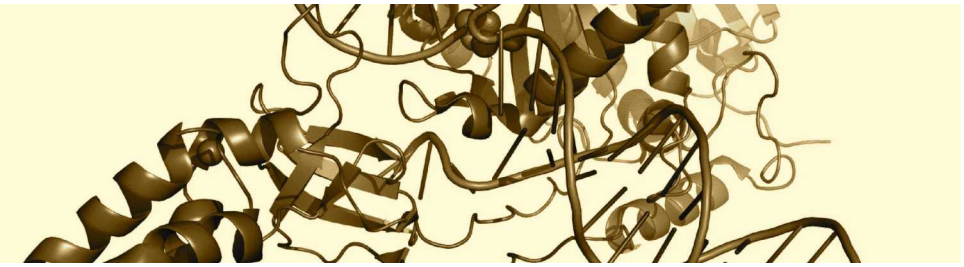
DFT2016 poll

organized by:
marcel swart
f. matthias bickelhaupt
miquel duran

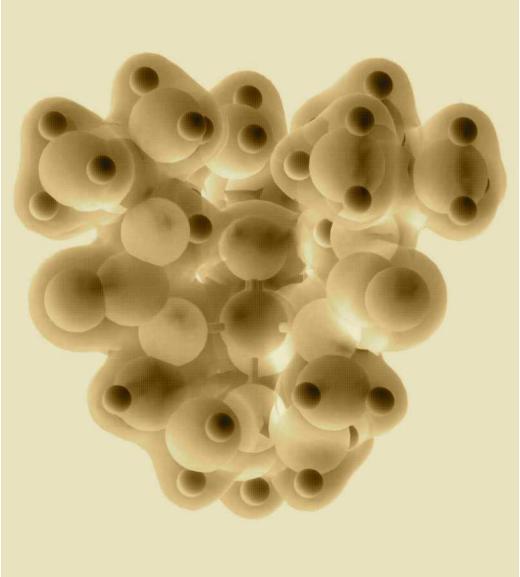


contents

The annual popularity poll for density functionals: **edition 2016**

The results are in. The top 3 remain the same as the past five years, while at the same time ωB97X-D and B3LYP-D consolidates their 4th and 5th position. The number of participants has increased 30% (99), but the total number of responses for the third with eleven properties (*reaction barriers; normal mode analysis; chiroptical properties; hydrogen bonds; excitation energies; main group elements; transition metals; relativistic elements; NMR shieldings/couplings; geometries; spin-state splittings*) has decreased slightly.

The following five functionals are promoted to the **Primera Divisió**: TPSSh, RPA, BLYP, OLYP, BHandH
thereby replacing the following five (that relegate to the **Segona Divisió**):
M06, PWPB96-D_3, RPBE, B3PW91, optB88-vdW.



5th consecutive win for PBE. top 3 remains the same.

origin of the online popularity poll of density functionals

Following a presentation by Matthias Bickelhaupt ("Hyper-valent 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.

a regular visitor to Girona

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.

"Yes, it is not scientifically sound, epistemologically correct, platonically unsullied. But at least it is fun. We should appreciate fun in chemistry."

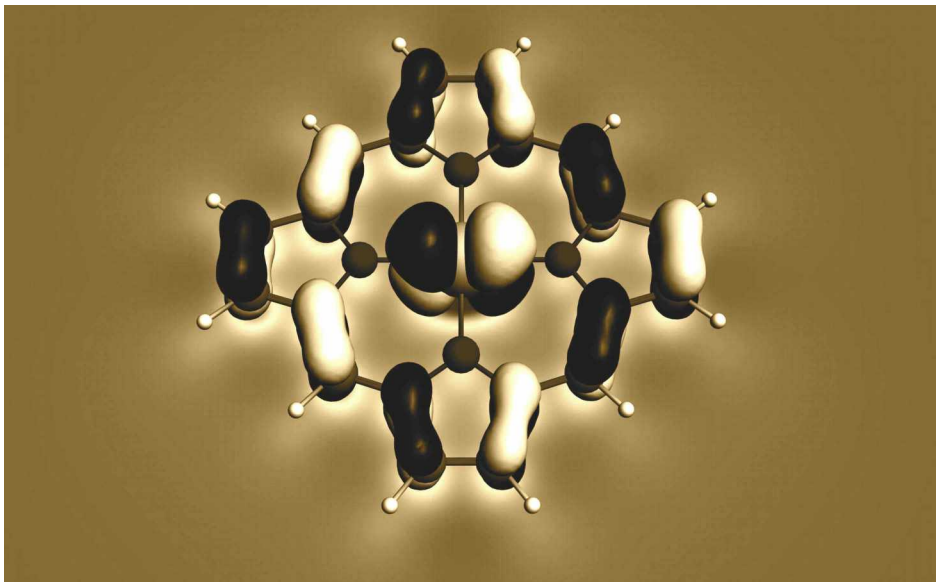
CCL mailing list, 2014

- *"No MCY"*
- *"tl;dr"*
- *"Do some real chemistry like Heisenberg in breaking bad, make some blue meth. Don't waste precious taxpayers money by just playing on your computers."*

Comments by participants, 2016

news-item

DFT2016 poll



the data

news-item

DFT2016 poll

Here are the raw data for the DFT2016 poll.

	functional	*year*	like	neutral	hate	empty	**points**
Primera Divisió							
1	**PBE**	1996	49	23	7	14	163
2	**PBE0 (PBE1PBE)**	1996	43	19	9	24	139
3	**B3LYP**	1994	33	24	20	20	103
4	**ωB97X-D**	2008	30	19	7	26	102
5	**B3LYP-D**	2006	23	26	14	25	81
6	**CAM-B3LYP**	2004	22	24	12	27	78
7	**BP86**	1988	20	23	10	30	73
8	**LDA**	1980	21	27	21	17	69
9	**M06-2X**	2008	24	16	22	25	66
10	**B97-D**	2006	15	27	8	30	64
11	**PW91**	1992	12	33	11	28	58
12	**HSE**	2003	10	33	9	28	54
13	**B2PLYP**	2006	12	27	10	29	53
14	**revPBE**	1998	11	27	9	31	51
15	**LC-ωPBE**	2006	10	25	7	32	48
16	**M06**	2008	18	17	25	24	46
17	**PWPB95-D3**	2011	6	32	8	32	42
18	**RPBE**	1999	7	30	9	28	42
19	**B3PW91**	1993	4	32	13	30	31
20	**optB88-vdW**	2010	3	24	10	32	23
Segona Divisió							
1	**TPSSh**	2003	17	19	6	37	64
2	**RPA**	2008	14	16	7	39	51
3	**BLYP**	1988	16	19	17	36	50
4	**OLYP**	2001	13	18	9	38	48
5	**BHandH**	1993	10	21	8	37	43
6	**LC-PBE**	2007	9	21	7	39	41
7	**revTPSS**	2009	10	20	9	37	41
8	**SSB-D**	2009	8	15	4	41	35
9	**revTPSS-D**	2009	8	20	10	39	34
10	**DSD-BLYP**	2010	6	17	6	40	29
11	**S12g**	2013	5	17	4	43	28
12	**S12h**	2013	5	17	4	42	28
13	**M06-L**	2006	10	16	19	36	27
14	**SAOP**	2000	6	15	7	40	26
15	**SCAN**	2015	3	21	5	40	25
16	**MVS**	2015	4	18	6	41	24
17	**PW6B95**	2005	4	18	7	41	23
18	**DSD-PBEP86**	2011	4	17	7	42	22
19	**LB94**	1994	3	20	7	40	22
20	**MN12L**	2012	5	18	14	40	19
21	**APBE**	2011	1	19	8	42	14
22	**mPW1K**	2000	1	18	10	41	11

with the addition of the third question, a wealth of data has been obtained, that will be useful for new researchers in the field

(continued)

paco 2016

functional	weight
PBE	0.1176
PBE0	0.1003
B3LYP	0.0743
wB97X-D	0.0736
B3LYP-D	0.0584
CAM-B3LYP	0.0563
BP86	0.0527
LDA	0.0498
M06-2X	0.0476
B97-D	0.0462
PW91	0.0418
HSE	0.0390
B2PLYP	0.0382
revPBE	0.0368
LC-wPBE	0.0346
M06	0.0332
PWPB95-D3	0.0303
RPBE	0.0303
B3PW91	0.0224
optB88-vdW	0.0166

These weights could be used with e.g. the GMTKN30 database by Grimme and co-workers to get a feel of how accurate the PACO2016 functional would be.

"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."

John Perdew, 2014

In 2015, for the first time we added a third question where the participants could indicate their preferred functionals for eleven different properties. Similar to last year, ca. 70% of the participants indeed indicated at least one preferred (or hated) functional for one or more properties. In total 1777 votes were cast, corresponding to an average of 17.9 per participant.

Shown below is a summary of the preferred or disliked functionals for each property. A full list of all functionals for all properties is available at:

www.marcelswart.eu/dft-poll

1. Reaction barriers

preferred:
M06-2X, PBE0, M06, ωB97X-D, B3LYP-D, PBE

disliked:
MN12L, APBE, B3LYP

2. Normal mode analysis

preferred:
BP86, B3LYP, PBE, LDA

disliked:
B2PLYP, M06, BHandH, APBE

3. Chiroptical properties

preferred:
CAM-B3LYP, LDA, TPSSh, LB94, PBE0

disliked:
B3LYP, BLYP, B3LYP-D, APBE

4. Hydrogen bonds

preferred:
ωB97X-D, B3LYP-D, LDA

disliked:
B3LYP, B3LYP*, OLYP, MN12L, M05-2X, M05, LB94, BHandH

5. Excitation energies

preferred:
CAM-B3LYP, LB94, PBE0, B2PLYP

disliked:
BLYP, B3LYP, PBE, APBE

6. Main group elements

preferred:
PBE, M06-2X, TPSSh, LDA, M06

disliked:
BHandH, APBE, MN12L, B3PW91

7. Transition metals

preferred:
PBE, PBE0, LDA, BP86, TPSSh

disliked:
APBE, BHandH, M06-2X

8. Relativistic elements

preferred:
PBE, PBE0, LDA, TPSSh, BP86

disliked:
B3LYP, B3LYP-D, BHandH

9. NMR shieldings/couplings

preferred:
PBE, PBE0, LDA, M06-2X, SAOP, TPSSh

disliked:
BHandH, B3LYP-D, APBE, BP86, MN12L

10. Geometries

preferred:
B3LYP, PBE, BP86, PBE0, LDA

disliked:
BHandH, APBE, MN12L

11. Spin-state splittings

preferred:
TPSSh, S12g, MVS, SSB-D, PBE0

disliked:
BP86, B3LYP-D, M06, BLYP, BHandH

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.

third question

The 2015 edition marked a change with respect to the previous editions: a THIRD question was added where participants can indicate for each functional on the list (both Primera and Segona Divisió), what is their preference for a total of 11 properties:

- Reaction barriers
- Normal modes analysis
- Chiroptical properties
- Hydrogen bonds
- Excitation energies
- Main group elements
- Transition metals
- Relativistic elements
- NMR shieldings, NMR couplings
- Geometries
- Spin-state splittings

For each of these one can choose between the following five preferences:

++	Love it
+	Like it
0	Neutral
-	Dislike it
--	Hate it

This is now reflected in the new Rule #8.

density functional theory is **exact**. density functional approximations are constantly being improved to reach the same level

rules and data

All rules and (raw) data are publicly available at:
www.marcelswart.eu/dft-poll

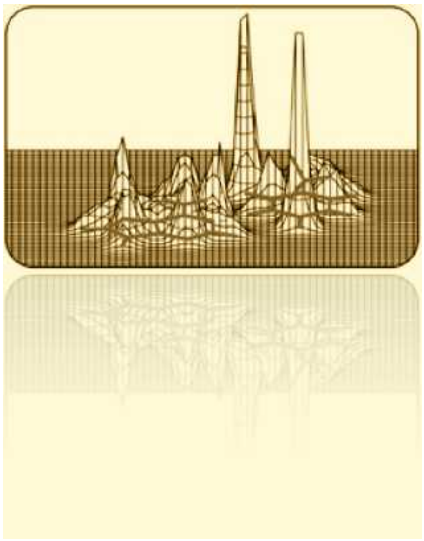
Primera Divisió 2016

ωB97X-D, B2PLYP, B3LYP, B3LYP-D, B97-D, BHandH, BLYP, BP86, CAM-B3LYP, HSE, LC-wPBE, LDA, M06-2X, OLYP, PBE, PBE0 (PBE1PBE), PW91, revPBE, RPA, TPSSh

Segona Divisió 2016

B3PW91, DSD-BLYP, DSD-PBEP86, LB94, LC-PBE, M06, M06-L, MN12L, MVS, optB88-vdW, PW6B95, PWPB95-D_3, revTPSS, revTPSS-D, RPBE, S12g, S12h, SAOP, SCAN, SSB-D

Suggestions are welcome (10 additional slots available in Segona Divisió), by sending a mail to: marcel.swart@udg.edu



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.

Girona, Amsterdam

Oct. 2016

Marcel Swart
ICREA & Univ. Girona
www.marcelswart.eu

Matthias Bickelhaupt
VU Univ. Amsterdam &
Radboud Univ. Nijmegen
www.few.vu.nl/~bickel

Miquel Duran
Univ. Girona
www.miquelduran.net

references

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Hohenberg-Kohn: *Phys. Rev. B 1964, 136, 864*

APBE: *Phys. Rev. Lett. 2011, 106, 186406*

B2PLYP: *J. Chem. Phys. 2006, 124, 034108*

B3LYP: *J. Phys. Chem. 1994, 98, 11623*

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wB97X-D: *Phys. Chem. Chem. Phys. 2008, 10, 6615*

B97-D: *J. Comput. Chem. 2006, 27, 1787*

BHandH: *J. Chem. Phys. 1993, 98, 1372*

BLYP: *Phys. Rev. A 1988, 38, 3098; Phys. Rev. B 1988, 37, 785*

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KT1: *J. Chem. Phys. 2003, 119, 3015*

LB94: *Phys. Rev. A 1994, 49, 2421*

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LC-PBE: *J. Chem. Phys. 2007, 126, 154105*

LDA: *Proc. Roy. Soc. (London) A 1929, 123, 714; Phys. Rev. 1951, 81, 385; Can. J. Phys. 1980, 58, 1200; Phys. Rev. B 1992, 45, 13244*

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M06, M06-2X: *Theor. Chem. Acc. 2008, 120, 215*

M06-L: *J. Chem. Phys. 2006, 125, 194101*

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