DFT2015 poll

organized by:
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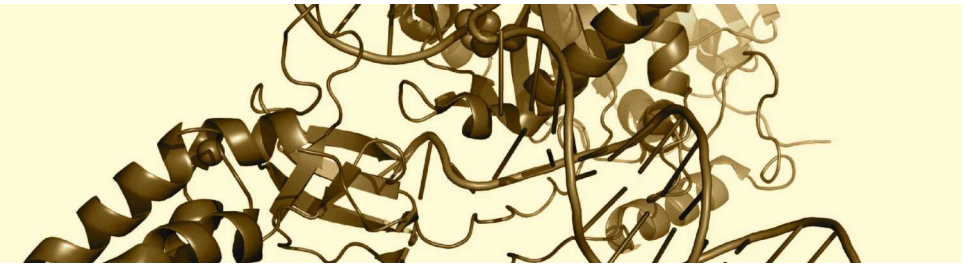
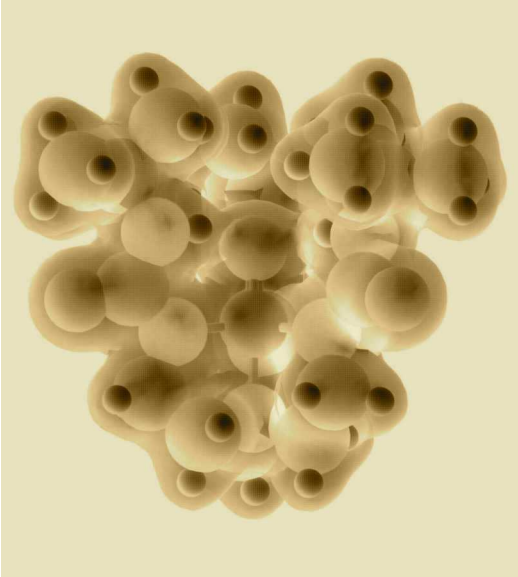


contents

The annual popularity poll for density functionals: **edition 2015**

The results are in. The top 3 remain the same as the past four years, while at the same time ωB97X-D consolidates its 4th position. The number of participants has been the lowest ever (76), which might be related to the addition of a third question with preferences of all functionals for a total of 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*).

The following five functionals are promoted to the **Primera Divisió**:
revPBE, LC-wPBE, optB88-vdW, PWPB95-D3, RPBE
thereby replacing the following five:
revTPSS, RPA, TPSSh, M06-L, BLYP.



4th consecutive win for PBE. top 3 remains the same.

> *"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**

origin of the online popularity poll of density functionals

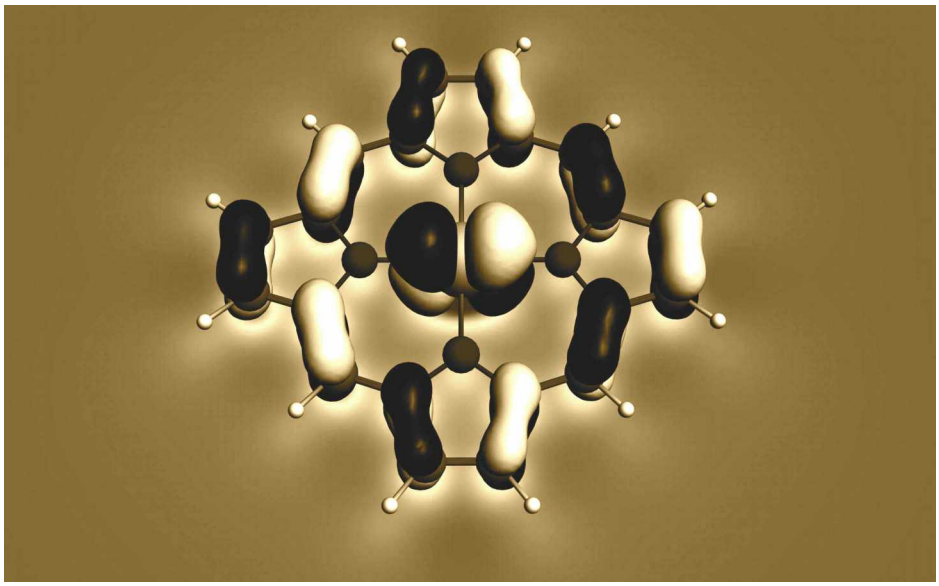
Following a presentation by Matthias Bickelhaupt ("Hypervalent versus Nonhypervalent Carbon", 27. 2. 2009) there was a discussion in Can Paco (the bar at the faculty of Chemistry at the University of Girona). Because the presentation showed the results for quite a number of density functionals, Miquel 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.

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.

news-item

DFT2015 poll



the data

news-item

DFT2015 poll

Here are the raw data for the DFT2015 poll.

	functional	*year*	like	neutral	hate	empty	**points**
Primera Divisió							
1	**PBE**	1996	36	18	3	19	123
2	**PBE0 (PBE1PBE)**	1996	34	19	2	21	119
3	**B3LYP**	1994	23	21	15	17	75
4	**ωB97X-D**	2008	22	11	4	39	73
5	**B3LYP-D**	2006	17	23	7	29	67
6	**LDA**	1980	20	14	13	29	61
7	**PW91**	1992	14	22	5	35	59
8	**B97-D**	2006	16	16	7	37	57
9	**M06-2X**	2008	20	10	13	33	57
10	**B2PLYP**	2006	16	14	6	40	56
11	**CAM-B3LYP**	2004	12	19	5	40	50
12	**HSE**	2003	12	17	3	44	50
13	**BP86**	1988	14	14	9	39	47
14	**M06**	2008	11	19	12	34	40
15	**B3PW91**	1993	10	17	8	41	39
16	**revTPSS**	2009	6	21	4	45	35
17	**RPA**	2008	8	13	5	50	32
18	**TPSSh**	2003	6	18	5	47	31
19	**M06-L**	2006	7	15	12	42	24
20	**BLYP**	1988	6	18	17	35	19
Segona Divisió							
1	**revPBE**	1998	9	15	4	48	38
2	**LC-ωPBE**	2006	9	14	4	49	37
3	**optB88-vdW**	2010	7	13	3	53	31
4	**PWPB95-D_3**	2011	5	12	3	56	24
5	**RPBE**	1999	5	13	4	54	24
6	**LC-PBE**	2007	5	13	5	53	23
7	**mPW1K**	2000	4	15	4	53	23
8	**revTPSS-D**	2009	4	15	4	53	23
9	**OLYP**	2001	5	11	6	54	20
10	**PW6B95**	2005	3	13	3	57	19
11	**DSD-BLYP**	2010	4	10	4	58	18
12	**SSB-D**	2009	4	9	5	58	16
13	**LB94**	1994	3	10	4	59	15
14	**DSD-PBEP86**	2011	3	9	4	60	14
15	**S12g**	2013	2	10	2	62	14
16	**S12h**	2013	2	10	2	62	14
17	**MN12L**	2012	2	13	6	55	13
18	**APBE**	2011	1	10	3	62	10
19	**SAOP**	2000	0	13	3	60	10
20	**BHandH**	1993	2	11	9	54	8
21	**τ-HCTH**	2002	1	11	6	58	8
22	**M05**	2005	2	15	13	46	8
23	**M05-2X**	2006	2	14	13	47	7
24	**B3LYP***	2001	2	10	11	53	5

(continued)

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

paco 2015

functional	weight
PBE	0.1104
PBE0 (PBE1PBE)	0.1068
B3LYP	0.0673
ωB97X-D	0.0655
B3LYP-D	0.0601
LDA	0.0548
PW91	0.0530
B97-D	0.0512
M06-2X	0.0512
B2PLYP	0.0503
CAM-B3LYP	0.0449
HSE	0.0449
BP86	0.0422
M06	0.0359
B3PW91	0.0350
revTPSS	0.0314
RPA	0.0287
TPSSh	0.0278
M06-L	0.0215
BLYP	0.0171

These weights could be used with e.g. the GMTKN30 database by Grimme and co-workers to get a feel of how accurate the PACO2015 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. Almost 70% of the participants indeed indicated at least one preferred (or hated) functional for one or more properties. In total 1729 votes were cast, corresponding to an average of 22.75 per participant (*however, the median value is 5.50*).

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:
B2PLYP, M06-2X, PBE0, PBE, ωB97X-D

disliked:
B3LYP, MN12L, M05, LB94, BLYP, BHandH, B3LYP*

2. Normal mode analysis

preferred:
B3LYP, PBE, M06-2X, BP86, PBE0

disliked:
MN12L, M05, LB94, B3LYP*, OLYP, M06-L

3. Chiroptical properties

preferred:
B2PLYP, CAM-B3LYP, PBE, PBE0

disliked:
B3LYP, B3LYP*, OLYP, MN12L, M06-L, M05, LB94

4. Hydrogen bonds

preferred:
B97-D, ωB97X-D, BP86, M06-2X, PBE, PBE0

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

5. Excitation energies

preferred:
CAM-B3LYP, PBE0, ωB97X-D, HSE

disliked:
B3LYP*, OLYP, MN12L, M06-L, M05, B3LYP-D, B3LYP

6. Main group elements

preferred:
PBE, B2PLYP, M06-2X, B3LYP, BP86, PBE0

disliked:
B3LYP*, MN12L, M06-L, M05

7. Transition metals

preferred:
PBE, BP86, PBE0, PW91, B97-D

disliked:
B3LYP*, B3LYP-D, M05, BHandH, MN12L, B3LYP

8. Relativistic elements

preferred:
PBE0, BP86, PBE, PW91

disliked:
B3LYP*, B3LYP, B3LYP-D, MN12L, M05-2X, M05, CAM-B3LYP, BHandH

9. NMR shieldings/couplings

preferred:
BP86, PBE, PBE0, PW91

disliked:
B3LYP*, B3LYP-D, B3LYP, MN12L, M06-L, M05, BHandH

10. Geometries

preferred:
PBE, M06-2X, B3LYP, BP86, PBE0

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

11. Spin-state splittings

preferred:
SSB-D, LDA, OLYP, PBE0

disliked:
B3LYP, B3LYP*, B3LYP-D, MN12L, M06-L, M06-2X, M05-2X, M05, 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

This year's edition marks a change with respect to the previous editions: a THIRD question is now 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

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

This is now reflected in the new Rule #8.

rules and data

All rules and (raw) data are publicly available at:

www.marcelswart.eu/dft-poll

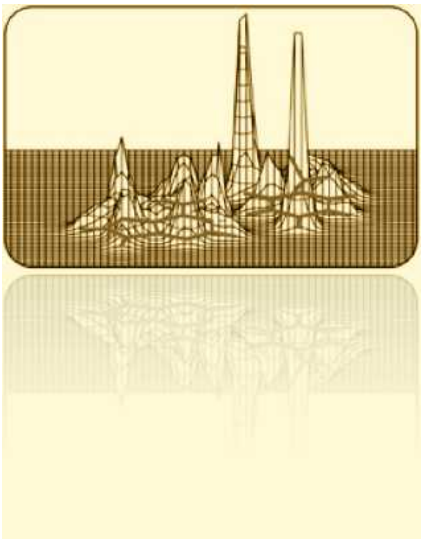
Primera Divisió 2016

ωB97X-D, B2PLYP, B3LYP, B3LYP-D, B3PW91, B97-D, BP86, CAM-B3LYP, HSE, LC-wPBE, LDA, M06, M06-2X, optB88-vdW, PBE, PBE0 (PBE1PBE), PW91, PWPB95-D_3, revPBE, RPBE

Segona Divisió 2016

APBE, BHandH, BLYP, DSD-BLYP, DSD-PBEP86, LB94, LC-PBE, M06-L, MN12L, mPW1K, OLYP, PW6B95, revTPSS, revTPSS-D, RPA, S12g, S12h, SAOP, SSB-D, TPSSh

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

Jan. 2016

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references

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*

B3LYP-D: *J. Phys. Chem. 1994, 98, 11623; J. Comput. Chem. 2006, 27, 1787*

B3LYP*: *Theor. Chem. Acc. 2001, 107, 48*

B3PW91: *J. Chem. Phys. 1993, 98, 5648*

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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HSE: *J. Chem. Phys. 2003, 118, 8207*

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

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

LC-wPBE: *J. Chem. Phys. 2006, 125, 234109*

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

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VSXC: *J. Chem. Phys. 1998, 109, 400*