DFT2012

Density functionals poll

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

"The non-empirical PBE functional is the surprising winner of this year."

List of **density 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 (PBE1PBE), PW91, PWPB95-D$_3$, 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, optB88-vdW, APBE
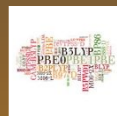
Origin of the online popularity poll of density functionals

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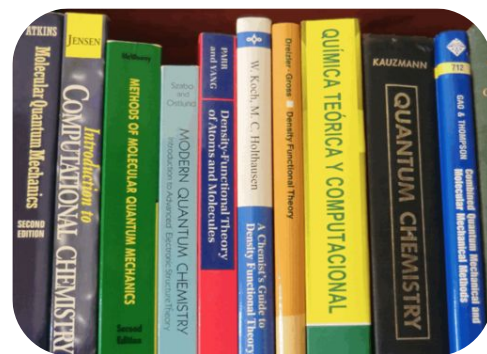
The aim of the online popularity poll is to probe the preferences of the computational chemistry and physics communities, and compile the quality of the "average" DFT computation.

Prof. Bickelhaupt: a regular visitor to Girona
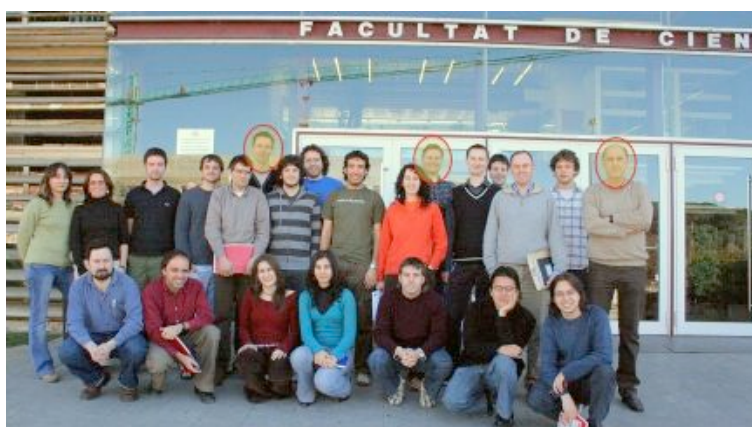
At least 50 research papers have resulted from the collaboration

There is a longstanding collaboration between the research groups of Prof. Bickelhaupt at the Vrije Universiteit Amsterdam (VUA), and the 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.
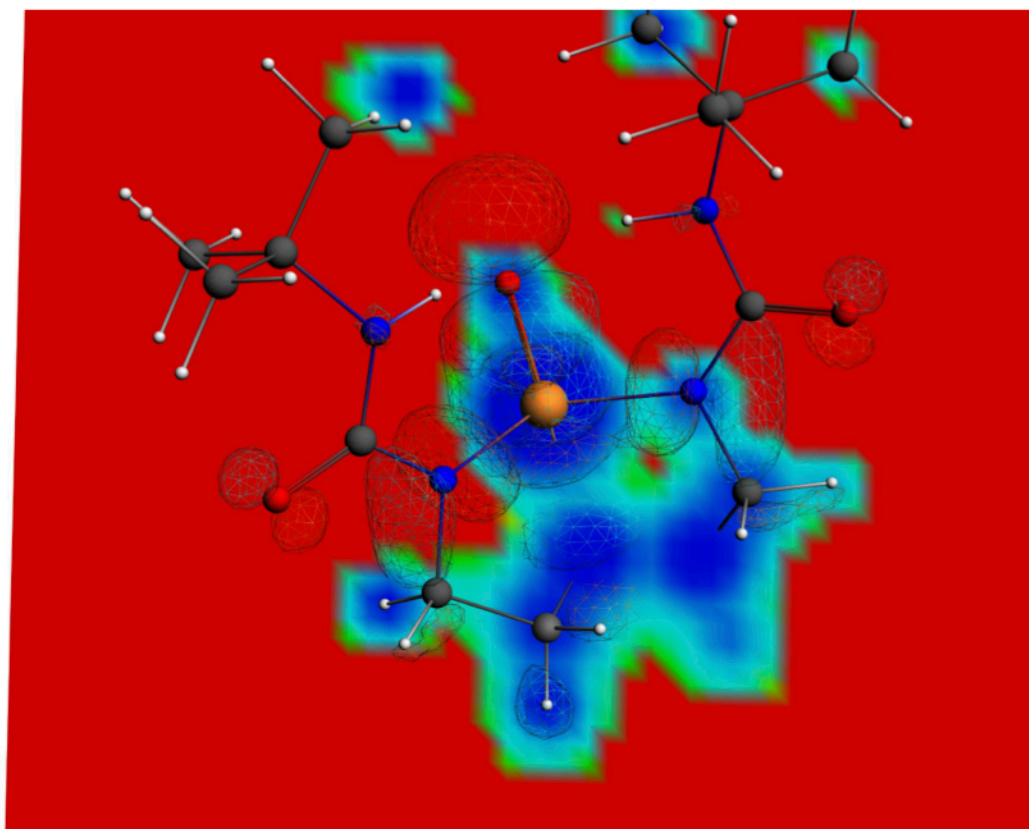
Rules for the popularity poll and the PACO functionals

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

Results of the **popularity poll**

	functional	year	cites	like	neutral	hate	empty	points
	Primera Divisió							
1	**PBE**	*1996*	*24231*	75	45	7	44	**263**
2	**PBE0**	*1996*	*3754*	70	40	11	50	**239**
3	**B3LYP**	*1994*	*25488*	66	36	32	37	**202**
4	**PW91**	*1992*	*9582*	45	43	11	72	**167**
5	**BP86**	*1988*	*909*	38	45	10	78	**149**
6	**B97-D**	*2006*	*85*	28	50	11	82	**123**
7	**B3LYP-D**	*2006*	*56*	29	50	21	71	**116**
8	**M06-2X**	*2008*	*389*	41	25	33	72	**115**
9	**BLYP**	*1988*	*1347*	28	48	18	77	**114**
10	**revPBE**	*1998*	*561*	25	44	11	91	**108**
11	**CAM-B3LYP**	*2004*	*1033*	23	45	11	92	**103**
12	**B2PLYP**	*2006*	*428*	21	44	12	94	**95**
13	**B3PW91**	*1993*	*1218*	21	45	14	91	**94**
14	**SSB-D**	*2009*	*39*	15	43	11	102	**77**
15	**TPSSh**	*2003*	*62*	12	48	12	99	**72**
16	**M06-L**	*2006*	*121*	22	36	33	80	**69**
17	**B3LYP***	*2001*	*397*	17	41	29	84	**63**
18	**PWPB95-D$_3$**	*2011*	*3*	11	41	11	108	**63**
19	**revTPSS-D**	*2009*	*66*	10	44	12	105	**62**
20	**revTPSS**	*2009*	*66*	9	45	14	103	**58**
	Segona Divisió							
1	**LDA**	*1980*	*11795*	42	34	24	71	**136**
2	**ωB97X-D**	*2008*	*402*	41	26	13	91	**136**
3	**HSE**	*2003*	*875*	31	28	10	102	**111**
4	**M06**	*2008*	*636*	24	33	28	86	**77**
5	**OLYP**	*2001*	*101*	16	34	14	107	**68**
6	**LC-wPBE**	2006	312	15	34	14	108	**65**
7	**LC-PBE**	2007	95	11	34	14	112	**53**
8	**SAOP**	2000	77	9	33	8	121	**52**
9	**PW6B95**	2005	19	11	33	15	112	**51**
10	**LB94**	1994	35	9	32	10	120	**49**
11	**RPBE**	1999	1796	9	38	16	108	**49**
12	**mPW1K**	2000	774	7	38	16	110	**43**
13	**M05-2X**	2006	945	15	32	35	89	**42**
14	**optB88-vdW**	2010	75	11	11	5	144	**39**
15	**APBE**	2011	13	4	36	9	122	**39**
16	**BHandH**	1993	57	8	35	22	106	**37**
17	**DSD-BLYP**	2010	25	7	29	13	122	**37**
18	**M05**	2005	243	10	36	33	92	**33**
19	**VSXC**	1998	43	3	34	18	116	**25**
20	**τ-HCTH**	2002	158	3	30	17	121	**22**
21	**X3LYP**	2004	79	5	31	25	110	**21**
22	**XLYP**	2004	4	0	29	25	117	**4**
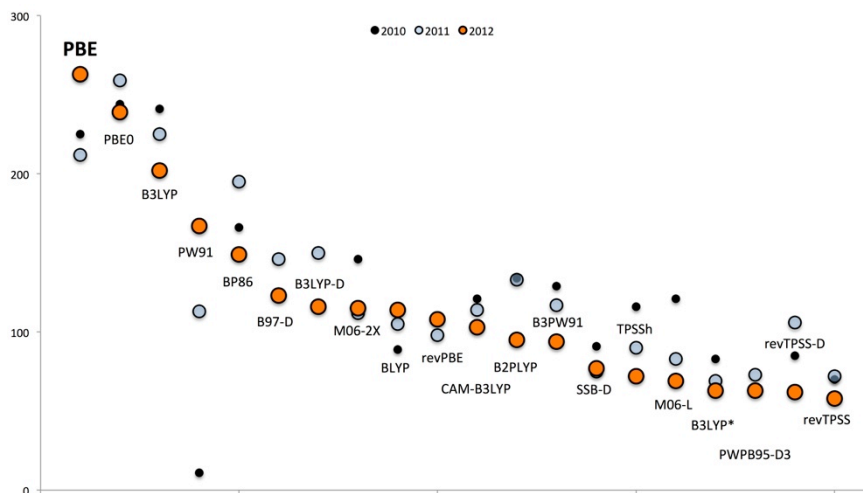
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Significance of the popularity poll results

For the first time, 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 first time that a GGA functional is beating hybrid functionals in popularity.

The total number of entries has increased significantly, from 142 in 2011 to 171 in 2012 (+20%). This increase is without any doubt related to the advertisement of the poll on the Psi-K mailing list, to attract a larger number of physicists to participate in the poll. Without any doubt, the participation of more physicists in the poll has made some changes.

Apart from the first place for PBE, the first place of LDA in the *Segona Divisió* (after relegating in the 2011 edition) is a clear sign of this. More surprising is the fact that the latest functionals by Perdew and co-workers (revTPSS, revTPSS-D) is relegating to the *Segona Divisió* in the 2013 edition. They will be accompanied by B3LYP*, M06-L and the PWPB95-D$_3$ functional.

Two functionals are excluded from the popularity poll 2013 (X3LYP and XLYP), unless suggested again (see rules on p. 3).

The composition of the *Primera Divisió* and *Segona Divisió* for the **year 2013** is given on p. 7. As usual, the online poll will be held from June 1 until October 1.
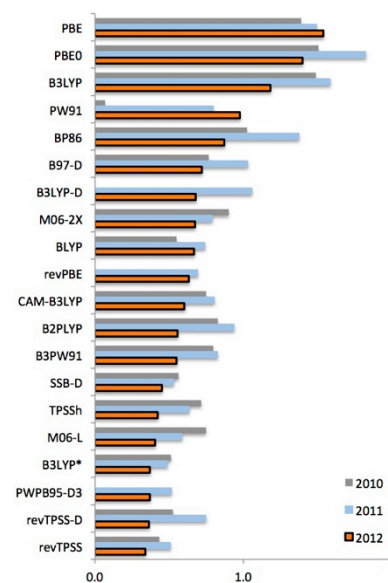
The average number of points decreases severely, from 0.82 to 0.69

Construction of the PACO2012 functional

| | w_{energy} | | |
	PACO2012	PACO2011	PACO2010
PBE	0.1150	0.0936	0.0943
PBE0	0.1044	0.1143	0.1022
B3LYP	0.0882	0.0993	0.1010
PW91	0.0730	-a	-a
BP86	0.0651	0.0861	0.0695
B97-D	0.0537	0.0645	0.0519
B3LYP-D	0.0507	-a	-a
M06-2X	0.0502	0.0494	0.0612
BLYP	0.0498	0.0464	0.0373
revPBE	0.0472	-a	-a
CAM-B3LYP	0.0450	0.0503	0.0507
B2PLYP	0.0415	0.0587	0.0561
B3PW91	0.0411	0.0517	0.0540
SSB-D	0.0336	0.0331	0.0381
TPSSh	0.0315	0.0397	0.0486
M06-L	0.0301	0.0366	0.0507
B3LYP*	0.0275	0.0305	0.0348
PWPB95-D$_3$	-b	-a	-a
revTPSS-D	0.0271	0.0468	-a
revTPSS	0.0253	-a	-a

a) not included in PACO2010/PACO2011; b) not available, therefore not taken into account

As usual, we prepared a *popularity adapted consensus object*, i.e. the PACO2012 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 PACO2011, PACO2012 together with the best and worst performing functionals are listed on p. 7.

Chemical systems used for checking interactions
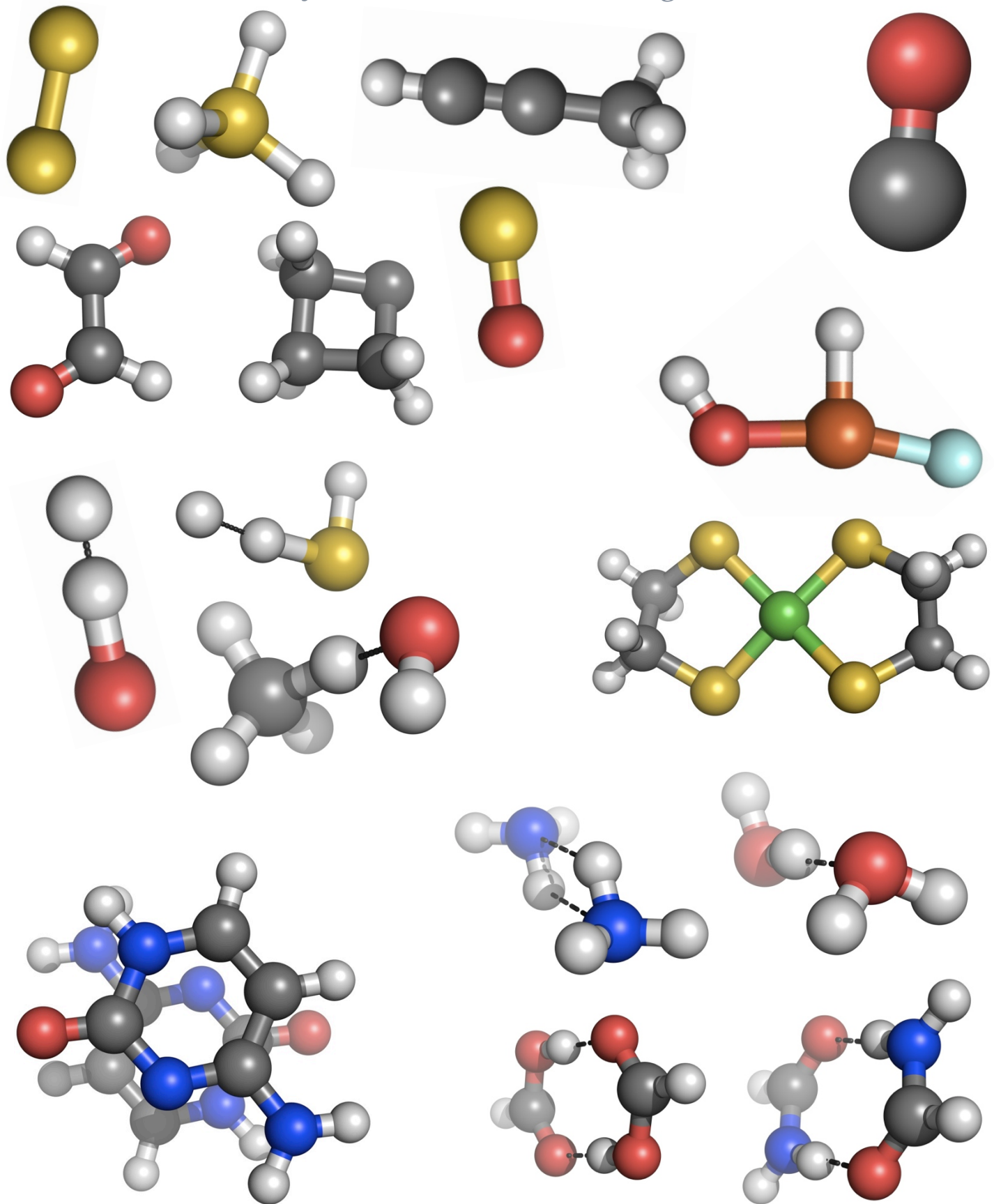
Check of **PACO2012** interactions

	reference	**PACO2012**	PACO2011	PACO2010	best	worst
AE6[a,b]					M06-2X	LDA
SiH_4	322.83	**319.24**	320.75	320.29	320.50	344.49
SiO	192.74	**187.34**	187.21	187.35	188.60	219.96
S_2	102.79	**105.84**	105.72	105.88	102.65	132.52
propyne	705.06	**709.25**	710.44	711.32	703.86	800.27
glyoxal	633.99	**641.16**	641.18	642.00	632.21	751.15
cyclobutane	1149.37	**1153.70**	1156.66	1158.05	1146.74	1302.09
MAD		**4.62**	5.07	5.66	2.04	73.95
BH6[a,b]					M06-2X	LDA
$OH+CH_4$ (fw)	6.54	**-0.46**	0.02	0.21	5.17	-16.89
$OH+CH_4$ (rv)	19.61	**12.01**	12.48	12.78	17.64	2.19
$H+OH$ (fw)	10.45	**3.89**	4.06	4.55	9.67	-2.04
$H+OH$ (rv)	12.90	**4.17**	4.76	4.76	11.35	-13.04
$H+H_2S$ (fw)	3.55	**-0.64**	-0.47	-0.13	4.23	-6.97
$H+H_2S$ (rv)	17.27	**13.72**	13.98	13.88	18.30	-0.31
MAD		**6.27**	5.92	5.71	1.23	17.90
Exc. states CO[c,d]					SAOP	B2PLYP
$^1\Pi,\ \sigma \rightarrow \pi^*$	8.51	**8.36**	8.38	8.37	8.55	8.59
$^1\Sigma^-,\ \pi \rightarrow \pi^*$	9.88	**9.71**	9.70	9.67	10.03	9.58
$^1\Delta,\ \pi \rightarrow \pi^*$	10.23	**10.01**	10.04	10.05	10.46	9.99
$^3\Pi,\ \sigma \rightarrow \pi^*$	6.32	**5.84**	5.86	5.87	6.28	5.70
$^3\Sigma^+,\ \pi \rightarrow \pi^*$	8.51	**8.00**	7.98	7.98	8.64	7.41
$^3\Delta,\ \pi \rightarrow \pi^*$	9.36	**8.71**	8.73	8.74	9.36	8.33
MAD		**0.36**	0.35	0.35	0.10	0.56
π-π stacking[a,e]	Ref. [51]				SSB-D	OLYP
Cyt_2	-9.93	**-3.64**	-3.68	-3.66	-9.69	+4.99
MAD		**6.29**	6.25	6.27	0.24	14.92
Spin-states[a]						
FeFHOH	5.4[f] ??	**13.19**	12.15	11.42	??	??
$Ni(EDT)_2^{2-}$	>0	**5.39**	4.44	3.49	??	??
MAD		**??**	??	??	??	??
H-bonding[a,g]					M06-2X	OLYP
ammonia	-3.17	**-2.65**	-2.62	-2.61	-3.17	-0.56
water	-5.02	**-4.72**	-4.71	-4.74	-5.13	-2.40
formic acid	-18.61	**-18.24**	-18.36	-18.44	-19.52	-11.40
formamide	-15.96	**-14.81**	-14.88	-14.93	-16.01	-8.66
MAD		**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

Although the weights of the different functionals in the PACO2012 functional have changed considerably compared to PACO2010/2011 (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 9%, while for BH6 it increases by 6%. 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-states keep increasing by ca. 1 kcal·mol⁻¹.

It will be interesting to see the performance for PACO2013, with the five new functionals included in the poll.

PRIMERA DIVISIÓ 2013

- ωB97X-D
- B2PLYP
- B3LYP
- B3LYP-D
- B3PW91
- B97-D
- BLYP
- BP86
- CAM-B3LYP
- HSE
- LDA
- M06
- M06-2X
- OLYP
- PBE
- PBE0
- PW91
- revPBE
- SSB-D
- TPSSh

SEGONA DIVISIÓ 2013

- APBE
- BHandH
- B3LYP*
- DSD-BLYP
- τ-HCTH
- LB94
- LC-ωPBE
- LC-PBE
- M05
- M05-2X
- M06-L
- mPW1K
- optB88-vdW
- PW6B95
- PWPB95-D₃
- revTPSS
- revTPSS-D
- RPBE
- SAOP
- VSXC

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.
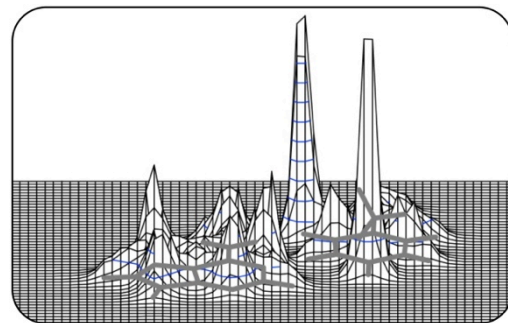
There exists a one-to-one relationship between the electron density and the <u>exact</u> energy.

"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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