DFT2022 poll

organized by:
marcel swart
f. matthias bickelhaupt
miquel duran
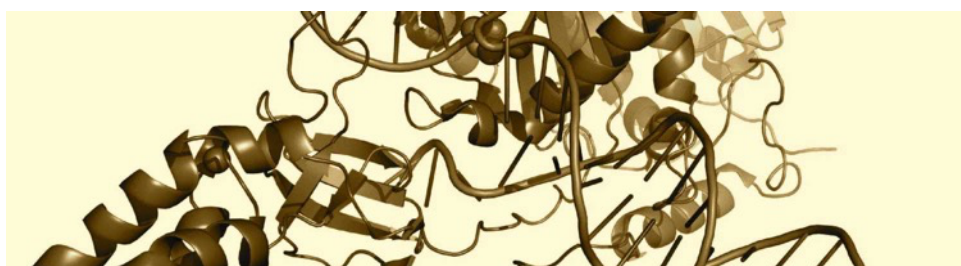
## contents

the data:
www.marcelswart.eu/dft-poll

The annual popularity poll for density functionals:
edition 2022

The 2022 results are in, with a large number of participation: 283 entries. Perdew's functionals remain at the top of the list (PBE **1**, PBE0 **2**, PBE-D **3**, PBEsol **5,** SCAN **6**), with ωB97X-D gaining track again in the *Primera Divisió* (jumping from number **11** to number **4**). HSE has lost its steam a bit, and is now found at number **7**, while PBEsol is slowly moving upwards (now at **5**). LDA maintains its top10 spot (now at place **8**), while the Minnesota functionals are losing steam (M06-2X at place **17**, joining M06 and M06-L in the *Segona Divisió* next year). (full results available online)

The following five functionals are promoted to the *Primera Divisió*:
r2SCAN-D4, ωB97M-V, ωB97X-V, B97-3c, B97M-V
thereby replacing the following five (that relegate to the *Segona Divisió*):
BP86, M06-2X, revPBE, optB88-vdW, RPBE.

There are ten places available for new suggestions to be included, of which five are taken by: r2SCAN-3c, MN12SX, MN15, revDSD-PBEP6, OPBE.

PBE continues its success

news-item

DFT2022 poll
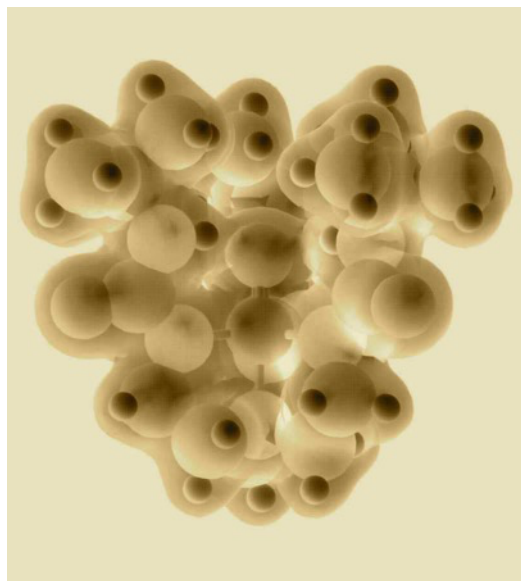
origin of the online popularity poll of density functionals

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.

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.

reviews/perspectives

Send a message to marcel.swart@udg.edu to have new reviews/perspectives included on the list

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.

Comments:
- "B3LYP is the"
- "AM05 is da shit!"
- " I do not know most of the functionals"

Girona, Amsterdam

October 2022

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

Matthias Bickelhaupt
Vrije Univ. Amsterdam &
Radboud Univ., Nijmegen
www.theochem.nl

Miquel Duran
Univ. Girona
www.miquelduran.net

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*

ωB97X-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-ωPBE: *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-D$_8$: *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*

τ-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*

Response to comments

- "I would like more differentiation maybe scale of 1-5, 1 is hate, 5 is like"

  The rules were set up 10 years ago and we see no reason for changing them.

- "Several interesting DFs missing including various DSD-, wB97X-2, MN15, M08HX, while some rather unusual were included e.g. DM21, S12g. Why?"

  DM21 attempts to solve the fractional electron problem, while S12g is one few spin-state consistent functionals. MN15 was included twice (2017, 2020) and was not among the best 20 in the *Segona Divisió*; next year it will get another chance.

Prologue from "Ab initio Molecular Orbital Theory", Warren J. Hehre, Leo Radom, Paul von R. Schleyer, John Pople, Wiley-Interscience 1986

PROLOGUE

The more progress physical sciences make, the more they tend to enter the domain of mathematics, which is a kind of centre to which they all converge. We may even judge the degree of perfection to which a science has arrived by the facility with which it may be submitted to calculation [1].

Adolphe Quetelet 1796–1874

This book helps to document the extent to which chemistry may now "be submitted to calculation."

The key to theoretical chemistry is molecular quantum mechanics. This is the science relating molecular properties to the motion and interactions of electrons and nuclei. Soon after its formulation in 1925 [2], it became clear that solution of the Schrödinger differential equation could, in principle, lead to direct quantitative prediction of most, if not all, chemical phenomena using only the values of a small number of physical constants (Planck's constant, the velocity of light, and the masses and charges of electrons and nuclei). Such a procedure constitutes an *ab initio* approach to chemistry, independent of any experiment other than determination of these constants. It was also early recognized that solution of the Schrödinger equation was a formidable if not completely impossible mathematical problem for any but the very simplest of systems.

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble [3].

P.A.M. Dirac 1902–1984

1
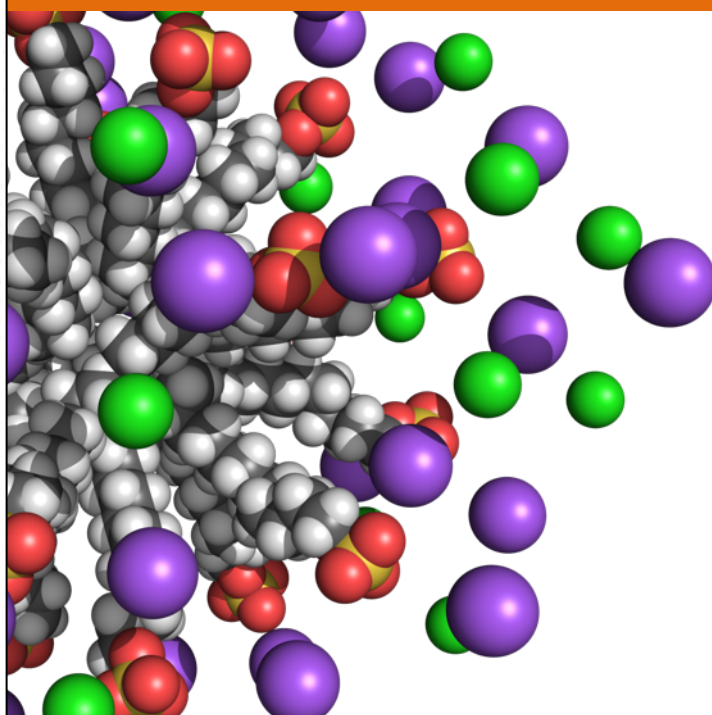
Additional comments

- "Density-functional theory, formerly an ab initio method, has successfully turned semi-empirical, let's put it this way."

  DFT is exact (Mel Levy). Density functional approximations (DFAs) remains *ab initio*, since all integrals can be computed. I.e., according to Hehre and co-workers in "Ab initio MO theory", the *ab initio* simply means that no experiments are needed to solve the Schrödinger equation except for a limited number of physical constants (see above).

- "I have used very few of the functional listed here. So, I used none of the above for most of the answers."