

# DFT2013

## Density functionals poll

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



### NEWS-ITEM, 2013

#### History and rules:



The origin of the popularity poll, as it was created after a visit of Matthias Bickelhaupt to the IQCC in Girona

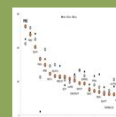
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The rules of the poll, and how the poll results are transformed into a measure how the computational chemistry community does

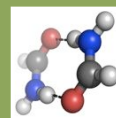
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*"The non-empirical PBE functional remains the clear winner of this year."*

## List of density functionals included in the poll

### Primera divisió 2013:

$\omega$ B97X-D, B2PLYP, B3LYP, B3LYP-D, B3PW91, B97-D, BLYP, BP86, CAM-B3LYP, HSE, LDA, M06, M06-2X, OLYP, PBE, PBE0 (PBE1PBE), PW91, revPBE, SSB-D, TPSSh

### Segona divisió 2013:

APBE, BHandH, B3LYP\*, DSD-BLYP,  $\tau$ -HCTH, LB94, LC- $\omega$ PBE, LC-PBE, M05, M05-2X, M06-L, mPW1K, optB88-vdW\*, PW6B95, PWPB95-D<sub>3</sub>, revTPSS, revTPSS-D, RPBE, SAOP, VSXC, RPA, S12g, S12h, KT1, DSD-PBEP86, BLOC

\*disqualified (see p. 4)

## 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,

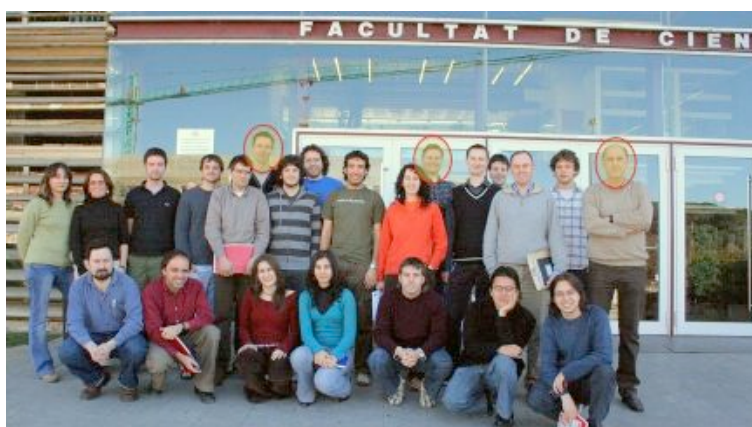
on Twitter, Facebook, blogs, etc. in order to get the maximum number of participants. The aims of this poll were: (i) to probe the "preference of the community", i.e., setting up a ranking of preferred DFT methods; and (ii) provide a compilation of the "de facto quality" that this implies for the "average 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 and physics communities, and compile the quality of the "average" DFT computation.*

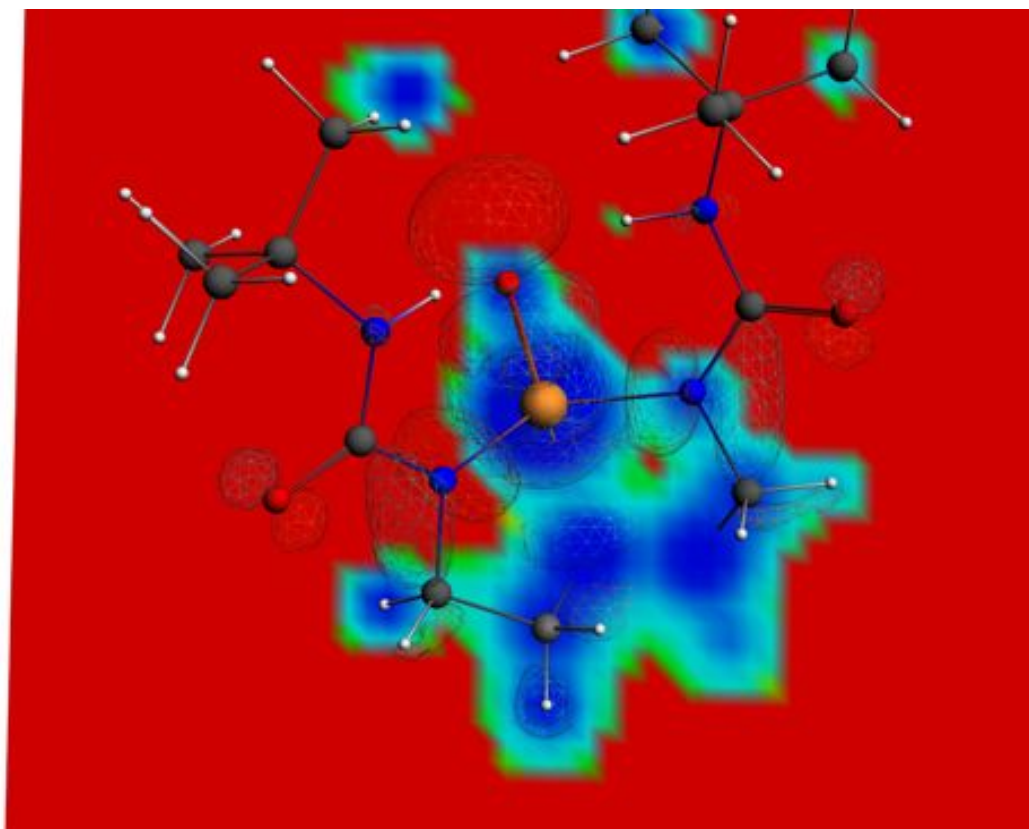
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### Prof. Bickelhaupt: a regular visitor to Girona



*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 IQCC in Girona. Since 1993, Prof. Matthias Bickelhaupt collaborates with Prof. Miquel Solà (IQCC) 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 IQCC 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 be relegated 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 ( $\text{SiH}_4$ ,  $\text{SiO}$ ,  $\text{S}_2$ , propyne, glyoxal, cyclobutane)
  - the BH6 set for six barrier heights (forward and reverse reaction of  $\text{OH}+\text{CH}_4$ ,  $\text{H}+\text{OH}$ ,  $\text{H}+\text{H}_2\text{S}$ )
  - the  $\pi$ - $\pi$  stacking energy of anti-parallel cytosine dimer
  - spin-state splitting of  $\text{FeFHOH}$  and  $\text{Ni}(\text{EDT})_2^{2-}$
  - excitation energies (singlet, triplet) of  $\text{CO}$
  - 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](http://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.
- 7) The organization of the DFT-poll reserves the right to disqualify density functionals in case of clear proof of cheating. This disqualification remains effective for the year following the year in which the cheating has been observed.

## Results\* of the popularity poll

	functional	year	like	neutral	hate	empty	points
<i>Primera Divisió</i>							
1	PBE	1996	109	46	7	32	366
2	PBE0 (PBE1PBE)	1996	96	27	4	67	311
3	B3LYP	1994	68	47	40	39	211
4	LDA	1980	65	37	31	61	201
5	PW91	1992	48	56	13	77	187
6	BP86	1988	49	34	22	89	159
7	HSE	2003	42	42	12	98	156
8	revPBE	1998	32	58	8	96	146
9	$\omega$ B97X-D	2008	38	41	11	104	144
10	B3LYP-D	2006	36	46	23	89	131
11	CAM-B3LYP	2004	28	53	9	104	128
12	M06-2X	2008	42	27	34	91	119
13	B97-D	2006	25	50	13	106	112
14	B2PLYP	2006	28	38	18	110	104
15	B3PW91	1993	20	58	15	101	103
16	M06	2008	30	44	36	84	98
17	TPSSh	2003	23	42	14	115	97
18	BLYP	1988	23	55	32	84	92
19	OLYP	2001	11	51	22	110	62
20	SSB-D	2009	9	40	17	128	50
<i>Segona Divisió</i>							
1	RPA	2008	22	32	5	135	93
2	LC- $\omega$ PBE	2006	18	33	7	136	80
3	RPBE	1999	16	33	7	138	74
4	BHandH	1993	13	43	11	127	71
5	B3LYP*	2001	19	34	20	121	71
6	M05-2X	2006	18	38	24	114	68
7	M06-L	2006	20	34	28	112	66
8	PWPB95-D <sub>3</sub>	2011	13	28	5	148	62
9	revTPSS-D	2009	9	36	6	143	57
10	LC-PBE	2007	9	39	10	136	56
11	revTPSS	2009	8	39	7	140	56
12	mPW1K	2000	10	35	10	139	55
13	SAOP	2000	11	29	7	147	55
14	PW6B95	2005	8	34	4	148	54
15	M05	2005	13	39	25	117	53
16	DSD-BLYP	2010	9	33	8	144	52
17	APBE	2011	9	31	9	145	49
18	$\tau$ -HCTH	2002	4	37	10	143	39
19	LB94	1994	7	28	11	148	38
20	DSD-PBEP86	2011	7	21	5	161	37
21	S12h	2013	4	29	7	154	34
22	KT1	2003	1	35	7	151	31
23	S12g	2013	3	28	7	156	30
24	VSXC	1998	1	37	13	143	27
25	BLOC	2013	6	7	1	180	24

\* the optB88-vdW functional has been disqualified from this year's result because of attempts to bias the outcome of the poll through repetitive *single-answer* entries (with only 1 option liked: optB88-vdW), which often were added at a pace of one per 8 seconds; a total of 56 of these *single-answer* optB88-vdW entries had been entered. The disqualification will be effective both for 2013 and 2014.

## ABOUT THE AUTHORS

## Marcel Swart

ICREA Research Professor at IQCC  
(Univ. Girona)

PhD 2002, Univ. Groningen

Research interests:  
theory, method development,  
molecular cages, spin states,  
(bio)inorganic chemistry

www.marcelswart.eu

## Matthias Bickelhaupt

Full Professor at  
Theoretical Chemistry  
(VU Univ. Amsterdam) &  
Institute of Molecules and Materials  
(Radboud Univ. Nijmegen)

PhD 1993, VU Univ. Amsterdam

Research interests:  
catalysis, S<sub>N</sub>2/E2 reactions,  
chemical bonding, DNA,  
molecular orbital analysis

www.few.vu.nl/~bickel

## Miquel Duran

Full Professor at IQCC  
(Univ. Girona)

PhD 1984, Univ. Aut. Barcelona

Research interests:  
influence electric fields on structure  
and reactivity, weak bonding,  
electron density methodology

www.miquelduran.net

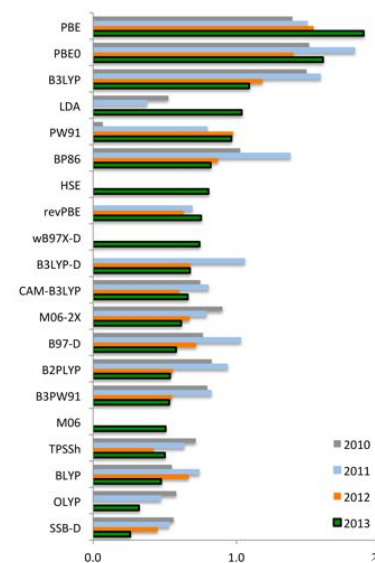
## Significance of the popularity poll results

For the second time in a row, the non-empirical PBE functional has been selected by the “computational chemistry and physics communities” as the most popular functional, before the PBE0 (the winner of the 2010 and 2011 editions) and B3LYP functionals. This is the second consecutive year that a GGA functional is beating hybrid functionals in popularity.

The total number of valid entries has increased significantly, from 171 in 2012 to 194 in 2013 (+13%). It should also be mentioned that 57 additional entries were not counted (56 because of the disqualification of *optB88-vdW*, see p. 4, and 1 because it was completely empty). It is remarkable that the  $\omega$ B97X-D and HSE functionals (both for the first

time in the *Primera Divisió*) continue their upward march, and are now at the 9<sup>th</sup> and 7<sup>th</sup> place respectively. This exemplifies the popularity of range-separated hybrid functionals in general nowadays. Five functionals will be promoted to the *Primera Divisió* of 2014: RPA, LC- $\omega$ PBE, RPBE, BHandH and B3LYP\*, replacing the following functionals: M06, TPSSh, BLYP, OLYP and SSB-D.

The composition of the *Primera Divisió* and *Segona Divisió* for the year 2014 is given on p. 7. The next online poll will, as usual, be held from June 1 until October 1.



The average number of points increases again, from 0.69 to 0.77

## Construction of the PACO2013 functional

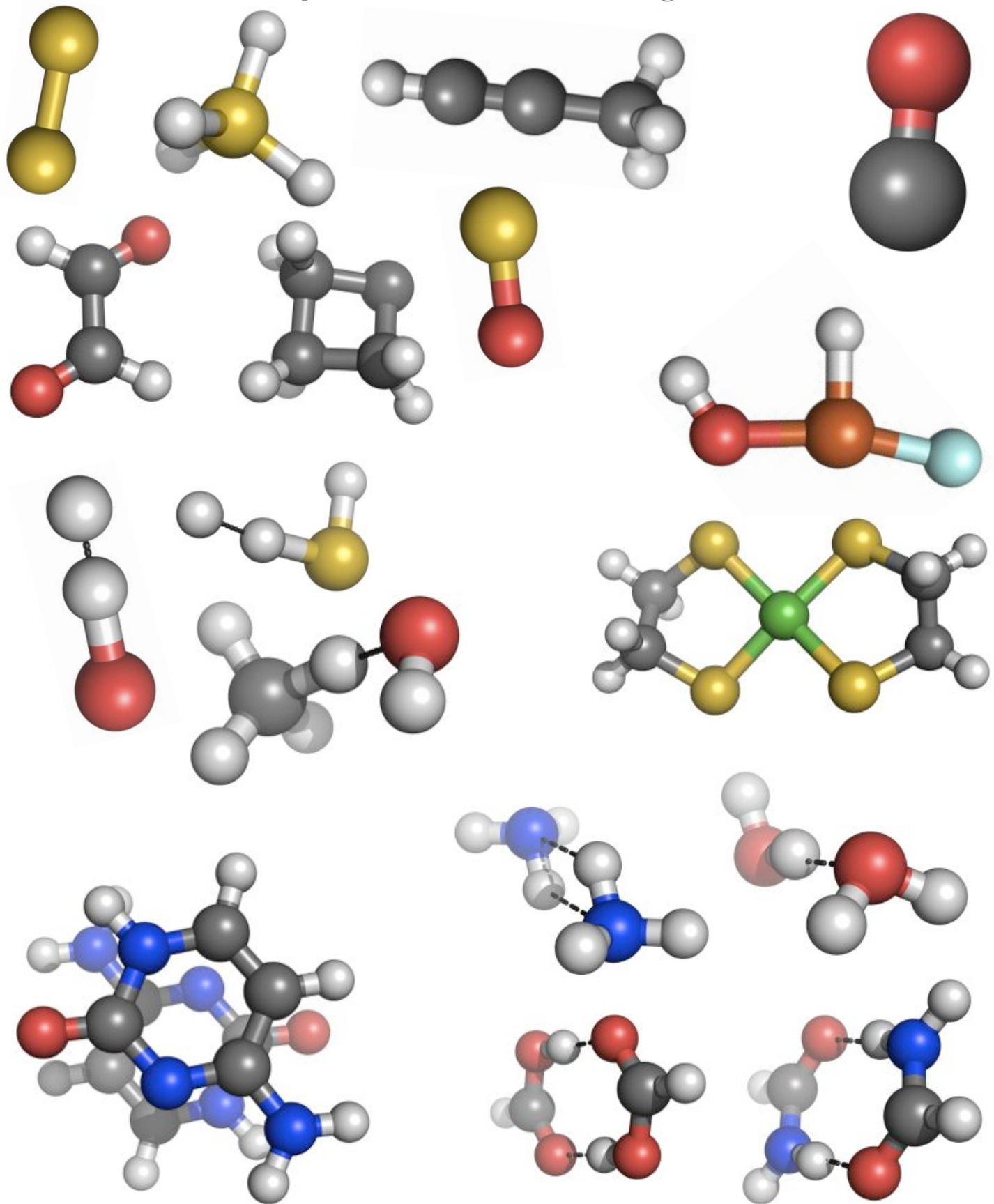
	$W_{\text{energy}}$			
	2013	2012	2011	2010
PBE	0.1230	0.1150	0.0936	0.0943
PBE0 (PBE1PBE)	0.1045	0.1044	0.1143	0.1022
B3LYP	0.0709	0.0882	0.0993	0.1010
LDA	0.0675	- <sup>a</sup>	0.0234	0.0356
PW91	0.0628	0.0730	- <sup>a</sup>	- <sup>a</sup>
BP86	0.0534	0.0651	0.0861	0.0695
HSE	0.0524	- <sup>a</sup>	- <sup>a</sup>	- <sup>a</sup>
revPBE	0.0490	0.0472	- <sup>a</sup>	- <sup>a</sup>
$\omega$ B97X-D	0.0484	- <sup>a</sup>	- <sup>a</sup>	- <sup>a</sup>
B3LYP-D	0.0440	0.0507	- <sup>a</sup>	- <sup>a</sup>
CAM-B3LYP	0.0430	0.0450	0.0503	0.0507
M06-2X	0.0400	0.0502	0.0494	0.0612
B97-D	0.0376	0.0537	0.0645	0.0519
B2PLYP	0.0349	0.0415	0.0587	0.0561
B3PW91	0.0346	0.0411	0.0517	0.0540
M06	0.0329	- <sup>a</sup>	- <sup>a</sup>	- <sup>a</sup>
TPSSh	0.0326	0.0315	0.0397	0.0486
BLYP	0.0309	0.0498	0.0464	0.0373
OLYP	0.0208	- <sup>a</sup>	0.0296	0.0394
SSB-D	0.0168	0.0336	0.0331	0.0381

a) not included in earlier editions

As usual, we prepared a popularity adapted consensus object, i.e. the PACO2013 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 the PACO201x functionals, together with the best and worst performing functionals, are listed on p. 7.

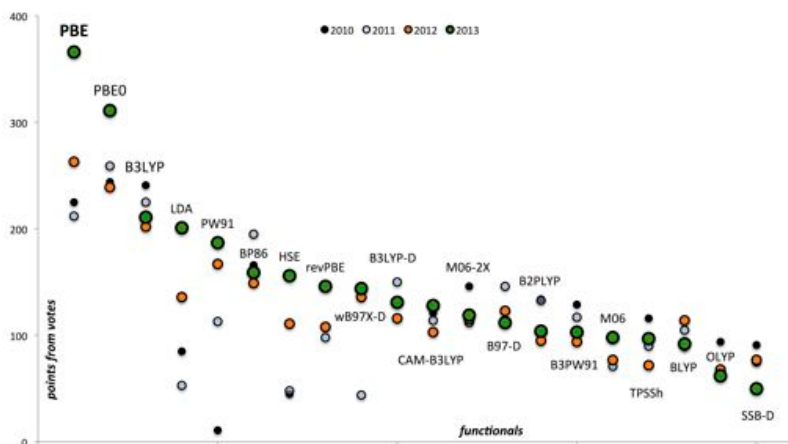
# Chemical systems used for checking interactions



## Check of PACO2013 interactions

	reference	2013	2012	2011	2010	best	worst
<b>AE6<sup>a,b</sup></b>						<i>M06-2X</i>	<i>LDA</i>
<i>SiH<sub>4</sub></i>	322.83	<b>319.57</b>	319.24	320.75	320.29	320.50	344.49
<i>SiO</i>	192.74	<b>189.80</b>	187.34	187.21	187.35	188.60	219.96
<i>S<sub>2</sub></i>	102.79	<b>107.72</b>	105.84	105.72	105.88	102.65	132.52
<i>propyne</i>	705.06	<b>715.40</b>	709.25	710.44	711.32	703.86	800.27
<i>glyoxal</i>	633.99	<b>649.49</b>	641.16	641.18	642.00	632.21	751.15
<i>cyclobutane</i>	1149.37	<b>1163.47</b>	1153.70	1156.66	1158.05	1146.74	1302.09
MAD		<b>8.51</b>	4.62	5.07	5.66	2.04	73.95
<b>BH6<sup>a,b</sup></b>						<i>M06-2X</i>	<i>LDA</i>
<i>OH+CH<sub>4</sub> (fw)</i>	6.54	<b>-1.56</b>	-0.46	0.02	0.21	5.17	-16.89
<i>OH+CH<sub>4</sub> (rv)</i>	19.61	<b>11.66</b>	12.01	12.48	12.78	17.64	2.19
<i>H+OH (fw)</i>	10.45	<b>4.11</b>	3.89	4.06	4.55	9.67	-2.04
<i>H+OH (rv)</i>	12.90	<b>2.88</b>	4.17	4.76	4.76	11.35	-13.04
<i>H+H<sub>2</sub>S (fw)</i>	3.55	<b>-0.65</b>	-0.64	-0.47	-0.13	4.23	-6.97
<i>H+H<sub>2</sub>S (rv)</i>	17.27	<b>12.71</b>	13.72	13.98	13.88	18.30	-0.31
MAD		<b>6.86</b>	6.27	5.92	5.71	1.23	17.90
<b>Exc. states CO<sup>c,d</sup></b>						<i>SAOP</i>	<i>B2PLYP</i>
<i><sup>1</sup>Π, σ → π*</i>	8.51	<b>8.33</b>	8.36	8.38	8.37	8.55	8.59
<i><sup>1</sup>Σ<sup>-</sup>, π → π*</i>	9.88	<b>9.67</b>	9.71	9.70	9.67	10.03	9.58
<i><sup>1</sup>Δ, π → π*</i>	10.23	<b>9.97</b>	10.01	10.04	10.05	10.46	9.99
<i><sup>3</sup>Π, σ → π*</i>	6.32	<b>5.85</b>	5.84	5.86	5.87	6.28	5.70
<i><sup>3</sup>Σ<sup>+</sup>, π → π*</i>	8.51	<b>8.03</b>	8.00	7.98	7.98	8.64	7.41
<i><sup>3</sup>Δ, π → π*</i>	9.36	<b>8.75</b>	8.71	8.73	8.74	9.36	8.33
MAD		<b>0.37</b>	0.36	0.35	0.35	0.10	0.56
<b>π-π stacking<sup>a,e</sup></b>						<i>ωB97X-D</i>	<i>OLYP</i>
<i>Cyt<sub>2</sub></i>	-9.93	<b>-3.93</b>	-3.64	-3.68	-3.66	-9.93	+4.99
MAD		<b>6.00</b>	6.29	6.25	6.27	0.00	14.92
<b>Spin-states<sup>a</sup></b>							
<i>FeFHOH</i>	5.4f ??	<b>13.44</b>	13.19	12.15	11.42	??	??
<i>Ni(EDT)<sub>2</sub><sup>-</sup></i>	>0	<b>6.59</b>	5.39	4.44	3.49	??	??
MAD		??	??	??	??	??	??
<b>H-bonding<sup>a,g</sup></b>						<i>M06-2X</i>	<i>OLYP</i>
<i>ammonia</i>	-3.17	<b>-2.78</b>	-2.65	-2.62	-2.61	-3.17	-0.56
<i>water</i>	-5.02	<b>-4.92</b>	-4.72	-4.71	-4.74	-5.13	-2.40
<i>formic acid</i>	-18.61	<b>-18.78</b>	-18.24	-18.36	-18.44	-19.52	-11.40
<i>formamide</i>	-15.96	<b>-15.24</b>	-14.81	-14.88	-14.93	-16.01	-8.66
MAD		<b>0.35</b>	0.58	0.55	0.51	0.27	4.93

a) in kcal mol<sup>-1</sup>; 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 PACO2011; g) reference data from *Phys. Chem. Chem. Phys.* **2006**, 8, 1985

PRIMERA  
DIVISIÓ 2014

- *ωB97X-D*
- *B2PLYP*
- *B3LYP*
- *B3LYP-D*
- *B3LYP\**
- *B3PW91*
- *B97-D*
- *BHandH*
- *BP86*
- *CAM-B3LYP*
- *HSE*
- *LC-ωPBE*
- *LDA*
- *M06-2X*
- *PBE*
- *PBE0*
- *PW91*
- *revPBE*
- *RPA*
- *RPBE*

SEGONA  
DIVISIÓ 2014

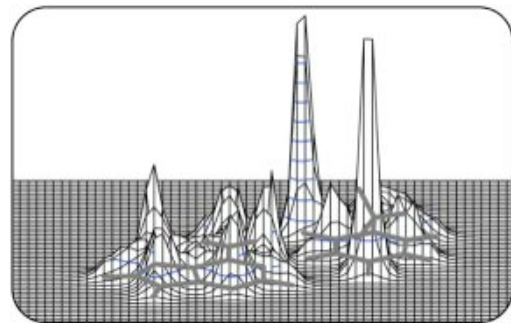
- *APBE*
- *BLYP*
- *DSD-BLYP*
- *DSD-PBEP86*
- *τ-HCTH*
- *LB94*
- *LC-PBE*
- *M05*
- *M05-2X*
- *M06*
- *M06-L*
- *mPW1K*
- *OLYP*
- *PW6B95*
- *PWPB95-D<sub>3</sub>*
- *revTPSS*
- *revTPSS-D*
- *SAOP*
- *SSB-D*
- *TPSSH*

## 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 exact 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 exact 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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