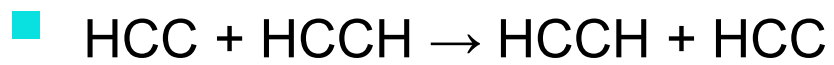
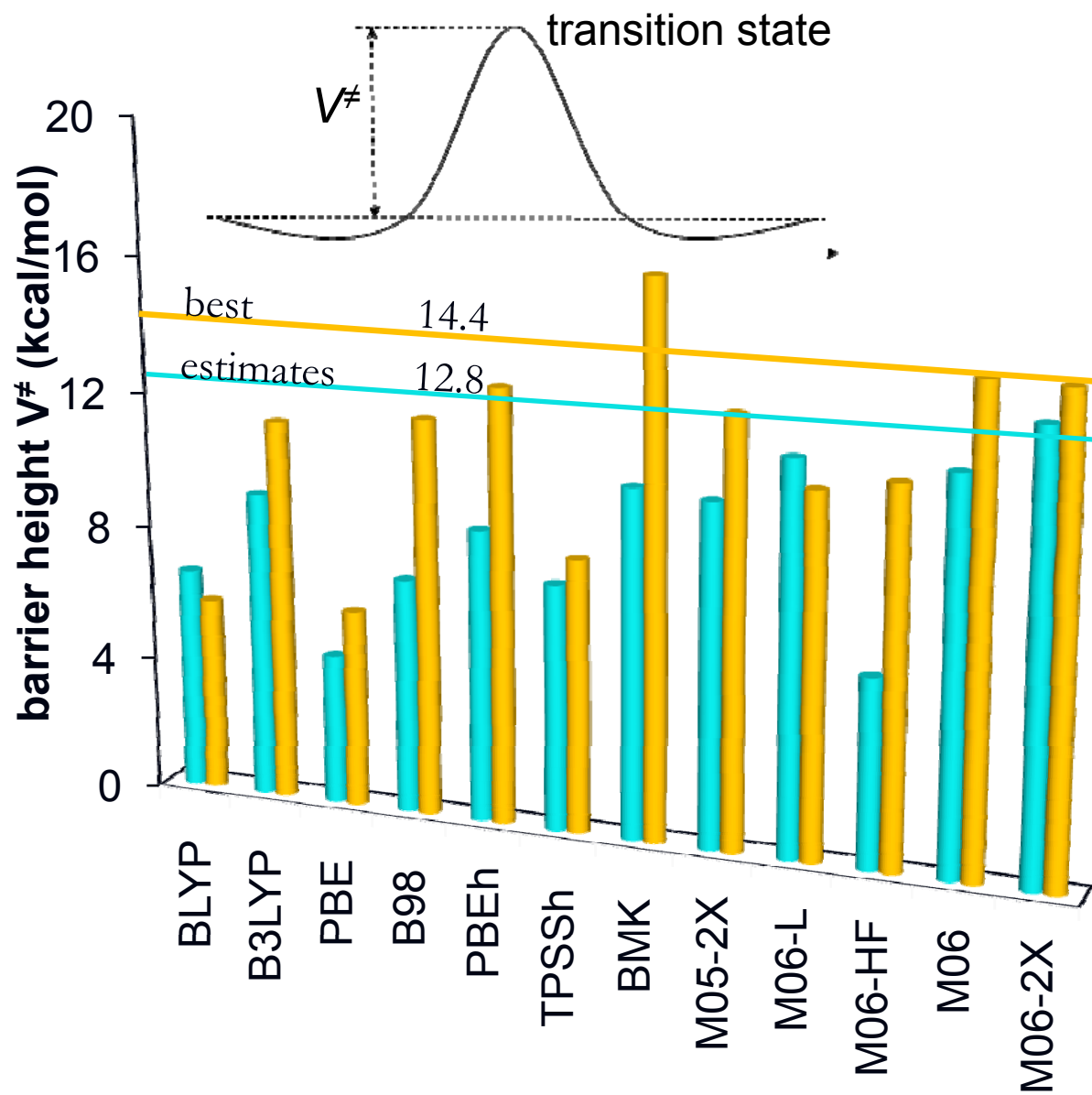


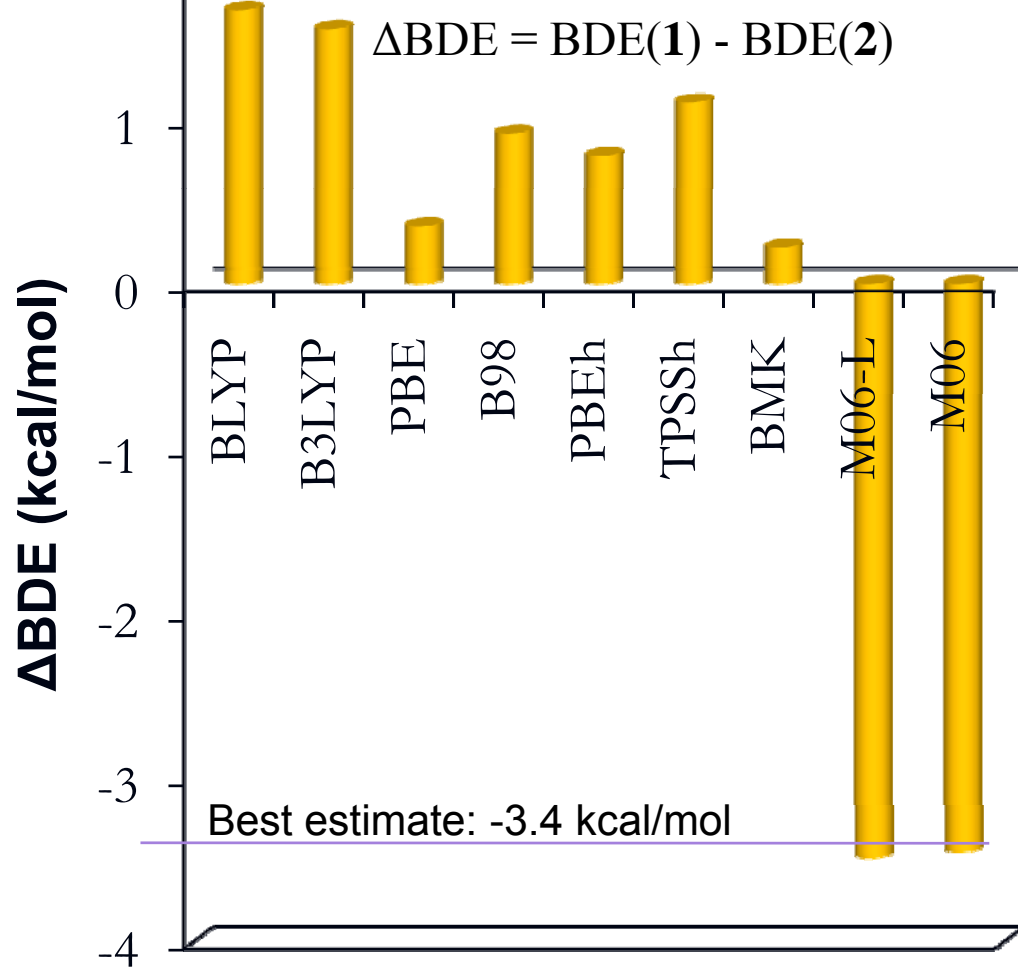
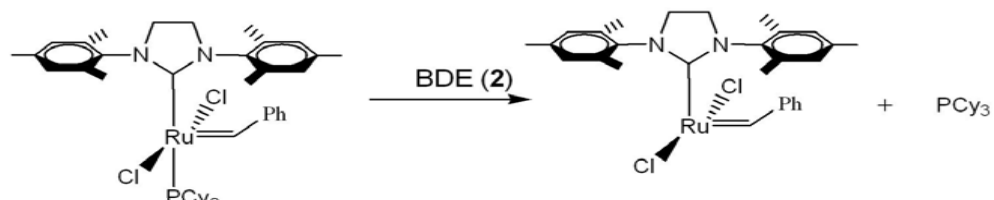
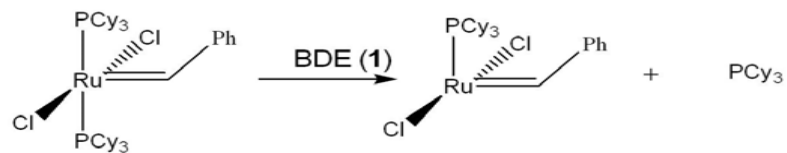
TMRE48:

A database of 48 reaction energies involving transition metals

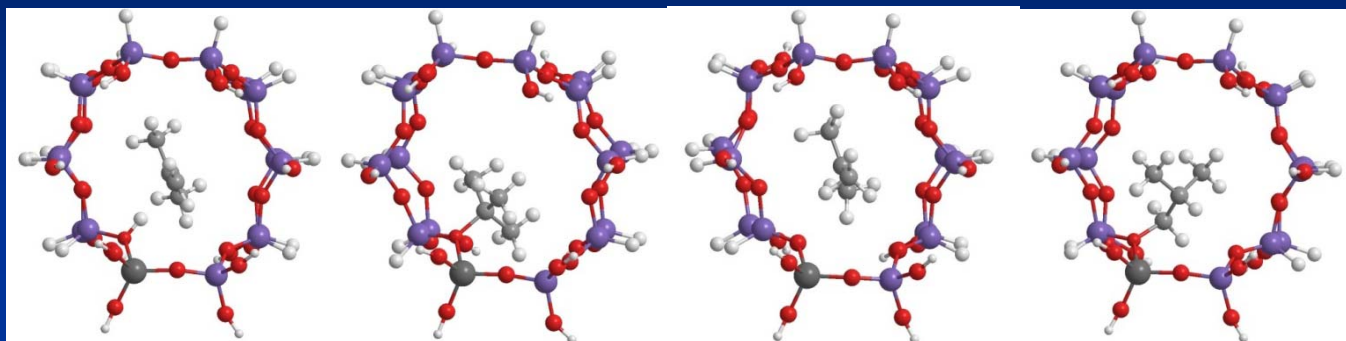








Adsorption energies (kcal/mol) of isobutene on a 16 T zeolite cluster



Method	π complex	tert-butoxide	tert-butyl carbenium ion	isobutoxide	MUE
Best estimate	15.1	13.9	-9.8	13.9	
M06-2X	12.7	16.6	-9.1	15.6	1.9
M06-L	14.4	15.6	-2.3	13.5	2.6
M06	13.3	16.0	-3.9	14.4	2.6
M06-HF	12.4	18.6	-12.5	18.8	3.7
PBEh	2.9	4.7	-15.6	4.7	9.1
TPSSh	-0.9	1.8	-17.7	1.6	12.1
B3LYP	-2.5	-5.5	-20.7	-4.8	16.6

Mean Unsigned Error (eV) for Excitation Energies

Valence excited
states

Rydberg excited
states

Charge transfer
excited states

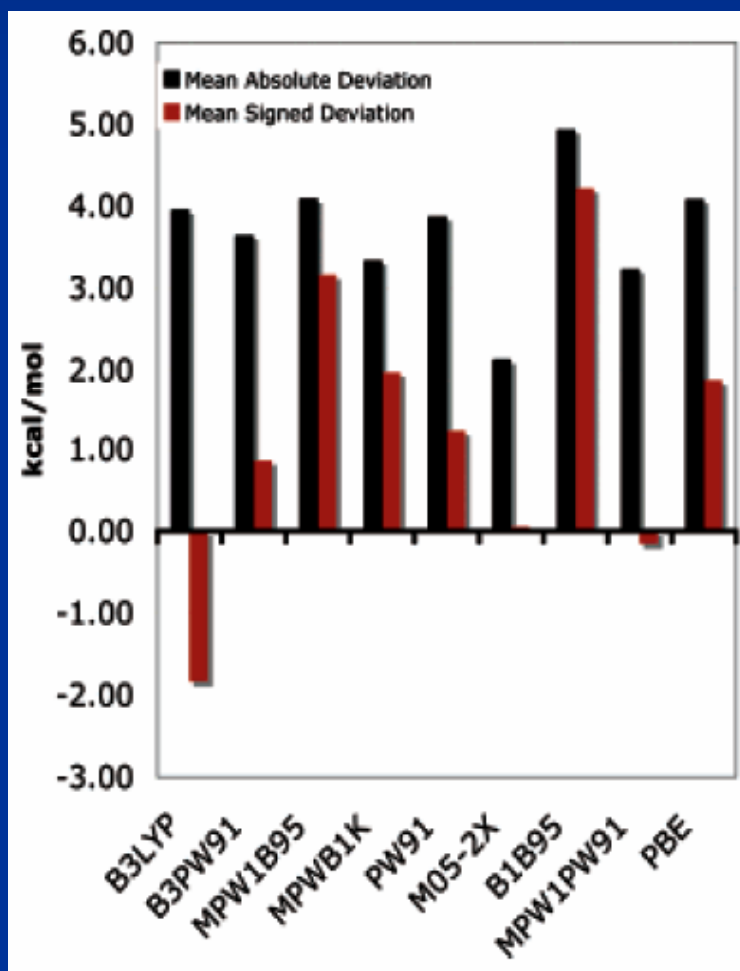
Overall

Method	VES21	RES20	CTE3	ES44
M06-HF	0.7	0.4	0.1	0.4
M06-2X	0.3	0.4	2.5	1.1
PBEh	0.3	0.9	4.1	1.8
B3LYP	0.3	1.1	4.4	1.9
M06	0.3	1.7	4.1	2.0
TPSSh	0.2	1.3	4.9	2.2
M06-L	0.3	1.6	5.4	2.5

Validations from other groups

I. Organic Energies

Wodrich, Matthew D.; Corminboeuf, Clemence; Schreiner, Peter R.; Fokin, Andrey A.; Von Schleyer, Paul. **How Accurate Are DFT Treatments of Organic Energies?** *Organic Letters* (2007), 9(10), 1851-1854.



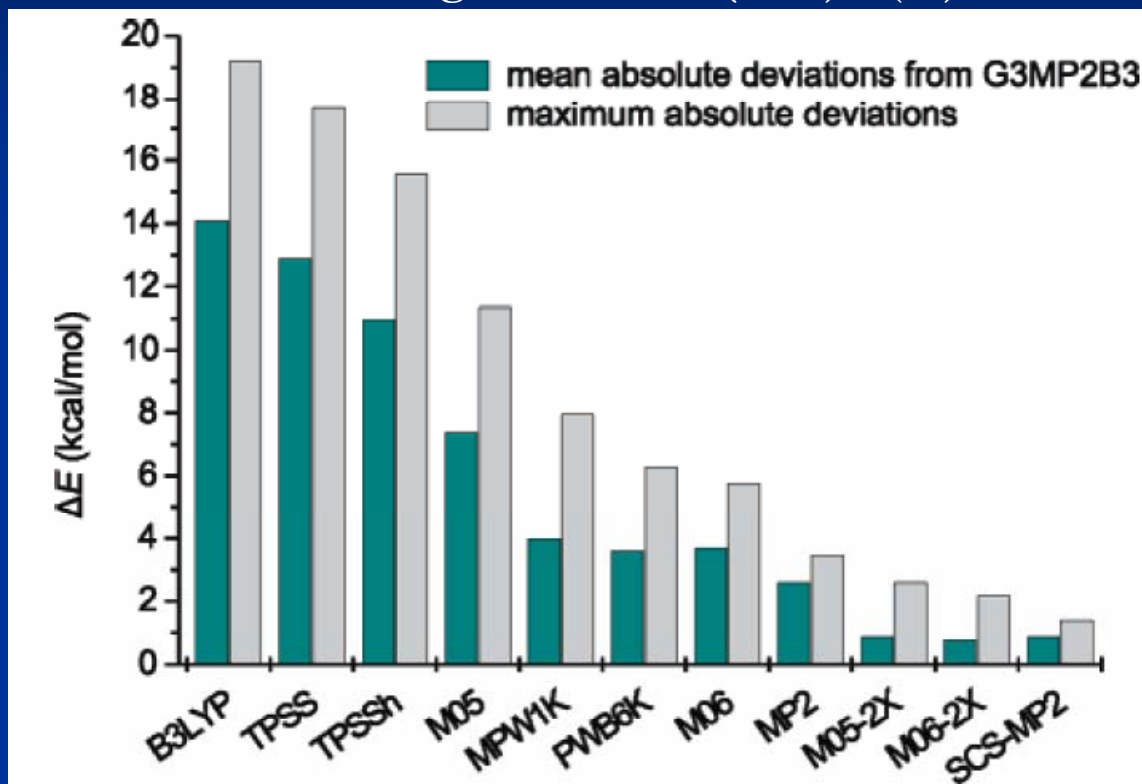
Abstract

Increasing awareness that popular functionals fail to describe many energies accurately has ended expectations of black-box DFT usage. The performance of nine density functionals, compared by computing the bond separation energies of 72 illustrative hydrocarbons with available experimental data, reveals that **only Zhao and Truhlar's recently proposed M05-2X functional, with a 2.13 kcal/mol average deviation from experiment, performs satisfactorily. B3LYP and other functionals show larger deviations.**

Validations from other groups

II. Conjugate Addition Reactions

Rokob, Tibor Andras; Hamza, Andrea; Papai, Imre. **Computing Reliable Energetics for Conjugate Addition Reactions**. *Organic Letters* (2007), 9(21), 4279 -4282.



Abstract

The performance of various density functionals along with second-order perturbation treatments has been tested for a set of conjugate addition reactions relevant to stereoselective organocatalysis. It is shown that B3LYP predictions seriously underestimate the reaction energies, whereas two newly designed functionals (M05-2X and M06-2X) and the SCS-MP2 method provide very accurate data. These new methods represent promising alternative approaches in future mechanistic studies.

Applications

Zhao, Y.; Truhlar, D. G. **How Well Can New-Generation Density Functionals Describe Protonated Epoxides Where Older Functionals Fail?** *J. Org. Chem.* (2007), 72(1), 295-298

Zhao, Y.; Truhlar, D. G. **Size-Selective Supramolecular Chemistry in a Hydrocarbon Nanoring** *J. Am. Chem. Soc.* (2007), 129(27), 8440-8442.

Ellingson, B. A.; Truhlar, D. G. **Explanation of the Unusual Temperature Dependence of the Atmospherically Important $\text{OH} + \text{H}_2\text{S} \rightarrow \text{H}_2\text{O} + \text{HS}$ Reaction and Prediction of the Rate Constant at Combustion Temperatures** *J. Am. Chem. Soc.*, (2007), ASAP Article

Pietra, F. **Why colchicine does not show mutarotation. With M05-2X density functional in the realm of tricky natural products** *J. Phys. Org. Chem.* (2007), ASAP Article

Summary

- M06-L is a local functional, and its locality allows one to use highly efficient algorithms to reduce the cost for large systems.
- M06 is a hybrid functional for general-purpose applications, and both M06-L and M06 are very suitable for applications in transition metal chemistry.
- M06-2X has improved performance for main-group thermochemistry, barrier heights, and noncovalent interactions as compared to M06-L and M06, but it is not suitable for describing transition metal chemistry.
- The M06-HF functional is designed to have full HF exchange because it provides the correct asymptotic behavior of the XC potential, which is important for long-range charge transfer excitations in electronic spectroscopy and some response properties such as polarizabilities of large conjugated molecules.

Technology Transfer and Software

The M06-class functionals have been implemented in:

- NWChem
- Gaussian03
- Jaguar
- ADF
- Q-Chem

<http://comp.chem.umn.edu/info/DFT.htm>

Future Plans

1. Implementation of the M06-class functionals in Plane Wave codes.
2. Application of the M06-class functionals for heterogeneous catalysis simulations.

Acknowledgment

ONR N00014-05-1-0538