DFT2014

Density functionals poll

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



*iCrea INSTITUCIÓ CATALANA DE RECERCA I ESTUDIS AVANÇATS

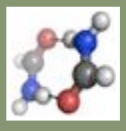
VRIJE UNIVERSITEIT AMSTERDAM

Universitat de Girona iQCC

NEWS-ITEM, 2014

History and rules:

Results:



Five years DFT poll:

Appendices:

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

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

Primera divisió 2014:

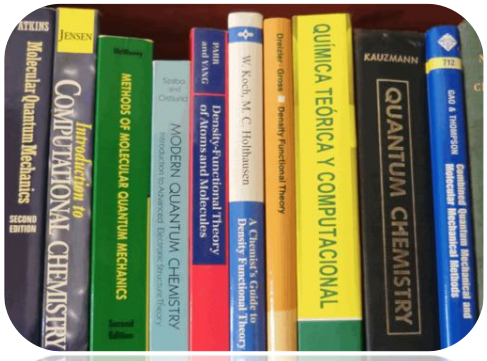
ωB97X-D, B2PLYP, B3LYP, B3LYP-D, B3LYP*, B3PW91, B97-D, BHandH, BP86, CAM-B3LYP, HSE, LC-ωPBE, LDA, M06-2X, PBE, PBE0 (PBE1PBE), PW91, revPBE, RPA, RPBE

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_3, revTPSS, revTPSS-D, SAOP, SSB-D, TPSSh, S12g, S12h, MN12L

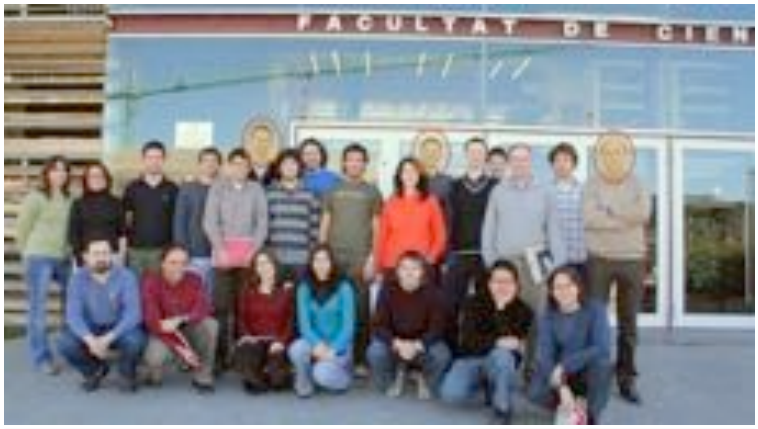
Origin of the online popularity poll of density functionals

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.



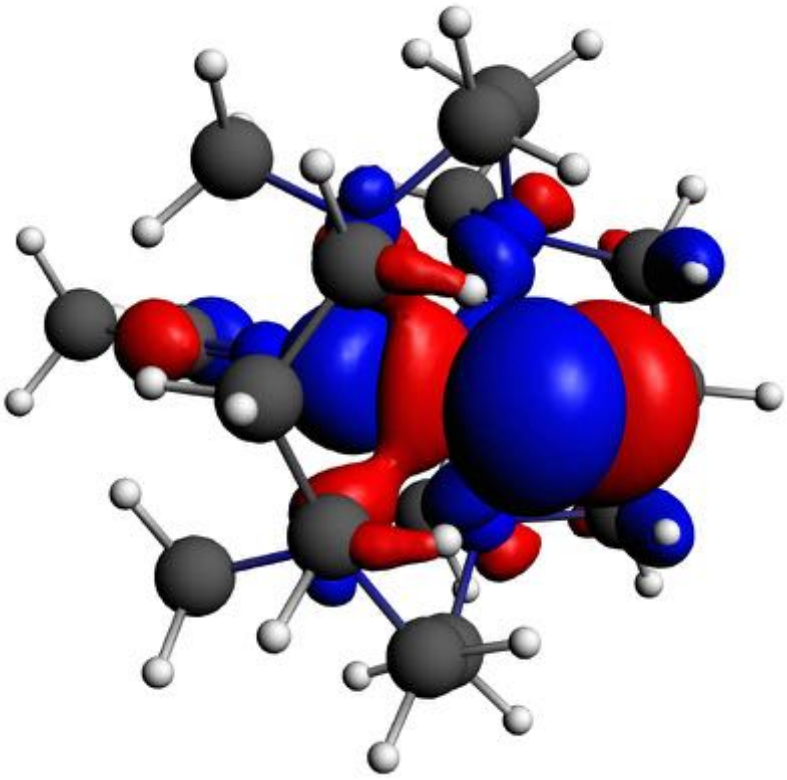
The aim of the online popularity poll is to probe the preferences of the computational chemistry and physics communities, and compile the quality of the "average" DFT computation.

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 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 $OH+CH_4$, $H+OH$, $H+H_2S$)*
   - *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.*

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
Primera Divisió							
1	**PBE**	1996	99	30	6	26	**321**
2	**PBE0 (PBE1PBE)**	1996	87	23	10	41	**274**
3	**B3LYP**	1994	56	44	33	28	**179**
4	**ωB97X-D**	2008	49	21	12	79	**156**
5	**PW91**	1992	38	47	13	63	**148**
6	**B3LYP-D**	2006	41	38	14	68	**147**
7	**LDA**	1980	50	33	37	41	**146**
8	**M06-2X**	2008	46	27	31	57	**134**
9	**CAM-B3LYP**	2004	39	29	14	79	**132**
10	**BP86**	1988	35	33	16	77	**122**
11	**HSE**	2003	29	47	12	73	**122**
12	**B97-D**	2006	26	39	13	83	**104**
13	**B2PLYP**	2006	24	33	18	86	**87**
14	**RPA**	2008	22	33	12	94	**87**
15	**B3PW91**	1993	21	40	19	81	**84**
16	**revPBE**	1998	19	42	17	83	**82**
17	**RPBE**	1999	18	34	18	91	**70**
18	**LC-ωPBE**	2006	15	37	13	96	**69**
19	**B3LYP***	2001	17	30	23	91	**58**
20	**BHandH**	1993	9	33	23	96	**37**
Segona Divisió							
1	**BLYP**	1988	30	37	20	74	**107**
2	**TPSSh**	2003	21	36	11	93	**88**
3	**M06**	2008	29	29	29	74	**87**
4	**M06-L**	2006	28	28	28	77	**84**
5	**revTPSS**	2009	17	30	10	104	**71**
6	**revTPSS-D**	2009	15	26	10	110	**61**
7	**LC-PBE**	2007	14	29	10	108	**61**
8	**OLYP**	2001	12	35	16	98	**55**
9	**M05-2X**	2006	14	27	27	93	**42**
10	**PWPB95-D_3**	2011	10	20	12	119	**38**
11	**mPW1K**	2000	7	30	15	109	**36**
12	**SSB-D**	2009	8	22	11	120	**35**
13	**DSD-BLYP**	2010	7	26	12	116	**35**
14	**PW6B95**	2005	7	25	12	117	**34**
15	**LB94**	1994	6	24	11	120	**31**
16	**τ-HCTH**	2002	6	24	13	118	**29**
17	**M05**	2005	9	27	26	99	**28**
18	**DSD-PBEP86**	2011	5	24	11	121	**28**
19	**SAOP**	2000	5	22	10	124	**27**
20	**APBE**	2011	3	26	11	121	**24**
21	**S12h**	2013	5	18	11	127	**22**
22	**S12g**	2013	5	19	12	125	**22**
23	**MN12L**	2012	2	11	10	138	**7**

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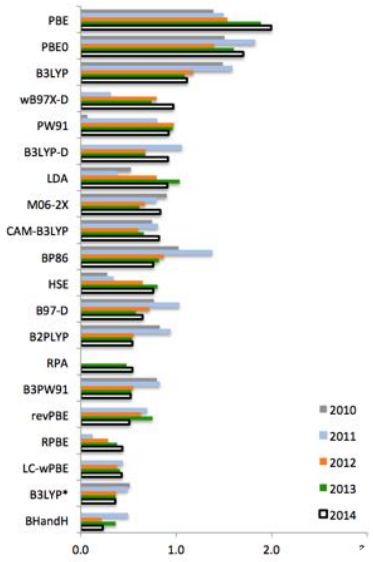
Significance of the popularity poll results

The non-empirical PBE functional has again 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 third consecutive year that this GGA functional is beating hybrid functionals in popularity.

The total number of valid entries in the poll decreased, from 194 in 2013 to 161 in 2014 (–17%). This is without any doubt due to the fact that this year SurveyMoz was used as *Online Survey Software* provider, and hence people could vote only once.

The ωB97X-D functional continues its upward march, and is now at the 4th place. This exemplifies the popularity of range-separated hybrid functionals in general nowadays. Five functionals will be promoted to the *Primera Divisió* of 2014: BLYP, TPSSh, M06, M06-L, revTPSS, replacing the following functionals: revPBE, RPBE, LC-ωPBE, B3LYP* and BHandH. Of these, BLYP, TPSSh, M06 and revTPSS had been present before in the *Primera Divisió* and are now returning there after having spent 1 or 2 years in the *Segona Divisió*.

The composition of the ***Primera Divisió*** and ***Segona Divisió*** for the **year 2015** is given on p. 7. The next online poll will, as usual, be held from June 1 until October 1. A third part will be added (see p. 8).



The average number of points increases slightly, from 0.77 to 0.79

Construction of the **PACO2014 functional**

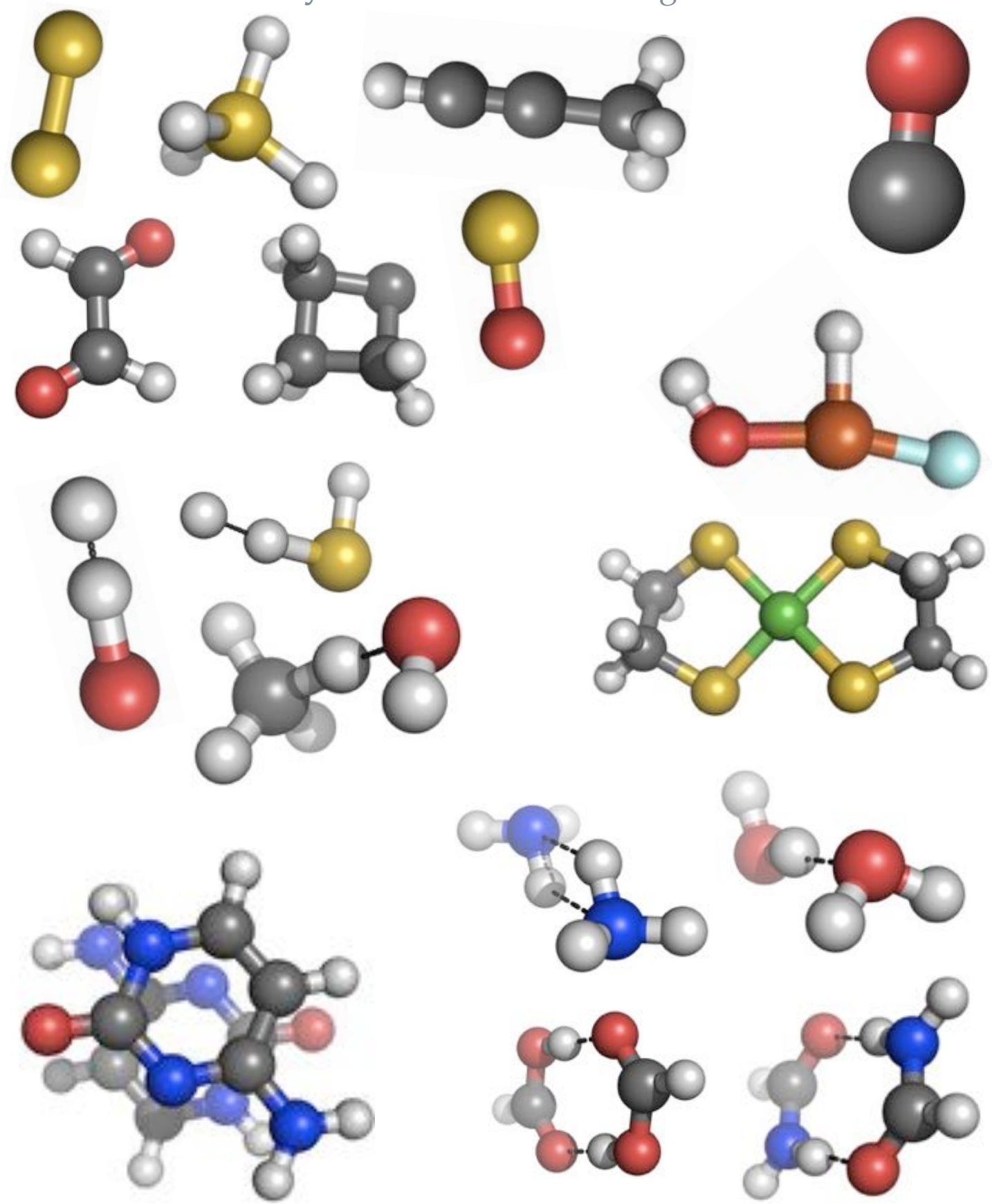
	w_{energy}				
	2014	*2013*	*2012*	*2011*	*2010*
PBE	0.1299	0.1230	0.1150	0.0936	0.0943
PBE0 (PBE1PBE)	0.1108	0.1045	0.1044	0.1143	0.1022
B3LYP	0.0724	0.0709	0.0882	0.0993	0.1010
ωB97X-D	0.0631	0.0484	-[a]	-[a]	-[a]
PW91	0.0599	0.0628	0.0730	-[a]	-[a]
B3LYP-D	0.0596	0.0440	0.0507	-[a]	-[a]
LDA	0.0591	0.0675	-[a]	0.0234	0.0356
M06-2X	0.0542	0.0400	0.0502	0.0494	0.0612
CAM-B3LYP	0.0534	0.0430	0.0450	0.0503	0.0507
BP86	0.0494	0.0534	0.0651	0.0861	0.0695
HSE	0.0494	0.0524	-[a]	-[a]	-[a]
B97-D	0.0421	0.0376	0.0537	0.0645	0.0519
B2PLYP	0.0352	0.0349	0.0415	0.0587	0.0561
RPA	-[b]	-[a]	-[a]	-[a]	-[a]
B3PW91	0.0340	0.0346	0.0411	0.0517	0.0540
revPBE	0.0332	0.0490	0.0472	-[a]	-[a]
RPBE	0.0282	-[a]	-[a]	-[a]	-[a]
LC-ωPBE	0.0278	-[a]	-[a]	-[a]	-[a]
B3LYP*	0.0234	-[a]	0.0275	0.0305	0.0348
BHandH	0.0149	-[a]	-[a]	-[a]	-[a]

a) not included in (some) earlier edition(s); b) not available, therefore not taken into account

As usual, we prepared a *popularity adapted consensus object*, i.e. the PACO2014 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.

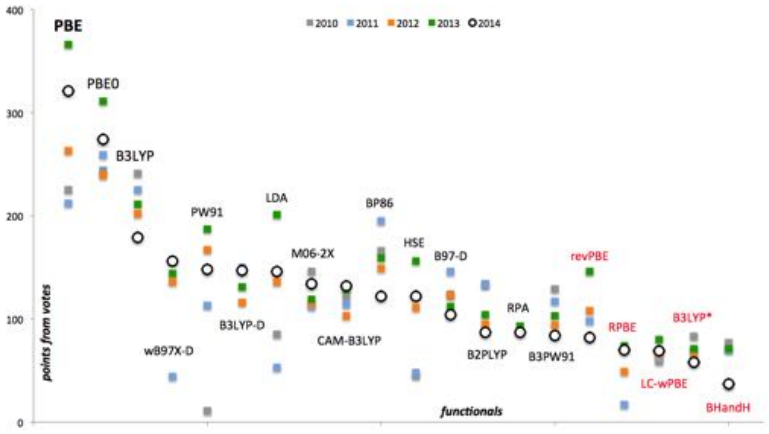
Chemical systems used for checking interactions



Check of **PACO2014** interactions

	reference	**2014**	2013	2012	2011	2010	best	worst
AE6[a,b]							*M06-2X*	*LDA*
SiH_4	*322.83*	**318.33**	319.57	319.24	320.75	320.29	320.50	344.49
SiO	*192.74*	**189.12**	189.80	187.34	187.21	187.35	188.60	219.96
S_2	*102.79*	**106.82**	107.72	105.84	105.72	105.88	102.65	132.52
propyne	*705.06*	**713.49**	715.40	709.25	710.44	711.32	703.86	800.27
glyoxal	*633.99*	**647.49**	649.49	641.16	641.18	642.00	632.21	751.15
cyclobutane	*1149.37*	**1160.63**	1163.47	1153.70	1156.66	1158.05	1146.74	1302.09
MAD		***7.56***	*8.51*	4.62	*5.07*	*5.66*	*2.04*	*73.95*
BH6[a,b]							*BHandH*	*LDA*
OH+CH_4 (fw)	*6.54*	**-1.19**	-1.56	-0.46	0.02	0.21	7.41	-16.89
OH+CH_4 (rv)	*19.61*	**11.98**	11.66	12.01	12.48	12.78	18.22	2.19
H+OH (fw)	*10.45*	**4.64**	4.11	3.89	4.06	4.55	9.51	-2.04
H+OH (rv)	*12.90*	**3.19**	2.88	4.17	4.76	4.76	12.05	-13.04
H+H_2S (fw)	*3.55*	**-0.27**	-0.65	-0.64	-0.47	-0.13	3.49	-6.97
H+H_2S (rv)	*17.27*	**12.92**	12.71	13.72	13.98	13.88	14.78	-0.31
MAD		***6.51***	*6.86*	6.27	*5.92*	*5.71*	*1.10*	*17.90*
Exc. states CO[c,d]							*SAOP*	*B2PLYP*
$^1\Pi$, $\sigma \rightarrow \pi^*$	*8.51*	**8.34**	8.33	8.36	8.38	8.37	8.55	8.59
$^1\Sigma^-$, $\pi \rightarrow \pi^*$	*9.88*	**9.69**	9.67	9.71	9.70	9.67	10.03	9.58
$^1\Delta$, $\pi \rightarrow \pi^*$	*10.23*	**10.01**	9.97	10.01	10.04	10.05	10.46	9.99
$^3\Pi$, $\sigma \rightarrow \pi^*$	*6.32*	**5.85**	5.85	5.84	5.86	5.87	6.28	5.70
$^3\Sigma^+$, $\pi \rightarrow \pi^*$	*8.51*	**8.02**	8.03	8.00	7.98	7.98	8.64	7.41
$^3\Delta$, $\pi \rightarrow \pi^*$	*9.36*	**8.74**	8.75	8.71	8.73	8.74	9.36	8.33
MAD		***0.36***	*0.37*	0.36	*0.35*	*0.35*	*0.10*	*0.56*
π-π stacking[a,e]							*ωB97X-D*	*OLYP*
Cyt_2	*-9.93*	**-4.22**	-3.93	-3.64	-3.68	-3.66	-9.93	+4.99
MAD		***5.71***	*6.00*	6.29	*6.25*	*6.27*	*0.00*	*14.92*
Spin-states[a]								
FeFHOH	*5.4[f] ??*	**13.13**	13.44	13.19	12.15	11.42	??	??
$Ni(EDT)_2^{2-}$	*>0*	**5.41**	6.59	5.39	4.44	3.49	??	??
MAD		***??***	*??*	??	*??*	*??*	*??*	*??*
H-bonding[a,g]							*M06-2X*	*OLYP*
ammonia	*-3.17*	**-2.84**	-2.78	-2.65	-2.62	-2.61	-3.17	-0.56
water	*-5.02*	**-4.97**	-4.92	-4.72	-4.71	-4.74	-5.13	-2.40
formic acid	*-18.61*	**-18.96**	-18.78	-18.24	-18.36	-18.44	-19.52	-11.40
formamide	*-15.96*	**-15.39**	-15.24	-14.81	-14.88	-14.93	-16.01	-8.66
MAD		***0.32***	*0.35*	0.58	*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 PACO2011; g) reference data from *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985



PRIMERA DIVISIÓ 2015

- *ωB97X-D*
- *B2PLYP*
- *B3LYP*
- *B3LYP-D*
- *B3PW91*
- *B97-D*
- *BLYP*
- *BP86*
- *CAM-B3LYP*
- *HSE*
- *LDA*
- *M06*
- *M06-2X*
- *M06-L*
- *PBE*
- *PBE0*
- *PW91*
- *revTPSS*
- *RPA*
- *TPSSh*

SEGONA DIVISIÓ 2015

- *APBE*
- *B3LYP**
- *BHandH*
- *DSD-BLYP*
- *DSD-PBEP86*
- *τ-HCTH*
- *LB94*
- *LC-ωPBE*
- *LC-PBE*
- *M05*
- *M05-2X*
- *mPW1K*
- *OLYP*
- *PW6B95*
- *PWPB95-D_3*
- *revPBE*
- *revTPSS-D*
- *RPBE*
- *SAOP*
- *SSB-D*

Summary of five years of DFT polling

After having organized the DFT poll for five years, it is time for some reflections on the outcome of the results and the status of the poll.

From the beginning we set the poll out to be anonymous. This would have two main advantages: (i) anyone willing to participate could do so easily, without having to pass through a complicated setup where one would have to register etc.; (ii) the participants would be able to give their preferences without having to fear negative feedback. To this day, it still works like that: the organizers do not know who are the participants, nor do they want to know. The only data known to the organizers are: the preferred functionals, and the date that this preference was given. Unfortunately, in the 2013 edition the organizers were forced to exclude one functional because of attempts to bias the outcome of the poll through repetitive single-answer entries. Therefore, the 2014 edition was taken using the SurveyMoz online software.

This year (2014) there has been a vivid discussion on the CCL list about the poll (see p. 9). One of the positive outcomes was a suggestion by Henry Rzepa (June 1, 2014) "*that in the future this poll be extended to indicate WHY any person indicates they LIKE a functional? As we all know, the choice of functional so often depends on what the property of interest is*".

The organizers investigated whether this would be possible technically (answer: yes), and therefore have decided to adapt the poll for this suggestion. Starting from the sixth edition in 2015, the poll will have a third part (next to the *Primera* and *Segona Divisió*) where for each functional one can indicate whether the participants like or dislike it for certain properties (*reaction barriers, normal modes, NMR shieldings, structures, spin-state splittings, etc.)*.

In the future this might be extended with a fourth part where the preferences for dispersion energy descriptions could be given.

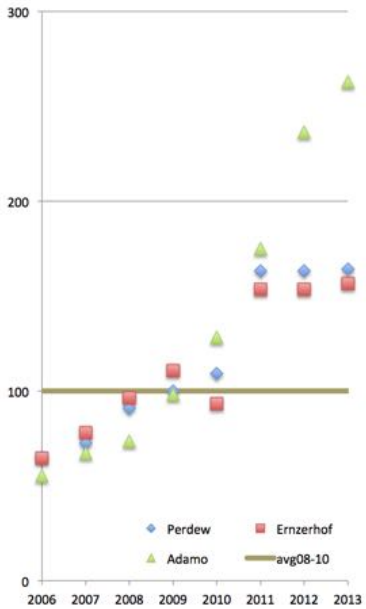
Anecdotes of five years of DFT polling

At the end of the first year we were not sure how to report the results. Obviously, this was not to be a regular science paper, but after long deliberations we thought it might enter the "News" items of a computational chemistry journal. The reviewers were however not so enthusiastic:

Reviewer 1: "*The topic of this paper is interesting, but the methodology must have some dreadful weakness. I talk to many quantum chemists all over the world every year. For most of them PBE0 is not even on the radar. […]*" (see Figure on the right; it is interesting to note how the number of citations for PBE0 increased by ca. 60% in the year after it "won" the first poll)

Reviewer 2: "*This paper is a bit hard to judge. […] It is a rather unique contribution ("one of a kind") that presents an unorthodox way of deciding on the merits of density functionals, and of constructing a good compromise functional. From a purist point of view, one might deplore such an approach: science is not a democracy. The truth is not decided by public vote! […] On the positive side, one might feel that computational chemists just need good functionals to study chemistry, and this contribution helps them to get an idea of current opinion on the matter. […] It is original, but it should not be followed by many of such 'polls'. […]*"

In the end, it was not accepted for publication; instead we decided to publish the results online in an annual news-item (available at www.marcelswart.eu/dft-poll).



*Normalized number of citations for PBE0 papers, **before** (2006-2010) and **after** (2011-2013) first news-item of DFT-poll*
[100 = average for 2008-2010]

What do people think about the poll

The enormous interest in the DFT poll becomes obvious every year in the first few days after the annual news-item has been published online: typically 400-600 visitors a day have a look at the results in the first week. Note that this is a multitude of the actual number of participants in the poll.

This year's announcement of the DFT poll on the CCL mailing list was followed by a vivid discussion about its merits cq. its flaws. Some researchers "*dislike strongly the idea of deciding the use of a functional by popularity*"[1], others "*see this popularity contest on DFT functionals as no more than a social media tool such as 'what are your colleagues reading these days?'*"[2] or "*think it's useful because if [they] see a functional that [they] don't know about used widely, [they're] going to investigate it. (Note not blindly use it, but investigate it.)*".[3] In order to stress the motivation for holding the poll, we as organizers felt we needed to add a statement as well,[4] since we "*are simply monitoring what happens in the field of DFT and comment on how the choice of the community differs from (or agrees with) reliable reference data. In that way, we do exactly what should be done, namely 'drive science through evidence and logic' or maybe even 'drive science back to evidence and logic' (because, against all basic principles of science, the community often just follows blindly a fashion)*".

Apart from how the poll may help novice researchers getting a grip on which functionals might be useful for their studies, one message described the other side of the poll as well: "*Yes, it is not scientifically sound, epistemologically correct, platonically unsullied. But at least it is fun. We should appreciate fun in chemistry*".[5]

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[1] www.ccl.net/cgi-bin/ccl/message-new?2014+06+01+003
[2] www.ccl.net/cgi-bin/ccl/message-new?2014+06+02+005
[3] www.ccl.net/cgi-bin/ccl/message-new?2014+06+02+008
[4] www.ccl.net/cgi-bin/ccl/message-new?2014+06+02+013
[5] www.ccl.net/cgi-bin/ccl/message-new?2014+06+03+011
[6] S. Bachrach, *WIREs Comput. Mol. Sci.* **2014**, *4*, 482-487
[7] www.ccl.net/cgi-bin/ccl/message-new?2014+06+02+014

Below we highlight some comments made by experienced researchers in the field who we asked for their opinion, and whether they are in favor or against the poll.

Henry Rzepa (Sept. 14, 2014): "*I still think the context of any vote cast is absolutely crucial. Perhaps what the community needs to develop is a public set of conformance test sets of molecules, one for each type of property?*"

Gustavo Scuseria (Sept. 14, 2014): "*I am not in favor or against the poll. It is interesting though that we need a contest to determine what is popular and useful. A cacophony of functionals have mushroomed in recent years, and I am very much afraid that uncontrolled approximations and rampant empiricism have taken over DFT*".

Andreas Savin (Sept. 14, 2014): "*I must shamefully confess that I do not know about the DFT popularity poll.*"

Andreas Savin (Sept. 17, 2014; after having received more information): "*I will not participate, as this poll is intended for people who apply DFT, and I do little in this direction, but I find it interesting. I am amused to see that B3LYP is not as popular as generally believed, and LDA has such a high rank. How does it compare to the number of citations?*".

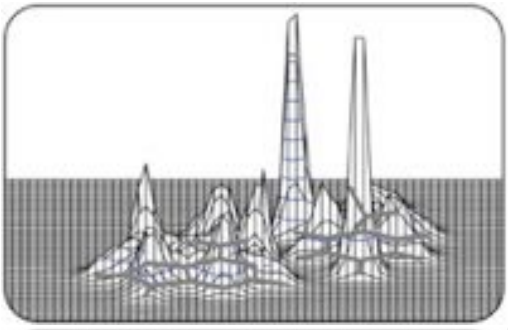
John Perdew (Sept. 14, 2014): "*The DFT popularity poll is somewhat like citation analysis: It measures (but in a different way) how well a functional has been received by a set of readers and users. There are many reasons why some functionals are received better than others: accuracy, reliability, wide applicability, computational efficiency, well-founded construction, availability in standard codes, reputation of the functional and its authors, historical priority, novelty, and even hype. The poll has to be seen as measuring all these things, and perhaps more. To the extent that the polled scientists use rational criteria, the results of the poll can point other scientists toward good or interesting functionals*".

Steven Bachrach (Sept. 15, 2014): "*Please feel free to quote me from the WIRES article and from CCL*". WIRES: "*It would be nice if we could somehow again reach some consensus regarding a uniform standard computational method that experts and nonexperts could rely upon for most situations. […]*".[6] CCL: "*I also think the poll has value in discerning trends, especially new functionals to appear on the list and ones that have fallen down or off*".[7]

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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