

# Delocalization Errors in Density Functionals and Implications for Main-Group Thermochemistry

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# Introduction – Delocalization Error

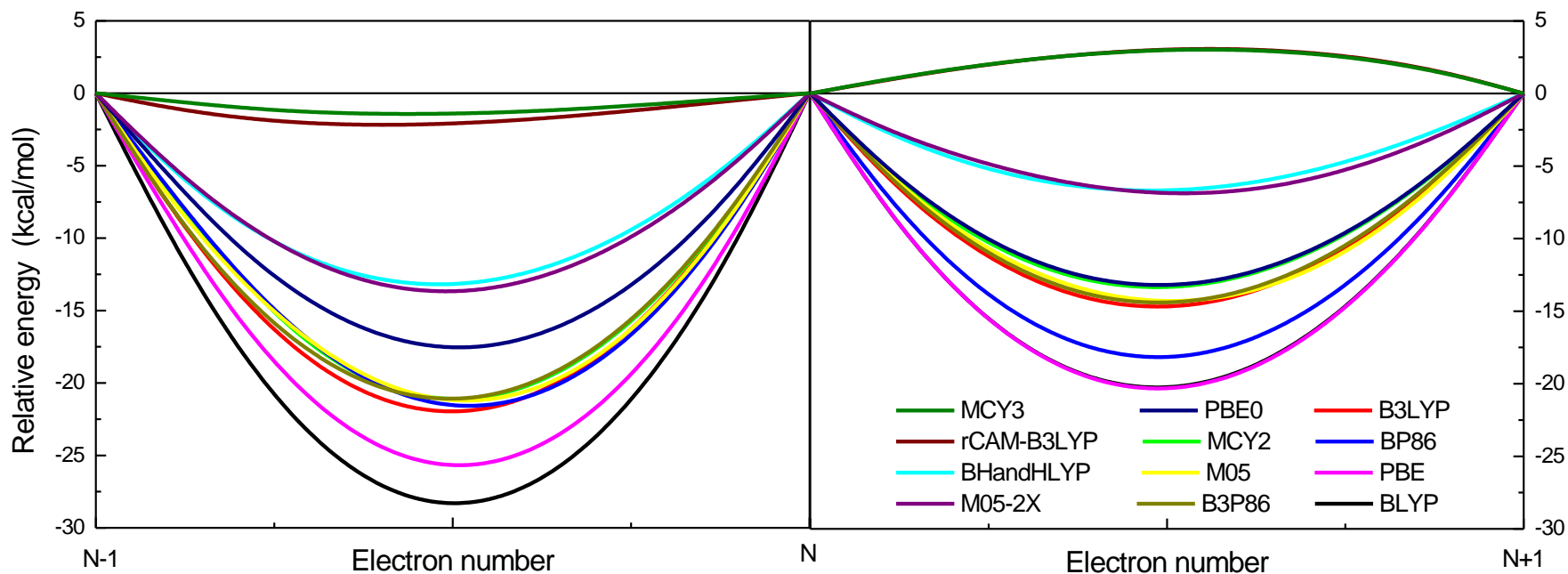
Generally, density-functional theory (DFT) methods predict highly accurate molecular geometries and reaction energies. Nevertheless, there are many situations in which the currently used approximate density functionals fail.

The failures of functionals can be understood by relating the errors to violation of basic conditions of the exact functional or of known physical constraints.

One such exact condition is the behaviour for systems with fractional charges. In plots of the electronic energy versus electron number, the exact functional should give piecewise straight lines between the integers.

However, most approximate density functionals give a convex interpolation of the energy as a function of fractional charge, which leads to an artificial tendency towards the delocalization of the electrons.

Plot of relative energy versus electron number (N) for the carbon atom showing the deviation from the exact straight-line between integers. N-1 indicates the cation and N+1 indicates the anion.

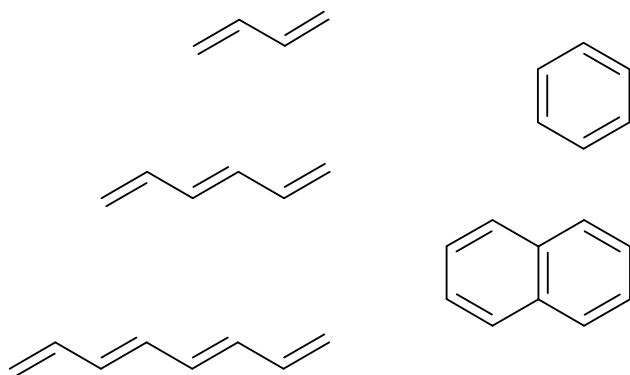
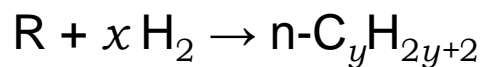


Delocalization error accounts for:

- incorrect dissociation limit of molecules and ions,
- over-stabilization of charge-transfer complexes,
- over-stabilization of some transition states,
- overestimation of polarizabilities of extended polymers,
- underestimation of HOMO-LUMO gaps in molecules.

It is also important for main-group thermochemistry, and causes over-stabilization of the delocalized electron densities seen in highly conjugated molecules.

For example, consider the mean errors (ME) in the enthalpy changes for 5 hydrogenation reactions, relative to experiment.



Method	ME (kcal/mol)
BLYP	24.9
PBE	23.8
MCY2	12.2
PBE0	11.9
B3LYP	7.3
BH&HLYP	-0.8
MCY3	2.7
rCAM-B3LYP	-6.8

In the present work, the difficulty of approximate density functionals in describing the energetics of Diels-Alder reactions and dimerization of aluminum complexes is analyzed.

We present a consistent view of these results from the perspective of delocalization error, although the interpretation is more subtle than in previous work. Two functionals free from electron delocalization error yield significantly more accurate results.

More generally, functionals free from electron delocalization error should be used for theoretical studies of reactions where there is a loss of extended conjugation or formation of highly branched or cage-like moieties.

# Methods

For all species, geometry optimizations and frequency calculations were performed with B3LYP/6-31G(2df,p).

Single-point energy calculations were performed with 6-311++G(3df,3pd) using 12 DFT methods:

BLYP	PBE
BPBE	PBE0
B3LYP	M05
BH&HLYP	M05-2X

“Conventional”  
GGA and  
hybrid  
functionals,  
Gaussian 03,  
NWchem

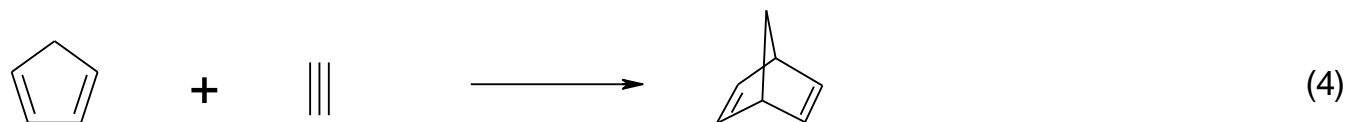
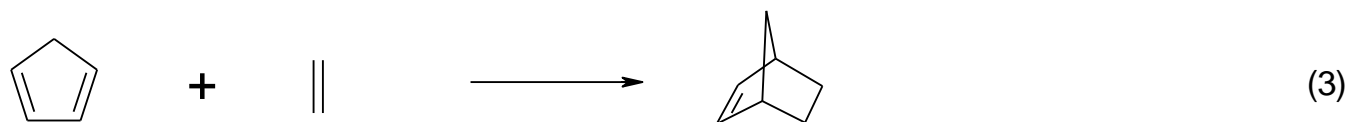
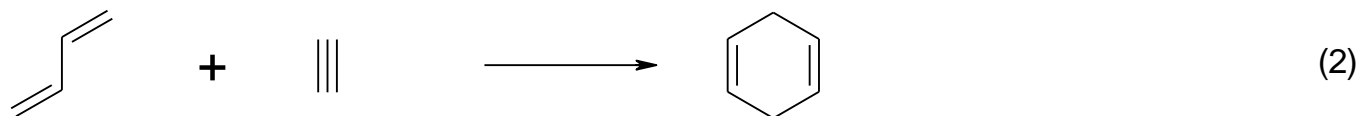
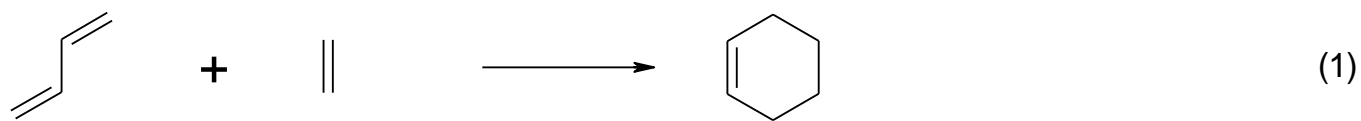
DF07 MCY2
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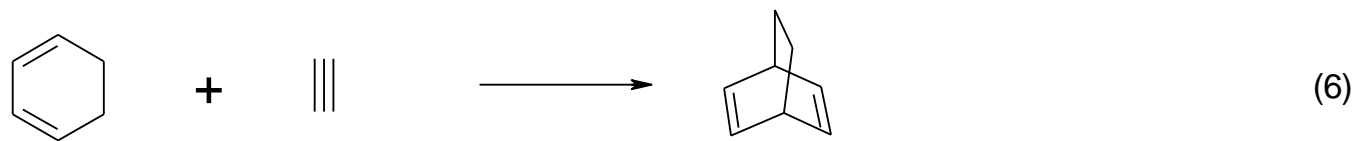
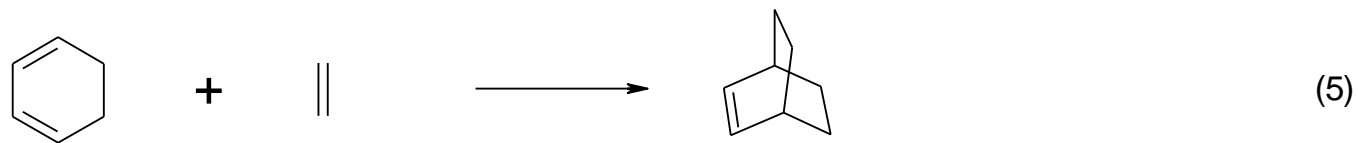
“Exact-exchange-  
based” functionals,  
NUMOL, CADPAC

MCY3 rCAM-B3LYP
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“Straight-line”  
functionals,  
CADPAC

## The Diels-Alder reactions.

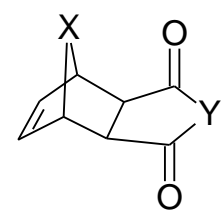




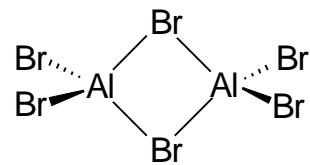
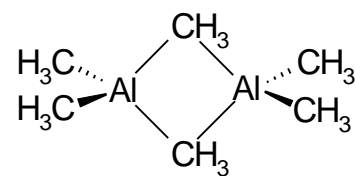
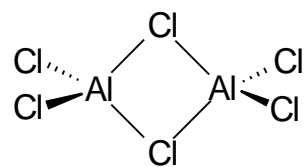
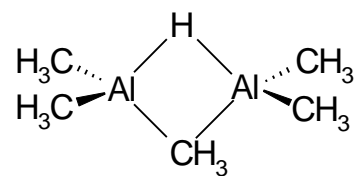
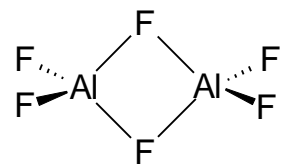
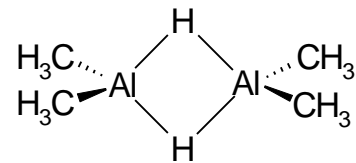
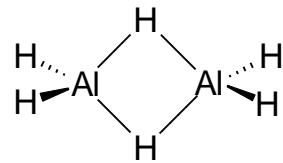
X=O, Y=NH (8)

X=CH<sub>2</sub>, Y=O (9)

X=CH<sub>2</sub>, Y=NH (10)



The bridge-bonded aluminium dimers.



Errors in electronic energy changes for the Diels-Alder reactions, relative to estimated CCSD(T)/CBS//PBE0/TZVP values (S. Grimme), in kcal/mol.

MAE: mean absolute error. ME: mean error.

Method	MAE	ME	Method	MAE	ME
BLYP	21.6	21.6	PBE	5.8	5.3
B3LYP	14.0	14.0	M05	4.4	4.1
DF07	12.8	12.8	PBE0	3.2	-0.9
MCY2	12.3	12.3	M05-2X	1.6	-1.2
BPBE	9.5	9.5	rCAM-B3LYP	2.6	-2.6
BH&HLYP	7.1	7.0	MCY3	3.4	-3.4

The errors are caused by destabilization of the bicyclic reaction products.

Calculated errors in dimerization enthalpies for the aluminium complexes, relative to experimental data, in kcal/mol.

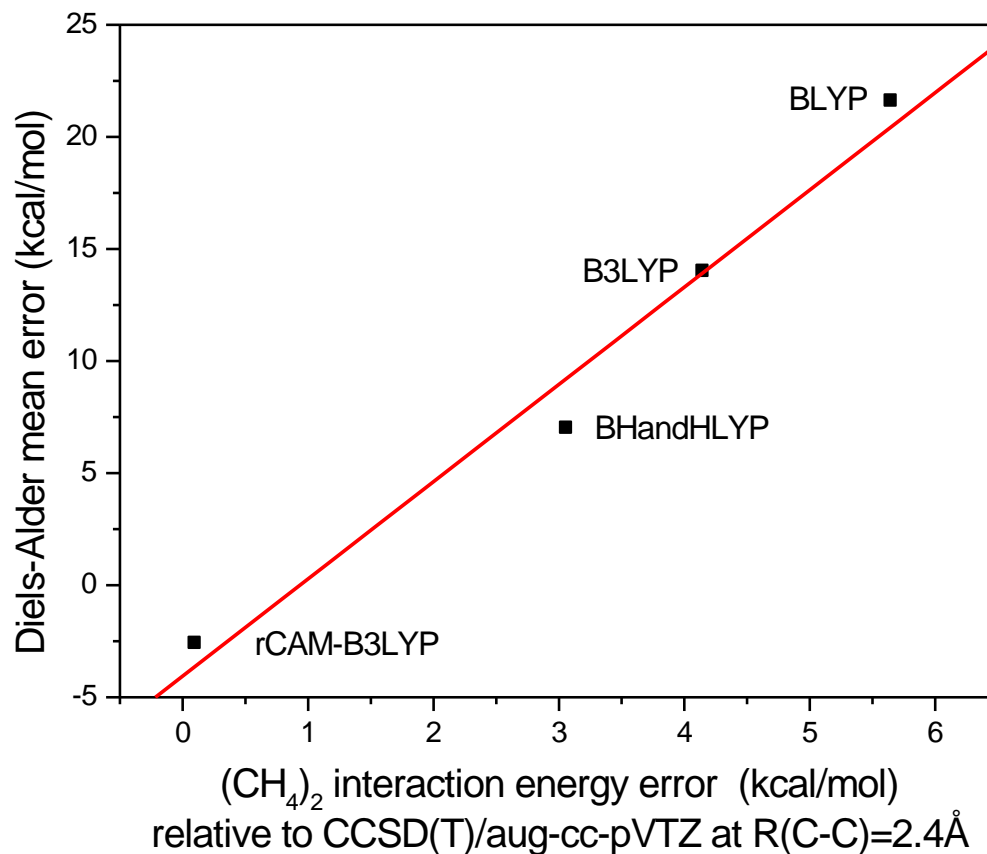
Method	MAE	ME	Method	MAE	ME
BLYP	11.1	11.1	PBE	3.8	3.1
B3LYP	8.0	8.0	M05	7.0	7.0
DF07	6.6	6.6	PBE0	2.4	1.5
MCY2	8.4	8.4	M05-2X	1.4	-1.3
BPBE	6.4	6.4	rCAM-B3LYP	2.7	2.0
BH&HLYP	5.8	5.8	MCY3	2.0	0.8

Most functionals destabilize the dimers due to underestimation of the of the Al-X bridge bond strength, with the general trend  $H < F < Cl < Br \approx CH_3$ .

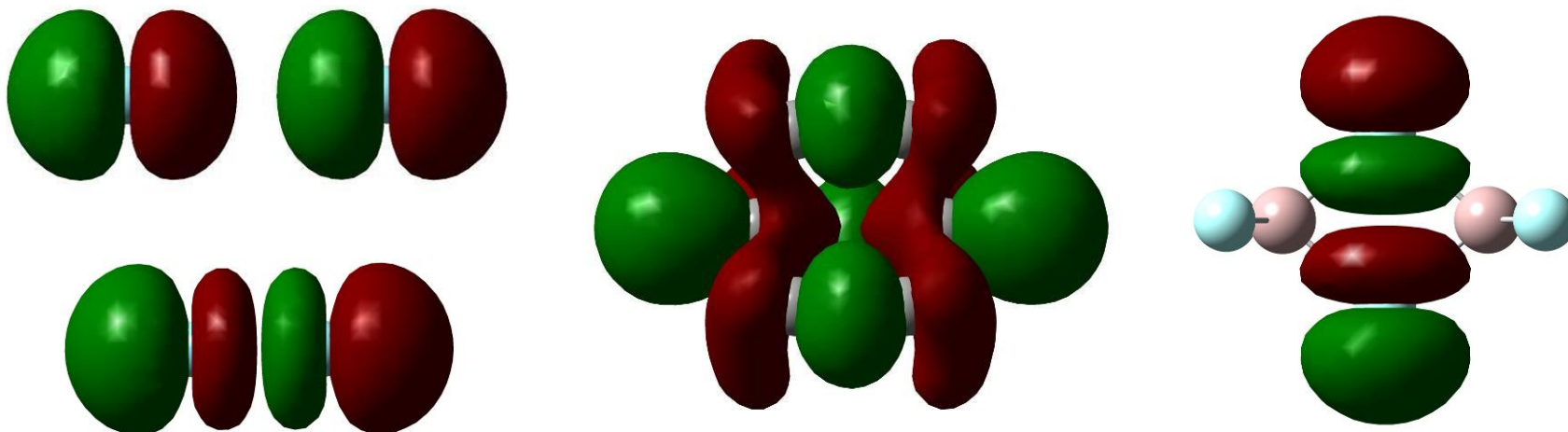
Why do most functionals tend to destabilize these cyclic and bicyclic systems?

In the Diels-Alder products, the bridgehead carbons are separated by 2.1-2.6 Å but are not bonded. This can be viewed as a van der Waals interaction at highly compressed distances.

There is a good correlation between the mean reaction energy errors and interaction energy errors for  $(\text{CH}_4)_2$ .



At short interatomic distances, non-bonded repulsion results in localization of the electron density since the orbitals become compressed.



The B3LYP argon dimer HOMO at interatomic separations of 4.0 Å (top left) and 2.0 Å (bottom left), the bicyclo[2,2,2]octane HOMO-2 (center) and the Al<sub>2</sub>F<sub>6</sub> F-F non-bonding orbital (right). The orbitals are displayed for isodensity contour values of  $\pm 0.02$  au.

# Summary

The majority of the functionals were found to under-bind the Diels-Alder reaction products and aluminum dimers, all of which involve cyclic or bicyclic moieties.

Our findings imply that there is a region of highly localized electron density in the reaction products that is under-stabilized by most functionals, and support the view that the errors are related to the electron delocalization error.

Delocalization error causes approximate functionals give too low energy for delocalized states or too high energy for localized states.

This interpretation allows us to understand better a wide range of errors in main-group thermochemistry obtained with popular density functionals.

