DFT2011

Density functionals poll

Organized by M. Swart, F.M. Bickelhaupt and M. Duran

NEWS-ITEM, 2011

History and rules:
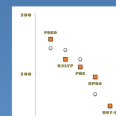
Results:

Appendices:

"Surprisingly, the PBE0 functional is for the second year in a row the winner."

List of **density functionals** included in the poll

Primera divisió 2011:

B2PLYP, B3LYP, B3LYP*, B3PW91, B97-D, BLYP, BP86, CAM-B3LYP, LDA, M05-2X, M06-2X, M06-L, mPW1K, OLYP, PBE, PBE0 (PBE1PBE), revTPSS-D, SAOP, SSB-D, TPSSh

Segona divisió 2011:

BHandH, HSE, LB94, LC-ωPBE, M05, PW91, revTPSS, tau-HCTH, X3LYP, XLYP, B3LYP-D, revPBE, PW6B95, PWPB95-D$_3$, DSD-BLYP, M06, ωB97X-D, LC-PBE, BMK, VSXC (VS98), TCA, revTCA, RPBE

Origin of the online popularity poll of density functionals

Following a presentation by Matthias Bickelhaupt ("*Hypervalent versus Nonhypervalent Carbon*", 27. 2. 2009) there was a discussion in *Can Paco* (the bar at the faculty of Chemistry at the University of Girona). Because the presentation showed the results for quite a number of density functionals, Miquel Duran suggested to take a number of these results, and use appropriate weights for them in order to obtain a "consensus" density functional result. In order to get the weights needed for this procedure, we have held annual online polls where people could indicate their preferences for a number of density functionals. The polls were announced on the CCL list, on Twitter, Facebook, blogs, etc. in order to get the maximum number of participants. The aims of this poll were: (i) to probe the "preference of the community", i.e., setting up a ranking of preferred DFT methods; and (ii) provide a compilation of the "*de facto* quality" that this implies for the "average DFT computation". Note that this poll does not cover everybody, only those who were motivated to take part in the poll and vote. Yet, we feel that the results do provide some insight in current preferences. And interestingly, these preferences do not always match with the best choice in terms of best agreement with accurate reference data.
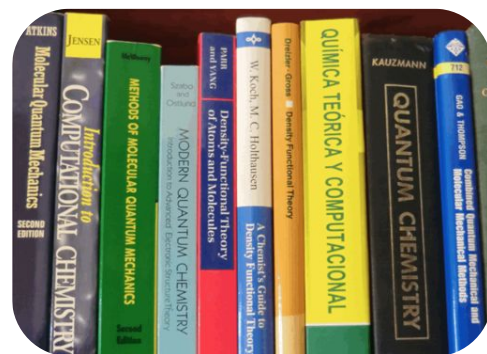
The aim of the online popularity poll is to probe the preferences of the computational chemistry community, and compile the quality of the "average" DFT computation.

Prof. Bickelhaupt: a regular visitor to Girona

At least 50 research papers have resulted from the collaboration

There is a longstanding collaboration between the research groups of Prof. Bickelhaupt at the Vrije Universiteit Amsterdam (VUA), and the IQC in Girona. Since 1993, Prof. Matthias Bickelhaupt collaborates with Prof. Miquel Solà (IQC) and has visited the University of Girona (UdG) every year since 1998 for joint investigations on the chemical bond, DNA, organic reactions, etc. Many members of the IQC have also gone to Amsterdam for short (3-month) or longer (post-doc) research stays, which has led to a very fruitful collaboration. This has recently been recognized by the rectorates of the VUA and UdG, and is now officially a collaboration between the universities. For the UdG, this is an important component of the Campus of Excellence that was awarded to it in 2011.
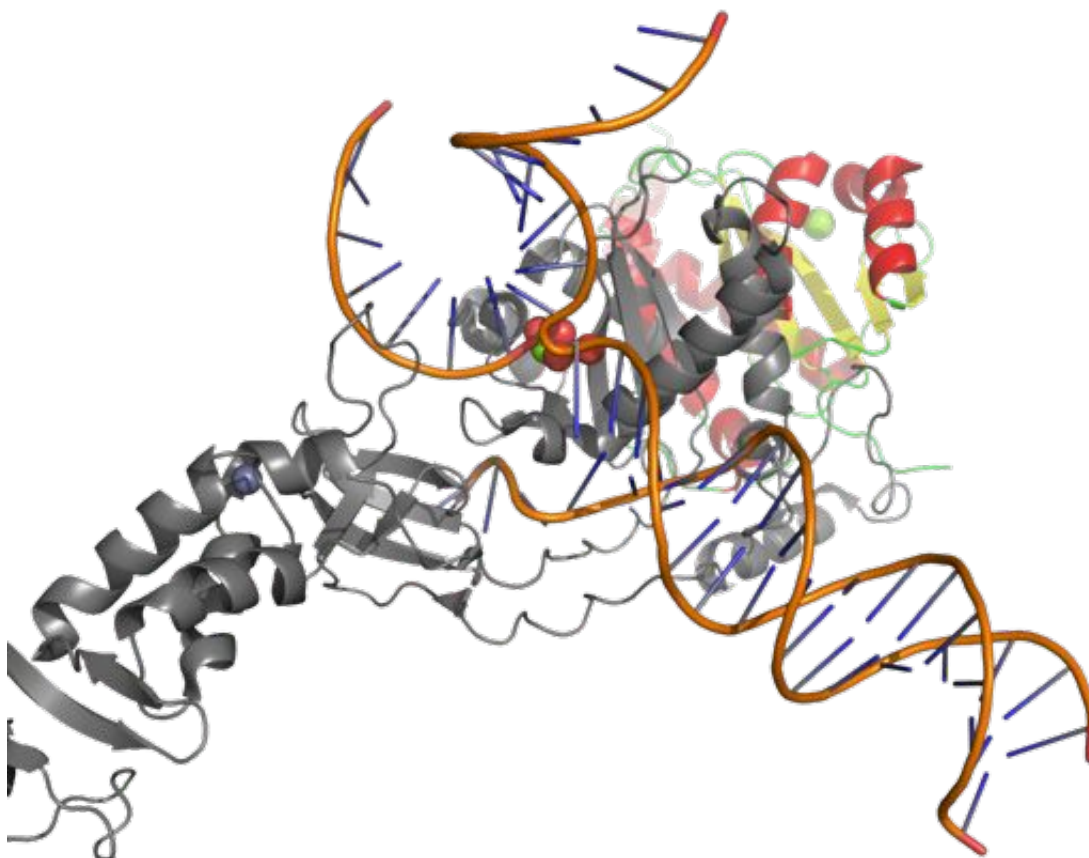
Rules for the popularity poll and the PACO functionals

1) *Points are given similar to football, i.e. a 'like' gives +3 points, 'neutral' +1 points, no answer at all ('Vot en blanc','None Of The Above') 0 points, 'hate' -1 points. A ranking of the functionals will be made by taking into account these points.*

2) *In case there are two or more functionals with the same number of points, the ordering will be decided by the following criteria: (i) most number of 'like's, (ii) least number of 'hate's, (iii) results from previous years (for future editions), (iv) year of publication of the functional (the younger, the better), (v) decision by organizers.*

3) *There will be a Primera Divisió with the 20 most popular functionals. At the end of each year, the 5 least popular of the Primera Divisió will relegate to the Segona Divisió.*
    Each year, only the 20 most popular functionals of the Segona Divisió will be kept. The five most popular ones of the Segona will be promoted to the Primera, while the 15 next will form the Segona for the next year together with the 5 relegated from the Primera.
    The other functionals will not take part in the poll for the year after (unless suggested again). There is a maximum of 10 additional suggestions for each year, which are added chronologically (after being suggested by mail to M. Swart).

4) *A new PACO functional will be constructed each year, by taking a weighted linear combination of the 20 functionals in the Primera Divisió. For those functionals that do not have an energy expression (e.g. SAOP, LB94), a weight of zero (except for the excitation energies) will be used for the construction of PACO20xx. In particular, the following energy expressions are obtained:*

    The weight of each functional is given by its number of points, divided by the total number of points of the 20 functionals in the Primera Divisió (using a value of 0 for those without an energy expression, see above). The sum of the weights is therefore one.

Note that with these PACO functionals we do not wish to ridicule the development of density functionals, which is hard and painstaking work, and often underestimated. Neither do we intend to mix different functionals for the sake of mixing, in the hope of reducing discrepancies. However, we do wish to help the community by getting a consensus current opinion on the many functionals, which may help the reader choose a functional for his/her own study on chemistry. As mentioned in the introduction, it can also be enlightening to compare the consensus current opinion with the actual performance.

5) *The PACO20xx functionals will be applied to a small number of typical chemical systems:*
    - *the AE6 set for six atomization energies (SiH$_4$, SiO, S$_2$, propyne, glyoxal, cyclobutane)*
    - *the BH6 set for six barrier heights (forward and reverse reaction of OH+CH$_4$, H+OH, H+H$_2$S)*
    - *the π-π stacking energy of anti-parallel cytosine dimer*
    - *spin-state splitting of FeFHOH and Ni(EDT)$_2$$^{2-}$*
    - *excitation energies (singlet, triplet) of CO*
    - *the hydrogen-bonding energies of four dimers (ammonia, water, formic acid, formamide)*

    For all of these coupled cluster CCSD(T) or experimental (reference) data are available.

6) *Each year, a new popularity poll will be held between June 1 and October 1, and will be announced on www.marcelswart.eu/dft-poll, on the CCL list, etc. and a short news item such as the current one about it will be published.*

Results of the **popularity poll**

	functional	year	cites	like	neutral	hate	empty	points
Primera Divisió								
1	**PBE0**	*1996*	*751*	81	22	6	33	**259**
2	**B3LYP**	*1994*	*23603*	73	30	24	15	**225**
3	**PBE**	*1996*	*1548*	61	36	7	38	**212**
4	**BP86**	*1988*	*838*	57	33	9	43	**195**
5	**B97-D**	*2006*	*44*	42	31	11	58	**146**
6	**B2PLYP**	*2006*	*75*	34	38	7	63	**133**
7	**B3PW91**	*1993*	*1137*	26	47	8	61	**117**
8	**CAM-B3LYP**	*2004*	*151*	29	38	11	64	**114**
9	**M06-2X**	*2008*	*242*	39	26	31	46	**112**
10	**revTPSS-D**	*2009*	*2*	22	42	2	76	**106**
11	**BLYP**	*1988*	*1270*	24	51	18	49	**105**
12	**TPSSh**	*2003*	*52*	19	40	7	76	**90**
13	**M06-L**	*2006*	*92*	27	31	29	55	**83**
14	**SSB-D**	*2009*	*23*	18	31	10	83	**75**
15	**B3LYP***	*2001*	*43*	22	27	24	69	**69**
16	**OLYP**	*2001*	*95*	14	39	14	75	**67**
17	**SAOP**	*2000*	*66*	7	42	6	87	**57**
18	**LDA**	*1980*	*10872*	17	34	32	59	**53**
19	**M05-2X**	*2006*	*227*	17	34	32	59	**53**
20	**mPW1K**	*2000*	*173*	9	38	14	81	**51**
Segona Divisió								
1	**B3LYP-D**	*2006*	*38*	44	31	13	54	**150**
2	**PW91**	*1992*	*488*	27	41	9	65	**113**
3	**revPBE**	*1998*	*22*	23	35	6	78	**98**
4	**PWPB95-D$_3$**	*2011*	*3*	18	25	6	93	**73**
5	**revTPSS**	*2009*	*2*	14	35	5	88	**72**
6	**M06**	2008	415	25	21	25	71	**71**
7	**BHandH**	1993	50	10	48	8	76	**70**
8	**LC-wPBE**	2006	43	12	34	8	88	**62**
9	**DSD-BLYP**	2010	4	13	27	6	96	**60**
10	**PW6B95**	2005	15	11	31	5	95	**59**
11	**HSE**	2003	625	8	32	8	94	**48**
12	**X3LYP**	2004	69	14	27	24	77	**45**
13	**wB97-XD**	2008	47	10	18	4	110	**44**
14	**M05**	2005	288	11	26	29	76	**30**
15	**LB94**	1994	31	5	28	13	96	**30**
16	**τ-HCTH**	2002	5	2	30	12	98	**24**
17	**LC-PBE**	2007	8	4	15	5	118	**22**
18	**RPBE**	1999	75	3	11	3	125	**17**
19	**VSXC**	1998	42	2	13	6	121	**13**
20	**XLYP**	2004	4	4	23	23	92	**12**
21	**BMK**	2004	341	1	14	6	121	**11**
22	**TCA**	2008	14	0	13	4	125	**9**
23	**revTCA**	2008	11	0	10	3	129	**7**
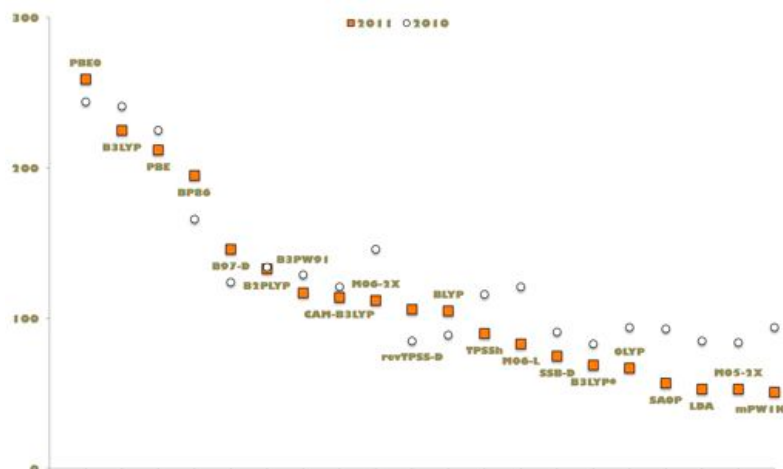
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Significance of the popularity poll results

For the second year in a row, the PBE0 functional has been selected by the "computational chemistry community" as the most popular functional, before the widely-used B3LYP functional.

Remarkably, the total number of people who *like*d PBE0 increased by 12.5%, even though the number of entries was ca. 12% <u>lower</u>. As a result, the total number of points for PBE0 increased (to 259, see Figure on p. 4). This is not so for the majority, because of the lower number of poll entries. However, the average number of points increases for all functionals in the top 10, except M06-2X (see Figure on the right). The average number of points for all functionals goes up slightly, from 0.79 to 0.82.

There are five functionals that will relegate to the *Segona Divisió* in the 2012 edition: OLYP, SAOP, LDA, M05-2X and mPW1K. They will be replaced by B3LYP-D, PW91, revPBE, PWPB95-D$_3$ and revTPSS. The promotion of PWPB95-D$_3$ is quite remarkable, given that it was published in the same year (2011) as the poll was held.

Three functionals are excluded from the popularity poll 2012 (BMK, TCA and revTCA), unless suggested again (see rules on p. 3).

The composition of the *Primera Divisió* and *Segona Divisió* for the **year 2012** is given on p. 7. As usual, the online poll will be held from June 1 until October 1.

The average number of points increases slightly, from 0.79 to 0.82

Construction of the **PACO2011 functional**

| | w$_{energy}$ | | w$_{td-dft}$ | |
	PACO2011	PACO2010	PACO2011	PACO2010
PBE0	0.1143	0.1022	0.1115	0.0984
B3LYP	0.0993	0.1010	0.0969	0.0972
PBE	0.0936	0.0943	0.0913	0.0907
BP86	0.0861	0.0695	0.0840	0.0669
B97-D	0.0645	0.0519	0.0629	0.0500
B2PLYP	0.0587	0.0561	0.0573	0.0540
B3PW91	0.0517	0.0540	0.0504	0.0520
CAM-B3LYP	0.0503	0.0507	0.0491	0.0488
M06-2X	0.0494	0.0612	0.0482	0.0589
revTPSS-D	0.0468	0.0[a]	0.0457	0.0[a]
BLYP	0.0464	0.0373	0.0452	0.0359
TPSSh	0.0397	0.0486	0.0388	0.0468
M06-L	0.0366	0.0507	0.0357	0.0488
SSB-D	0.0331	0.0381	0.0323	0.0367
B3LYP*	0.0305	0.0348	0.0297	0.0335
OLYP	0.0296	0.0394	0.0289	0.0379
SAOP	0.0[b]	0.0[b]	0.0245	0.0375
LDA	0.0234	0.0356	0.0228	0.0343
M05-2X	0.0234	0.0352	0.0228	0.0339
mPW1K	0.0225	0.0394	0.0220	0.0379

a) has only recently (End 2011) become available in g09, therefore not taken into account for PACO2010;
b) no energy expression, therefore not taken into account

As usual, we prepared a *popularity adapted consensus object*, i.e. the PACO2011 functional. It was obtained by taking the points from the online poll for the *Primera Divisió*, and giving each of the functionals in it a weight corresponding to their points (see Rules on p. 3). These weights are listed here on the left.

With these weights, we have carried out an analysis of the performance for a series of chemical interactions within a set of molecules (shown on p. 6). The results of PACO2010, PACO2011 together with the best and worst performing functionals are listed on p. 7.

Chemical systems used for checking interactions
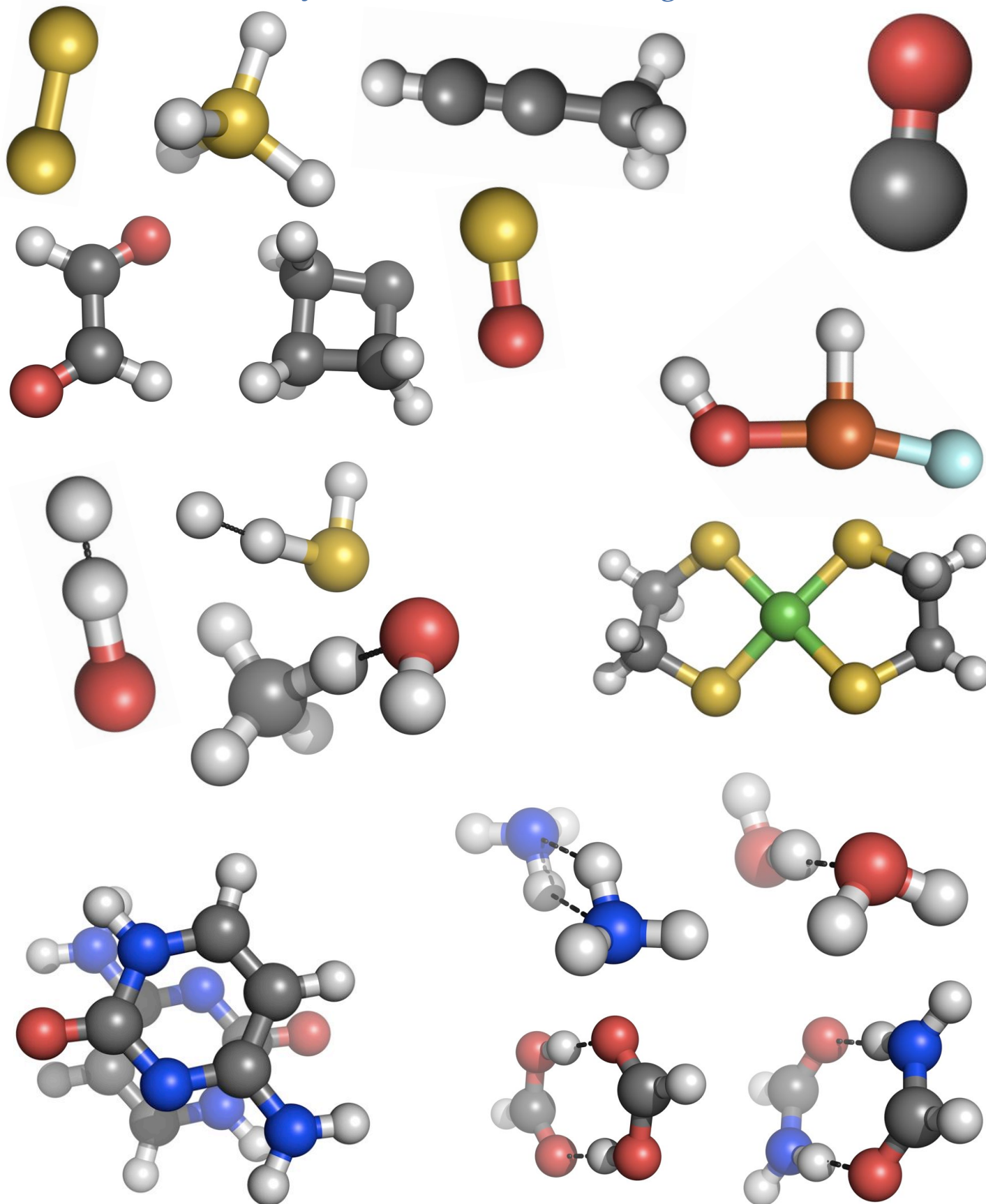
Check of **PACO2011** interactions

	reference	PACO2011	PACO2010	best	worst
AE6[a,b]				M06-2X	LDA
SiH_4	322.83	**320.75**	320.29	320.50	344.49
SiO	192.74	**187.21**	187.35	188.60	219.96
S_2	102.79	**105.72**	105.88	102.65	132.52
propyne	705.06	**710.44**	711.32	703.86	800.27
glyoxal	633.99	**641.18**	642.00	632.21	751.15
cyclobutane	1149.37	**1156.66**	1158.05	1146.74	1302.09
MAD		**5.07**	5.66	2.04	73.95
BH6[a,b]				M06-2X	LDA
$OH+CH_4$ (fw)	6.54	**0.02**	0.21	5.17	-16.89
$OH+CH_4$ (rv)	19.61	**12.48**	12.78	17.64	2.19
H+OH (fw)	10.45	**4.06**	4.55	9.67	-2.04
H+OH (rv)	12.90	**4.76**	4.76	11.35	-13.04
$H+H_2S$ (fw)	3.55	**-0.47**	-0.13	4.23	-6.97
$H+H_2S$ (rv)	17.27	**13.98**	13.88	18.30	-0.31
MAD		**5.92**	5.71	1.23	17.90
Excited states CO[c,d]				SAOP	B2PLYP
$^1\Pi, \sigma \rightarrow \pi^*$	8.51	**8.38**	8.37	8.55	8.59
$^1\Sigma^-, \pi \rightarrow \pi^*$	9.88	**9.70**	9.67	10.03	9.58
$^1\Delta, \pi \rightarrow \pi^*$	10.23	**10.04**	10.05	10.46	9.99
$^3\Pi, \sigma \rightarrow \pi^*$	6.32	**5.86**	5.87	6.28	5.70
$^3\Sigma^+, \pi \rightarrow \pi^*$	8.51	**7.98**	7.98	8.64	7.41
$^3\Delta, \pi \rightarrow \pi^*$	9.36	**8.73**	8.74	9.36	8.33
MAD		**0.35**	0.35	0.10	0.56
π-π stacking[a,e]	Ref. [51]			SSB-D	OLYP
Cyt_2	-9.93	**-3.68**	-3.66	-9.69	+4.99
MAD		**6.25**	6.27	0.24	14.92
Spin-states[a]					
FeFHOH	5.4[f] ??	**12.15**	11.42	??	??
$Ni(EDT)_2^{2-}$	>0	**4.44**	3.49	??	??
MAD		**??**	??	??	??
H-bonding[a,g]				M06-2X	OLYP
ammonia	-3.17	**-2.62**	-2.61	-3.17	-0.56
water	-5.02	**-4.71**	-4.74	-5.13	-2.40
formic acid	-18.61	**-18.36**	-18.44	-19.52	-11.40
formamide	-15.96	**-14.88**	-14.93	-16.01	-8.66
MAD		**0.55**	0.51	0.27	4.93

a) in kcal·mol⁻¹; b) reference data from J. Phys. Chem. A 2003, 107, 8996; c) in eV; d) reference data from J. Chem. Phys. 2000, 112, 1344 and J. Chem. Phys. 2001, 114, 652; e) reference data from. J. Phys. Chem. B 2004, 108, 5466; f) from news-item PACO2010; g) reference data from Phys. Chem. Chem. Phys. 2006, 8, 1985

Although the weights of the different functionals in the PACO2011 functional have changed considerably compared to PACO2010 (see Table on p. 5), the performance for the different chemical interactions is more or less similar. The *mean absolute deviation* (MAD) values are very alike, with the only exception of the AE6 and BH6 sets. For AE6, the MAD value drops by 10%, while for BH6 it increases by 4%. Weak interactions and excited states are equally well represented. For spin states, there are not yet reliable reference data to compare with, but it is remarkable that the spin-state splittings increase by ca. 1 kcal·mol⁻¹.

It will be interesting to see the performance for PACO2012, with the five new functionals included in the poll.

PRIMERA DIVISIÓ 2012

- *B2PLYP*
- *B3LYP*
- *B3LYP**
- *B3LYP-D*
- *B3PW91*
- *B97-D*
- *BLYP*
- *BP86*
- *CAM-B3LYP*
- *M06-2X*
- *M06-L*
- *PBE*
- *PBE0*
- *PW91*
- *PWPB95-D3*
- *revPBE*
- *revTPSS*
- *revTPSS-D*
- *SSB-D*
- *TPSSh*

SEGONA DIVISIÓ 2012

- *ωB97X-D*
- *BHandH*
- *DSD-BLYP*
- *τ-HCTH*
- *HSE*
- *LB94*
- *LC-ωPBE*
- *LC-PBE*
- *LDA*
- *M05*
- *M05-2X*
- *M06*
- *mPW1K*
- *OLYP*
- *PW6B95*
- *RPBE*
- *SAOP*
- *VSXC*
- *X3LYP*
- *XLYP*

Density Functional Theory in a nutshell

In 1964, Hohenberg and Kohn published theorems that laid the basis for density functional theory (DFT). Together with the Kohn-Sham scheme published a year later in 1965, these form the basic framework of DFT. In these papers, it was shown that there exists a one-to-one relation between the energy and density, i.e. it is in principle possible to obtain directly the <u>exact</u> energy from the electron density. But, the mathematical formulation that delivers this energy is unknown, although it can be constructed numerically from an exact (accurate) wavefunction for a concrete system. It was not until the 1980s that the first reasonable approximations were proposed. Apart from the Local Density Approximation (LDA), the Generalized Gradient Approximation (GGA), hybrid functionals containing a portion of *exact* (Hartree-Fock) exchange, meta-GGA functionals, double hybrid functionals, local hybrid functionals, and the hybrid meta-GGA functionals, there are now also the range-separated hybrid functionals.

In 1998, Walter Kohn received the Nobel prize in Chemistry for his work on DFT.
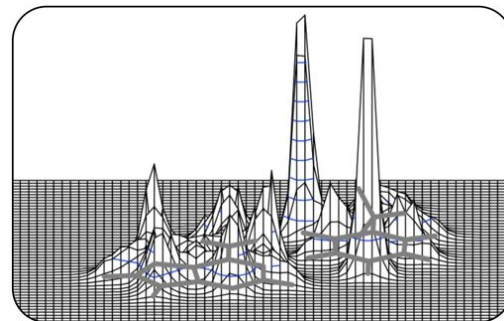
There exists a one-to-one relationship between the electron density and the <u>exact</u> energy.

"the total electron density defines the number of electrons in the system; the cusps in the density define the nuclear coordinates; the derivative of the density at a cusp defines the nuclear charge at that cusp and thus the configuration of the elements; therefore, the system is fully defined"
(Bright-Wilson, 1965)

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TCA: *J. Chem. Phys. 2008, 128, 034101*
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