May 6, 2010

Reference energies and gradients for the MOHLYP and MOHLYP2 functionals

Ke Yang and Donald G. Truhlar

The MOHLYP functional[1] is a combination of the metal-adjusted OptX exchange functional[2] with half of the Lee-Yang-Parr (LYP) correlation functional.[3] The MOHLYP2[4] functional has the same functional form as MOHLYP, but uses different parameters.

The gradient enhancement for the OptX exchange functional[2] is

$$F(s) = 1.05151 - \frac{b}{C_F}\left(\frac{\gamma s^2}{1+\gamma s^2}\right)^2$$

where $\gamma = 0.006$, $b = 1.43169$, C_F is from the LSDA, and s is the reduced gradient. The MOHLYP functional replaces 1.05151 by 1.0 to restore the uniform electron gas (UEG) limit, and the parameter b was optimized to be 1.292.[1] The MOHLYP functional scales the gradient correction part of the LYP correlation functional by a factor of 0.5.

The MOHLYP2 functional was first used[4] under the name of MOHLYP, but after that it has properly been called MOHLYP2 to distinguish it from MOHLYP. MOHLYP2 has good performance for barrier heights,[4] but it is not recommended for general use. The MOHLYP2 functional changes b from 1.292 to 1.8498, and it scales the entire LYP correlation functional by a factor of 0.5.[5]

References

1. Schultz, N. E.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 11127.

2. Handy, N. C.; Cohen, A. J. *Mol. Phys.* **2001**, *99*, 403.

3. Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

4. Zheng, J.; Zhao, Y.; Truhlar, D. G. *J. Chem. Theory. Comput.* **2009**, *5*, 808.

5. http://comp.chem.umn.edu/Truhlar/docs/852U.pdf

Reference energies and gradients

Tables 1 and 2 present reference energies and forces for CH_3 (open shell, doublet) and H_2O (closed shell, singlet) with the 6-31+G** basis set and a pruned (99, 590) grid.

Geometry of CH_3 (in Å)

****

C 0.000000 0.000000 0.000000

H 0.000000 1.078000 0.000000

H 0.933000 -0.539000 0.000000

H -0.933000 -0.539000 0.000000

****

Geometry of H_2O (in Å)

****

O 0.000000 0.000000 0.000000

H 0.000000 0.000000 0.956914

H 0.926363 0.000000 -0.239868

****

Table 1. Reference energies (hartrees) and forces (hartree/bohr) for CH_3

MOHLYP	E=	-39.637917		
			Forces	
		X	Y	Z
	C	0.000000	0.000310	0.000000
	H	0.000000	0.013343	0.000000
	H	0.011904	-0.006827	0.000000
	H	-0.011904	-0.006827	0.000000
MOHLYP2	E=	-39.808055		
			Forces	
		X	Y	Z
	C	0.000000	0.000302	0.000000
	H	0.000000	0.010359	0.000000
	H	0.009317	-0.005331	0.000000
	H	-0.009317	-0.005331	0.000000

Table 2. Reference energies (hartrees) and forces (hartree/bohr) for H_2O

MOHLYP	E=	-76.112148		
			Forces	
		X	Y	Z
	O	-0.018236	0.000000	-0.014115
	H	-0.001213	0.000000	0.020404
	H	0.019448	0.000000	-0.006288
MOHLYP2	E=	-76.372562		
			Forces	
		X	Y	Z
	O	-0.013919	0.000000	-0.010774
	H	-0.000270	0.000000	0.014726
	H	0.014189	0.000000	-0.003953