Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information for

# DSD-PBEP86: In search of the best double-hybrid DFT with spin-component scaled MP2 and dispersion corrections

## Theoretical Method

For the W4-08 and DBH24 sets we used the aug'-pc3 basis set of Jensen,[1-5] with diffuse functions on non-hydrogen atoms and adding a high exponent d function for the W4-08 in order to properly account for high oxidation states. For the rest we used the Weigend and Ahlrichs Def2 bases:[6,7] Def2-TZVP for S22 and Grubbs, as the size of the molecules made it arduous to climb to a quadruple-ζ type of functions. Following past practice, we added half the counterpoise correction in the S22 set to correct for the basis set superposition error, exploiting the well-known finding that uncorrected weak interaction energies converge from above, and corrected ones from below, in function of the basis se [8,9]); Def2-QZVP was applied to MB, and Def2-QZVPP to the Pd set.

The Def2-QZVP basis set was used throughout the S130 set for the D3BJ parametrization. In addition, we applied one-half the counterpoise correction for the S22 and RG6 sets. The W4-11 set was calculated with aug-pc3+d; HFREQ27 with aug-pc2+2d and aug-pc3+d.

For the validation sets, we used the aug'-pc3+d basis set for NHTBH38, HTBH38, H-Bonds and vdW. For Pericyclic the aug'-pc2+2d basis set was used, and for Alkanes pc3.

The MP2 energies were calculated with the default "frozen core" correlation calculation, with only the valence electrons in the active space. For the transition metals, also the n-1 s and p atomic orbitals were included in the active space.

All the DH calculations including D2 dispersion corrections were carried out using an in-house modified Gaussian09 version,[10] which includes the dispersion correction. D3BJ dispersion corrections were calculated with the DFTD3 software.[11]

## LDA Alternatives

We briefly considered LDA correlation parametrizations other than VWN5. Perdew-Zunger,[12] while yielding slightly different total energies, yields essentially indistinguishable reaction energies, and it can reasonably be assumed that the same will hold true for the Perdew-Wang parametrization[13] (not implemented in Gaussian). For the VWN3 parametrization we do find a degradation in performance: unlike the others which are fitted to quantum Monte Carlo simulations of the uniform electron gas,[14] VWN3 is fitted to RPA (random phase approximation[15]) data for the same: RPA can be regarded as a crude approximation to CCSD.[16]

## Examples of DSD-PBEP86 input for Gaussian09, Gaussian 03, Molpro, ORCA, and Q-CHEM.

- *Gaussian09 [10]*

```
#p b2plyp/cc-pVTZ
iop(3/125=0250005300,3/78=0430004300,3/76=0300007000,3/74=1004)

Example G09 input

0 1
o
h 1 r
h 1 r 2 th

r=0.957
th=104.5
```

IOP(3/74) selects the functional (1004 corresponds to PBE-P86), overriding the default b-lyp; IOP(3/125) chooses $c_S$ and $c_O$ (0250005300 means 25% same spin and 53 % opposite spin MP2); IOP(3/78) gives the DFT correlation (in this case 43% P86); and IOP(3/76) the amount of DFT and exact exchange (30% PBE and 70% HF for this example).

- *Gaussian03 [17]*

```
#P pbep86/cc-pVTZ int(grid=fine)
IOp(3/74=1004,3/78=0430004300,3/76=0300007000) extraoverlay

8/10=4/1;9/16=-3/6;

Example G03 input

0 1
o
h 1 r
h 1 r 2 th

r=0.957
th=104.5
```

Total energy has to be extracted as SCF energy + 0.25*(E2alpha-alpha + E2beta-beta) + 0.53*E2alpha-beta.

- *Molpro [18]*

```
gthresh,energy=1d-9,grid=1d-6
geom={
o;
h,1,r;
h,1,r,2,th
}
r=0.957 ang
th=104.5 deg
basis=vtz
percenthf=70.0
percentDFTc=43.0
percentPTab=53.0
percentPTss=25.0
{rks,pbex,p86
exchange,percenthf*0.01
dftfactor,1.00-percenthf*0.01,percentDFTc*0.01}
ekohnsham=energy
mp2
eab=EMP2_SING+EMP2_TRIP/3d0
ess=2d0*EMP2_TRIP/3d0
ecorrmp2val=(eab*percentPTab+ess*percentPTss)*0.01
edsdpbep86val=ekohnsham+ecorrmp2val
```

- *Orca [19]*

```
* xyz 0 1
C 0.0 0.0 0.0
O 0.0 0.0 1.1314
*
! DFT aug-cc-pVTZ
%method
Exchange x_PBE
Correlation c_P86
LDAOpt C_VWN5
ScalHFX 0.70
ScalDFX 0.30
ScalGGAC 0.43
ScalLDAC 0.43
ScalMP2C 1.00
FrozenCore FC_ELECTRONS
end
%mp2
DoSCS True
Ps 0.53
Pt 0.25
end
```

- *Q-CHEM [20]*

```
$comment
DSD-PBEP86
$end
$molecule
0 1
O
H 1 R
H 1 R 2 TH
R=0.957
TH=104.5
$end
$rem
BASIS = aug-cc-pVTZ
CORRELATION = MP2
DH = 1
DH_OS = 510000
DH_SS = 230000
EXCHANGE = general
GUI = 0
JOB_TYPE = SP
SCF_FINAL_PRINT = 1
$end
$xc_functional
X HF 0.68
X PBE 0.32
C P86 0.45
$end
```

*Optionally one might add*

```
$empirical_dispersion
S6 0.29
$end
```

*in this case the following line should be added to the $rem block*

```
DFT_D = EMPIRICAL_GRIMME
```

1. F. Jensen, *J. Chem. Phys.*, 2001, **115**, 9113.
2. F. Jensen, *J. Chem. Phys.*, 2002, **116**, 7372.
3. F. Jensen, *J. Chem. Phys.*, 2002, **117**, 9234.
4. F. Jensen and T. Helgaker, *J. Chem. Phys.*, 2004, **121**, 3463.
5. F. Jensen, *J. Phys. Chem. A*, 2007, **111**, 11198-11204.
6. A. Schäfer, C. Huber, and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829.
7. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.
8. A. Karton, A. Tarnopolsky, J.-F. Lamère, G. C. Schatz, and J. M. L. Martin, *J. Phys. Chem. A*, 2008, **112**, 12868-12886.
9. T. Schwabe and S. Grimme, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3397.
10. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr.,

J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision B.01*, Gaussian, Inc., Wallingford CT, 2009. See also: http://www.gaussian.com

11. S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, *“DFT-D3 - A dispersion correction for DFT-functionals”; http://toc.uni-muenster.de/DFTD3*, .
12. J. P. Perdew and A. Zunger, *Phys. Rev. B*, 1981, **23**, 5048.
13. J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244.
14. D. Ceperley, *Phys. Rev. B*, 1978, **18**, 3126.
15. J. Oddershede, *Advances in Quantum Chemistry* 1978, **11**, 275-352.
16. G. E. Scuseria, T. M. Henderson, and D. C. Sorensen, *J. Chem. Phys.*, 2008, **129**, 231101
17. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Rob, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03* (Gaussian, Inc., Wallingford, CT, 2003). See also: http://www.gaussian.com
18. H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, and A. Wolf, MOLPRO 2010.1. See also: http://www.molpro.net
19. Frank Neese, F. ORCA – an ab initio, Density Functional and Semiempirical program package, Version 2.6. University of Bonn, 2008. See also: http://www.thch.uni-bonn.de/tc/orca/
20. Y.Shao, L. Fusti–Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S. T. Brown, A.T.B. Gilbert, L.V. Slipchenko, S.V. Levchenko, D.P. O’Neill, R.A. DiStasio Jr., R.C. Lochan, T.Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y.Lin, T. Van Voorhis, S. H. Chien, A. Sodt, R. P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E. F. C. Byrd, H. Daschel, R. J. Doerksen, A. Dreuw, B. D. Dunietz, A.D. Dutoi, T.R.. Furlani, S. R. Gwaltney, A. Heyden, S. Hirata, C.-P. Hsu, G. E. Kedziora, R.Z. Khaliullin, P. Klunzinger, A. M. Lee, M. S. Lee, W.Z. Liang, I. Lotan, N. Nair, B. Peters, E. I. Proynov, P. A. Pieniazek, Y. M. Rhee, J. Ritchie, E. Rosta, C. D. Sherrill, A. C. Simmonett, J. E. Subotnik, H. L. Woodcock III, W. Zhang, A. T. Bell, A. K. Chakraborty, D. M. Chipman, F. J. Keil, A. Warshel, W. J. Hehre, H. F. Schaefer III, J. Kong, A. I. Krylov, P.M.W. Gill and M.Head-Gordon. Phys. Chem. Chem. Phys., 8, 3172 (2006). See also: http://www.q-chem.com

Table 1: List of abbreviations.

| | Abbreviation | Significance |
|---|---|---|
| **Methods:** | | |
| | DH | Double Hybrid |
| | DSD | Dispersion corrected, SCS, DH |
| | DOD | Dispersion corrected, SOS, DH |
| | SCS | Spin Component Scaled |
| | SOS | Scaled Opposite Spin |
| | D2 | 2nd generation dispersion correction |
| | D3BJ | 3rd generation dispersion correction, with Becke-Johnson damping function. |
| **Coefficients** | | |
| | $c_O$ | Opposite spin MP2 coefficient. |
| | $c_S$ | Same spin MP2 coefficient. |
| | $c_X$ | DFT exchange coefficient. |
| | $c_C$ | DFT correlation coefficient. |
| | $s_6$ | Linear scaling of the $r^{-6}$ component in D2 or D3BJ. |
| | $s_8$ | Linear scaling of the $r^{-8}$ component in D3BJ. |
| | $a_1$, $a_2$ | D3BJ damping function parameters. |
| **Training sets** | | |
| | W4-08 | Total atomization energies |
| | DBH24 | Main group reaction barriers |
| | S22 | van der Waals and H-bonded systems |
| | Pd | Oxidative addition reactions on a Pd atom |
| | Grubbs | Metathesis reactions on Ru complexes |
| | MB | Mindless Benchmark (main group random thermochemistry). |
| **Training sets for D3BJ optimization (S130)** | | |
| | RG6 | Rare gases dimers. |
| | ACONF | N-alkane conformers. |
| | ADIM6 | Alkane dimers from ethane to n-heptane. |
| | S22 | van der Waals and H-bonded systems. |
| | CYCONF | Cysteine conformers. |
| | SCONF | Sugar conformers. |
| | PCONF | Small peptide conformers. |
| | S22+ | Extended S22 set (at two stretched geometries). |
| **Validation sets** | | |
| | NHTBH38 | Non Hydrogen Transfer Barrier Heights |
| | HTBH38 | Hydrogen Transfer Barrier Heights |
| | H-Bonds | H-bonded dimers |
| | vdW | van der Waals dimers |
| | Pericyclic | Pericyclic reactions. |
| | Alkanes | Alkanes thermochemistry and isomerization. |
| | HFREQ27 | Harmonic frequencies of small molecules. |
| | W4-11 | Atomization energies (extension of W4-08). |

Table 2: Statistical errors (in kcal/mol) over the training sets for the DSD-DFT with different functional combinations, in their optimal parameters.[a]

| Exchange | S | | | | B88 | | | | | PBE | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Correlation | VWN5 | P86 | LYP | PBE | VWN5 | LYP | PBE | P86 | PW91 | VWN5 | LYP | PBE | P86 | PW91 |
| Grubbs | 0.96 | 1.45 | 1.06 | 1.63 | 1.60 | 1.10 | 1.37 | 1.10 | 1.29 | 1.64 | 1.13 | 1.18 | 0.99 | 1.12 |
| W4-08[b] | 2.58 | 3.16 | 3.03 | 3.61 | 3.55 | 2.69 | 2.61 | 2.39 | 2.54 | 3.31 | 2.67 | 2.64 | 2.33 | 2.57 |
| non MR | 2.30 | 3.02 | 2.82 | 3.58 | 3.20 | 2.25 | 2.43 | 2.03 | 2.34 | 3.04 | 2.36 | 2.56 | 2.07 | 2.44 |
| MR | 3.93 | 3.90 | 4.06 | 3.74 | 5.21 | 4.57 | 3.55 | 3.94 | 3.56 | 4.65 | 4.07 | 3.09 | 3.52 | 3.26 |
| DBH24 | 1.38 | 2.31 | 1.85 | 2.76 | 1.96 | 1.09 | 1.34 | 1.09 | 1.31 | 1.57 | 1.17 | 1.33 | 1.11 | 1.29 |
| s22[c] | 0.33 | 0.42 | 0.33 | 0.51 | 0.93 | 0.44 | 0.61 | 0.45 | 0.58 | 1.01 | 0.64 | 0.48 | 0.40 | 0.45 |
| Pd | 1.27 | 1.71 | 1.36 | 1.74 | 1.53 | 0.95 | 1.55 | 1.54 | 1.48 | 1.34 | 0.88 | 1.37 | 1.37 | 1.22 |
| MB | 4.47 | 5.12 | 5.63 | 4.83 | 6.05 | 4.51 | 3.51 | 3.50 | 3.50 | 5.63 | 4.41 | 3.49 | 3.51 | 3.59 |
| Mean | 1.83 | 2.36 | 2.21 | 2.51 | 2.60 | 1.80 | 1.83 | 1.68 | 1.78 | 2.42 | 1.82 | 1.75 | 1.62 | 1.71 |

| Exchange | mPW | | | | HSE | | | | O | X | TPSS | B98 | BMK | $\tau$HCTH | HCTH407 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Correlation | LYP | PW91 | P86 | PBE | PBE | PW91 | P86 | LYP | LYP | LYP | | | | | |
| Grubbs | 1.12 | 1.15 | 1.02 | 1.21 | 1.09 | 1.05 | 0.91 | 1.08 | 1.63 | 1.11 | 1.45 | 0.77 | 3.36 | 1.69 | 1.99 |
| W4-08[b] | 2.64 | 2.48 | 2.28 | 2.55 | 2.63 | 2.56 | 2.34 | 2.70 | 2.50 | 2.66 | 2.50 | 2.92 | 3.50 | 2.98 | 2.83 |
| non MR | 2.27 | 2.32 | 1.97 | 2.40 | 2.53 | 2.44 | 2.05 | 2.36 | 2.07 | 2.25 | 2.24 | 2.52 | 2.96 | 3.01 | 2.82 |
| MR | 4.30 | 3.31 | 3.65 | 3.31 | 3.21 | 3.21 | 3.68 | 4.21 | 4.29 | 4.43 | 3.76 | 4.72 | 5.83 | 2.84 | 2.88 |
| DBH24 | 1.11 | 1.26 | 1.12 | 1.29 | 1.32 | 1.29 | 1.10 | 1.17 | 1.30 | 1.10 | 1.43 | 1.55 | 4.01 | 2.50 | 2.20 |
| s22[c] | 0.52 | 0.48 | 0.40 | 0.51 | 0.44 | 0.43 | 0.36 | 0.63 | 0.68 | 0.47 | 0.65 | 0.54 | 1.15 | 1.57 | 2.35 |
| Pd | 0.92 | 1.42 | 1.51 | 1.48 | 1.24 | 1.19 | 1.28 | 0.83 | 1.27 | 0.93 | 2.07 | 2.33 | 2.24 | 1.31 | 1.02 |
| MB | 4.53 | 3.50 | 3.43 | 3.51 | 3.53 | 3.52 | 3.61 | 4.57 | 4.29 | 4.50 | 4.47 | 4.10 | 3.93 | 4.93 | 4.90 |
| Mean | 1.81 | 1.72 | 1.63 | 1.76 | 1.71 | 1.67 | 1.60 | 1.83 | 1.94 | 1.80 | 2.09 | 2.04 | 3.03 | 2.50 | 2.55 |

[a] Including D2 dispersion correction.
[b] Full W4-08 set, and discrimination between high- and low- multireference systems.
[c] Including one half the counterpoise correction.

Table 3: Parameters of the DSD-DFT with different functional combinations, with D2 dispersion correction.

| Exchange | S | | | | B88 | | | | | PBE | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Correlation | VWN5 | P86 | LYP | PBE | VWN5 | LYP | PBE | P86 | PW91 | VWN5 | LYP | PBE | P86 | PW91 |
| $c_S$ | 0.11 | 0.00 | 0.00 | 0.00 | 0.72 | 0.43 | 0.13 | 0.24 | 0.15 | 0.67 | 0.40 | 0.12 | 0.23 | 0.14 |
| $c_O$ | 0.58 | 0.74 | 0.68 | 0.77 | 0.48 | 0.46 | 0.51 | 0.49 | 0.50 | 0.47 | 0.50 | 0.53 | 0.51 | 0.51 |
| $s_6$ | 0.28 | 0.14 | 0.17 | 0.17 | 0.48 | 0.35 | 0.54 | 0.41 | 0.53 | 0.44 | 0.28 | 0.42 | 0.29 | 0.40 |
| $c_C$ | 0.34 | 0.22 | 0.29 | 0.22 | 0.48 | 0.55 | 0.56 | 0.49 | 0.56 | 0.48 | 0.5 | 0.51 | 0.45 | 0.52 |
| $c_X$ | 0.29 | 0.23 | 0.25 | 0.22 | 0.24 | 0.29 | 0.35 | 0.33 | 0.35 | 0.26 | 0.28 | 0.34 | 0.32 | 0.34 |

| Exchange | mPW | | | | HSE | | | | O | X | TPSS | B98 | BMK | τHCTH | HCTH407 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Correlation | LYP | PW91 | P86 | PBE | PBE | PW91 | P86 | LYP | LYP | LYP | | | | | |
| $c_S$ | 0.41 | 0.14 | 0.24 | 0.12 | 0.12 | 0.15 | 0.23 | 0.40 | 0.38 | 0.42 | 0.30 | 0.34 | 0.35 | 0.41 | 0.43 |
| $c_O$ | 0.48 | 0.51 | 0.51 | 0.51 | 0.52 | 0.52 | 0.50 | 0.49 | 0.47 | 0.47 | 0.57 | 0.56 | 0.79 | 0.56 | 0.55 |
| $s_6$ | 0.31 | 0.47 | 0.34 | 0.48 | 0.39 | 0.39 | 0.27 | 0.26 | 0.58 | 0.33 | 0.28 | 0.00 | 0.14 | 0.30 | 0.52 |
| $c_C$ | 0.53 | 0.54 | 0.46 | 0.54 | 0.52 | 0.52 | 0.46 | 0.51 | 0.55 | 0.54 | 0.45 | 0.55 | 0.31 | 0.46 | 0.52 |
| $c_X$ | 0.29 | 0.35 | 0.32 | 0.35 | 0.34 | 0.34 | 0.32 | 0.28 | 0.31 | 0.29 | 0.3 | 0.22 | 0.1 | 0.29 | 0.29 |

Table 4: Optimal parameters and statistical errors (in kcal/mol) for DOD-DFT.

| | B-LYP | PBE-PBE |
|---|---|---|
| $c_S$ | 0 | 0 |
| $c_O$ | 0.54 | 0.51 |
| $s_6$ | 0.98 | 0.53 |
| $c_C$ | 0.59 | 0.56 |
| $c_X$ | 0.36 | 0.38 |
| Grubbs | 1.50 | 1.18 |
| W4-08 | 4.53 | 2.92 |
| non MR | 4.42 | 2.85 |
| MR | 5.13 | 3.31 |
| DBH24 | 1.11 | 1.10 |
| s22 | 2.06 | 0.52 |
| Pd | 1.56 | 1.35 |
| MB | 6.15 | 3.95 |
| Mean | 2.82 | 1.84 |

Table 5: RMSD for the S130 set of long range interactions with DSD-PBEP86 (in kcal/mol), with different dispersion correction methods.

| | Raw[a] | D2[b] | D3BJ[c] |
|---|---|---|---|
| RG6 | 0.24 | 0.09 | 0.06 |
| ACONF | 0.30 | 0.12 | 0.02 |
| ADIM6 | 1.62 | 0.19 | 0.12 |
| S22 | 1.29 | 0.26 | 0.21 |
| CYCONF | 0.14 | 0.11 | 0.18 |
| SCONF | 0.51 | 0.23 | 0.26 |
| PCONF[d] | 0.98 | 0.30 | 0.25 |
| S22+ | 0.70 | 0.14 | 0.11 |
| RMSD[e] | 0.63 | 0.16 | 0.13 |

[a] No dispersion correction.
[b] With $s_6$=0.29.
[c] With $s_6$=0.418, $a_2$=5.65 (optimal parameters).
[d] With TZVPP basis set.
[e] With a weight of 20 for the RG6 set.

Table 6: RMSD for the validation sets (in kcal/mol). Unless specified, all the functionals include D2 dispersion correction.

| DSD-DFT | B98 | B LYP | B P86 | B PBE | B PW91 | HSE PBE | mPW LYP | MPW PW91 | O LYP | PBE LYP | PBE PBE | S VWN5 | TPSS | X LYP | PBE P86 | PBE-P86 D3BJ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NHTBH38 | 2.74 | 2.08 | 2.09 | 2.12 | 2.06 | 2.06 | 2.07 | 2.00 | 2.32 | 2.14 | 2.06 | 2.21 | 2.47 | 2.04 | 1.99 | 2.18 |
| HTBH38 | 1.29 | 1.14 | 1.13 | 1.07 | 1.05 | 1.15 | 1.14 | 1.12 | 1.05 | 1.10 | 1.14 | 1.28 | 1.07 | 1.08 | 1.21 | 1.12 |
| H-Bonds | 0.41 | 0.45 | 0.28 | 0.34 | 0.31 | 0.33 | 0.56 | 0.28 | 0.31 | 0.62 | 0.30 | 0.62 | 0.24 | 0.49 | 0.42 | 0.38 |
| vdW | 0.49 | 0.43 | 0.31 | 0.38 | 0.36 | 0.33 | 0.53 | 0.30 | 0.29 | 0.60 | 0.30 | 0.45 | 0.32 | 0.45 | 0.42 | 0.47 |
| Pericyclic | | | | | | | | | | | | | | | | |
| ref W1 | 2.76 | 3.15 | 3.22 | 2.97 | 2.99 | 2.59 | 2.85 | 2.76 | 3.45 | 2.72 | 2.58 | 1.93 | 3.38 | 2.87 | 2.06 | 2.05 |
| ref CBS | 1.87 | 2.06 | 2.01 | 2.01 | 1.98 | 1.79 | 1.85 | 1.82 | 2.23 | 1.74 | 1.80 | 1.71 | 2.07 | 1.85 | 4.16 | 1.58 |
| ref Exp | 3.52 | 3.65 | 3.73 | 3.87 | 3.82 | 3.50 | 3.40 | 3.60 | 4.02 | 3.29 | 3.56 | 3.06 | 3.86 | 3.40 | 2.82 | 2.51 |
| Alkanes | | | | | | | | | | | | | | | | |
| TAEs | 10.89 | 3.48 | 3.18 | 2.24 | 2.64 | 1.18 | 0.80 | 1.57 | 7.28 | 1.09 | 1.74 | 2.48 | 4.10 | 0.42 | 0.99 | 1.07 |
| Isom. | 0.07 | 0.40 | 0.45 | 0.50 | 0.47 | 0.29 | 0.31 | 0.37 | 0.52 | 0.32 | 0.32 | 0.22 | 0.21 | 0.33 | 0.25 | 0.16 |

Table 7: RMSD for the complete W4-11 validation set (140 molecules), and discriminated between non multi-reference (124 molecules) and multi-reference (16 molecules) character systems, in kcal/mol. Unless specified, all the functionals include D2 dispersion correction.

| | B98 | B LYP | B P86 | B PBE | B PW91 | HSE PBE | mPW LYP | mPW PW91 | mPW P86 | mPW PBE | PBE PW91 | PBE LYP | PBE PBE | S VWN5 | TPSS | X LYP | PBE P86 | PBE-P86 D3BJ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| All | 3.16 | 2.95 | 2.41 | 2.75 | 2.66 | 2.82 | 2.80 | 2.62 | 2.41 | 2.73 | 2.73 | 2.83 | 2.81 | 2.93 | 2.77 | 2.78 | 2.44 | 2.48 |
| non-MR | 2.65 | 2.55 | 1.91 | 2.49 | 2.27 | 2.59 | 2.31 | 2.28 | 1.81 | 2.40 | 2.42 | 2.32 | 2.51 | 2.61 | 2.03 | 2.10 | 1.92 | 1.92 |
| MR | 2.67 | 2.45 | 2.50 | 2.20 | 2.40 | 2.14 | 2.58 | 2.29 | 2.66 | 2.29 | 2.27 | 2.61 | 2.26 | 2.31 | 2.92 | 2.83 | 2.55 | 2.61 |

Table 8: RMSD (in $cm^{-1}$) for the HFREQ27 set with selected methods.

| DSD<br>Basis set | S-VWN5<br>apc2+2d | B-LYP<br>apc2+2d | B-P86<br>apc2+2d | PBE-P86<br>apc2+2d | mPW-P86<br>apc2+2d | B-P86<br>apc3+d | PBE-P86<br>apc3+d |
|---|---|---|---|---|---|---|---|
| Unscaled: | | | | | | | |
| RMSD | 18.93 | 31.78 | 21.02 | 19.65 | 20.64 | 17.85 | 16.71 |
| MSD | 10.78 | 20.31 | 9.45 | 8.8 | 9.84 | 7.5 | 6.9 |
| Scaled: | | | | | | | |
| RMSD | 15.08 | 20.48 | 17.47 | 16.56 | 16.85 | 15.53 | 14.82 |
| MSD | 0.85 | -0.99 | -0.85 | -0.36 | -0.66 | -0.13 | 0.23 |
| Scaling factor | 0.9948 | 0.9889 | 0.9946 | 0.9952 | 0.9945 | 0.9960 | 0.9965 |