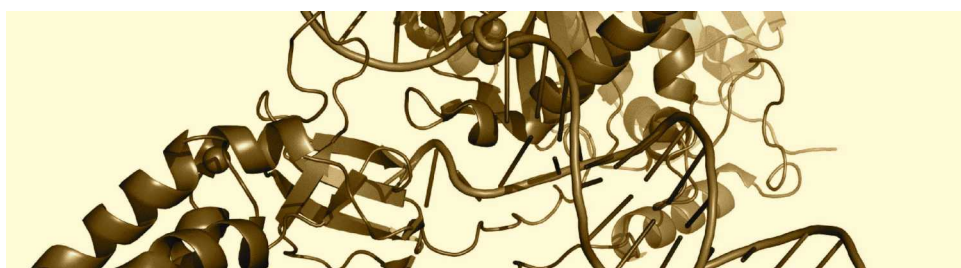


DFT2017 poll

organized by:
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the data:

www.marcelswart.eu/dft-poll

The annual popularity poll for density functionals: edition 2017

The results are in. And they are **exciting!** We have a new number one: PBE0 (aka. PBE1PBE), with the former number 1 still going strong at 2 (PBE), while ω B97X-D and B3LYP-D move upwards to the 3rd and 4th position. Big loser is B3LYP that **drops to position 7**. 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 stayed steady.

The following five functionals are promoted to the **Primera Divisió**: PBE-D, ω B97X-V, ω B97M-V, PWPB96-D₃, B97M-V thereby replacing the following five (that relegate to the **Segona Divisió**): BLYP, RPA, OLYP, LDA, BHandH.

PBE0 (PBE1PBE) returns to the top after six years

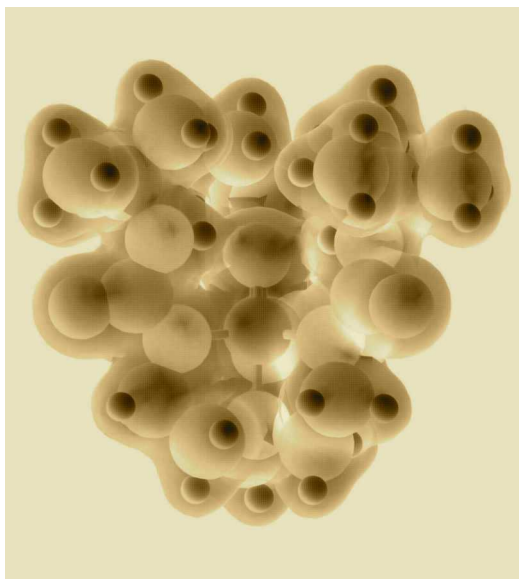
origin of the online popularity poll of density functionals

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

- *“TPSSh is 3good5you -> Don Truhlar”*
- *“I used just two types of functionals, B3LYP and B3PW91, so I polled these types only.”*

Comments by participants, 2017

“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

news-item

DFT2017 poll

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

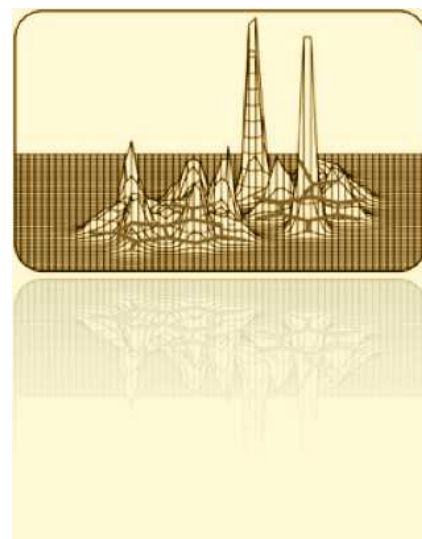
Primera Divisió 2018

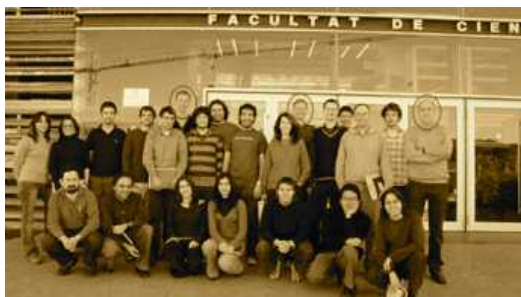
B2PLYP, B3LYP, B3LYP-D, B97-D, B97M-V, BP86, CAM-B3LYP, HSE, LC-wPBE, M06-2X, PBE, PBE-D, PBE0 (PBE1PBE), PW91, PWPB95-D₃, revPBE, TPSSh, wB97M-V, wB97X-D, wB97X-V

Segona Divisió 2018

B3PW91, BHandH, BLYP, DSD-BLYP, DSD-PBEP86, LC-PBE, LDA, M06, M06-L, OLYP, optB88-vdW, PW6B95, revTPSS, revTPSS-D, RPA, RPBE, S12g, 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

May 2018

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references

- Kohn-Sham**: *Phys. Rev. A* 1965, 140, 1133
- 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
- BP86**: *Phys. Rev. A* 1988, 38, 3098; *Phys. Rev. B* 1986, 33, 8822
- CAM-B3LYP**: *Chem. Phys. Lett.* 2004, 393, 51
- DSD-BLYP**: *J. Phys. Chem. C* 2010, 114, 20801
- DSD-PBEP86**: *Phys. Chem. Chem. Phys.* 2011, 13, 20104
- 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
- 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
- M05**: *J. Chem. Phys.* 2005, 123, 161103
- M05-2X**: *J. Chem. Theory Comput.* 2006, 2, 364
- M06, M06-2X**: *Theor. Chem. Acc.* 2008, 120, 215
- M06-L**: *J. Chem. Phys.* 2006, 125, 194101
- mPW1K**: *J. Phys. Chem. A* 2000, 104, 4811
- MVS**: *PNAS* 2015, 112, 685
- OLYP**: *Mol. Phys.* 2001, 99, 403; *Phys. Rev. B* 1988, 37, 785
- optB88-vdW**: *J. Phys.-Condens. Mat.* 2010, 22, 022201
- PBE**: *Phys. Rev. Lett.* 1996, 77, 3865
- PBE0**: *J. Chem. Phys.* 1996, 105, 9982; *J. Chem. Phys.* 1999, 110, 5029; *J. Chem. Phys.* 1999, 110, 6158
- PW6B95**: *J. Phys. Chem. A* 2005, 109, 5656
- PW91**: *Phys. Rev. B* 1992, 46, 6671
- PWPB95-D₃**: *J. Chem. Theory Comput.* 2011, 7, 291
- revPBE**: *Phys. Rev. Lett.* 1998, 80, 890
- revTPSS, revTPSS-D**: *Phys. Rev. Lett.* 2009, 103, 026403; $s_6=0.7282$ (revTPSS-D)
- RPA**: *J. Chem. Phys.* 2008, 129, 114105
- RPBE**: *Phys. Rev. B* 1999, 59, 7413
- S12g, S12h**: *Chem. Phys. Lett.* 2013, 580, 166
- SAOP**: *J. Chem. Phys.* 2000, 112, 1344
- SCAN**: *Phys. Rev. Lett.* 2015, 115, 036402
- SSB-D**: *J. Chem. Phys.* 2009, 131, 094103
- t-HCTH**: *J. Chem. Phys.* 2002, 116, 9559
- TPSSh**: *Phys. Rev. Lett.* 2003, 91, 146401; *J. Chem. Phys.* 2003, 119, 12129
- VSXC**: *J. Chem. Phys.* 1998, 109, 400