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# Simple computational chemistry

вторник, 21 июня 2016 г.

## DFT advices

We have gathered some information from computational chemistry forums, which can be helpful for you. It should be noted that the following text cannot be considered as a professional guide; such guides will possibly appear in the future.

### 1. The choice of a DFT functional

First of all, you should read this manual:

[Which functional should I choose? \(2008\)](#)

One of the theses in this book is that the GGA functionals are usually more universal (let's say, closer to "Ab initio") than the hybrid functionals (this statement, however, has some weak points). This also means that the errors with these functionals are more systematic: for example, the PBE functional usually overestimates the bond lengths and underestimates the vibrational frequencies. In our opinion, if you choose between, e.g., the PBE and B3LYP functionals, you should note that the latter should be more accurate for most organic molecules, but it should be less accurate in some problematic cases; so, the PBE functional is more reliable. Because of that, at one forum we found the following advice (written in 2010): always use the PBE functional and don't worry. It is CGA, so it must be more universal than, e.g., the B3LYP functional.

It is written in this manual that the B3LYP functional has shown good results for organic molecules, but it is worse for transition metal compounds and for large molecules. TPSSh probably is a good functional for transition metal compounds (according to this manual).

The B3LYP functional is commonly used in chemistry, while the PBE, PBE0 functionals are commonly used in applications to extended systems (materials) [13].

Here is another compilation on the subject:

[The annual popularity poll for density functionals: edition 2015](#)

Обо мне

Grigoriy Andrienko



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Here is a screenshot from this paper:

Here are the raw data for the DFT2015 poll.

	functional	year	like	neutral	hate	empty	points
<i>Primera Divisió</i>							
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	$\omega$ B97X-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
<i>Segona Divisió</i>							
1	revPBE	1998	9	15	4	48	38
2	LC- $\omega$ PBE	2006	9	14	4	49	37
3	optB88-vdW	2010	7	13	3	53	31
4	PWPB95-D <sub>3</sub>	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	$\tau$ -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

It is not clear from this list, whether the dispersion correction should be always used. However, at other forums we found the advices to use the dispersion correction always if possible. In Ref. [1] you can see that the  $\omega$ B97X-D is the best single-component functional, while PBE0-D3 perform almost as well. Besides that, on the CCL list one can read that B3LYP-D3 is usually better than B3LYP.

Dispersion correction is the interaction of induced dipoles. This correction becomes important if two parallel benzene rings interact (stacking). So, the dispersion correction is important for computing

such molecules as tetraphenylporphyrin, bilirubin, etc.

Here is a list of favorable and non-favorable DFT functionals from the DFT 2015 poll for computing particular properties:

Properties	"Preferred"	"Disliked"
1. Reaction barriers	B2PLYP, M06-2X, PBE0, PBE, $\omega$ B97X-D	B3LYP, MN12L, M05, LB94, BLYP, BHandH, B3LYP*
2. Normal mode analysis	B3LYP, PBE, M06-2X, BP86, PBE0	MN12L, M05, LB94, B3LYP*, OLYP, M06-L
3. Chiroptical properties	B2PLYP, CAM-B3LYP, PBE, PBE0	B3LYP, B3LYP*, OLYP, MN12L, M06-L, M05, LB94
4. Hydrogen bonds	B97-D, $\omega$ B97X-D, BP86, M06-2X, PBE, PBE0	B3LYP, B3LYP*, OLYP, MN12L, M05-2X, M05, LB94, BHandH
5. Excitation energies	CAM-B3LYP, PBE0, $\omega$ B97X-D, HSE	B3LYP*, OLYP, MN12L, M06-L, M05, B3LYP-D, B3LYP
6. Main group elements	PBE, B2PLYP, M06-2X, B3LYP, BP86, PBE0	B3LYP*, MN12L, M06-L, M05
7. Transition metals	PBE, BP86, PBE0, PW91, B97-D	B3LYP*, B3LYP-D, M05, BHandH, MN12L, B3LYP
8. Relativistic elements	PBE0, BP86, PBE, PW91	B3LYP*, B3LYP, B3LYP-D, MN12L, M05-2X, M05, CAM-B3LYP, BHandH
9. NMR shieldings / couplings	BP86, PBE, PBE0, PW91	B3LYP*, B3LYP-D, B3LYP, MN12L, M06-L, M05, BHandH
10. Geometries	PBE, M06-2X, B3LYP, BP86, PBE0	B3LYP*, MN12L, M05, LB94, M05-2X, BHandH
11. Spin-state splittings	SSB-D, LDA, OLYP, PBE0	B3LYP, B3LYP*, B3LYP-D, MN12L, M06-L, M06-2X, M05-2X, M05, BHandH

With all due respect to the creators of the above list, we must mention that we tried to compute the properties of bilirubin molecule (having intermolecular H-bonds) using the PBE, B3LYP and  $\omega$ B97XD functionals, and we found that the PBE functional is the worst at describing intermolecular H bonds (the PMR spectra computed using the PBE/6-311G(D,P) method are in poorer agreement with the experimental ones than the PMR spectra computed using the B3LYP/6-311G(D,P) or  $\omega$ B97XD/6-311G(D,P) methods). So, we found that the PBE functional is not good at describing H-bonds, in contrast to the conclusions drawn above. So, we think that you should not fully trust these tables.

Another [post](#) from CCL states the following:

- Recommended GGA methods: revPBE-D3, B97-D3
- Recommended meta-GGA methods: oTPSS-D3, TPSS-D3
- Hybrid functionals: PW6B95-D3, M062X-D3
- Double-hybrids are the most accurate DFT methods on the market: DSD-BLYP-D3, DSD-PBEP86-D3, PWPB95-D3

In Ref. [2], a thorough energy benchmark study of various density

functionals (DFs) was carried out. The authors write:

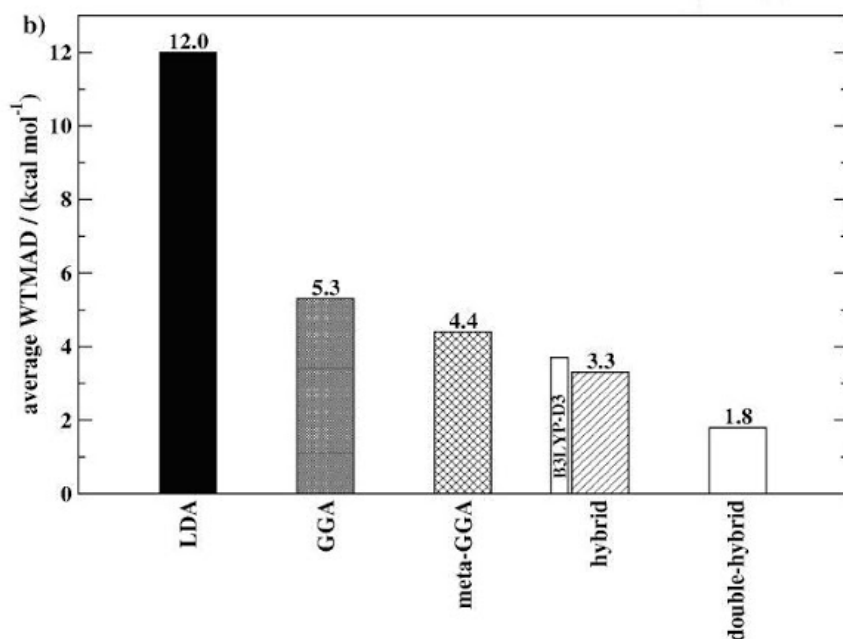
"In summary, we recommend on the GGA level the B97-D3 and revPBE-D3 functionals. The best meta-GGA is oTPSS-D3 although meta-GGAs represent in general no clear improvement compared to numerically simpler GGAs. Notably, the widely used B3LYP functional performs worse than the average of all tested hybrids and is also very sensitive to the application of dispersion corrections."

"The  $\omega$ B97X-D functional seems to be a promising method. The most robust hybrid is Zhao and Truhlar's PW6B95 functional in combination with DFT-D3".

"If higher accuracy is required, double-hybrids should be applied. The corresponding DSD-BLYP-D3 and PWPB95-D3 variants are the most accurate and robust functionals of the entire study."

The tests in this paper were performed on GMTKN30 set – this set covers mainly molecules containing main group elements, mostly organic ([link](#)).

So, the double-hybrids seem to be the best DFT methods at the moment. This is illustrated by the following chart from the aforementioned paper:



Another advantage of PBE is that this functional is "cheap".

Note that the PBE and PBE0 methods are quite different: PBE is a CGA, while PBE0 is a hybrid method. However, if one compares e.g. BP86, BLYP, BPW91 functionals (GGA) with PBE0, he finds that PBE0 is "less semi-empirical".

Here is another comparison of DFT functionals. In Ref. [3], a few DFT functionals were benchmarked for 14 compounds (calculation of vertical excitation energies by TDDFT and their comparison to

experiment). Here are two pictures from this paper:

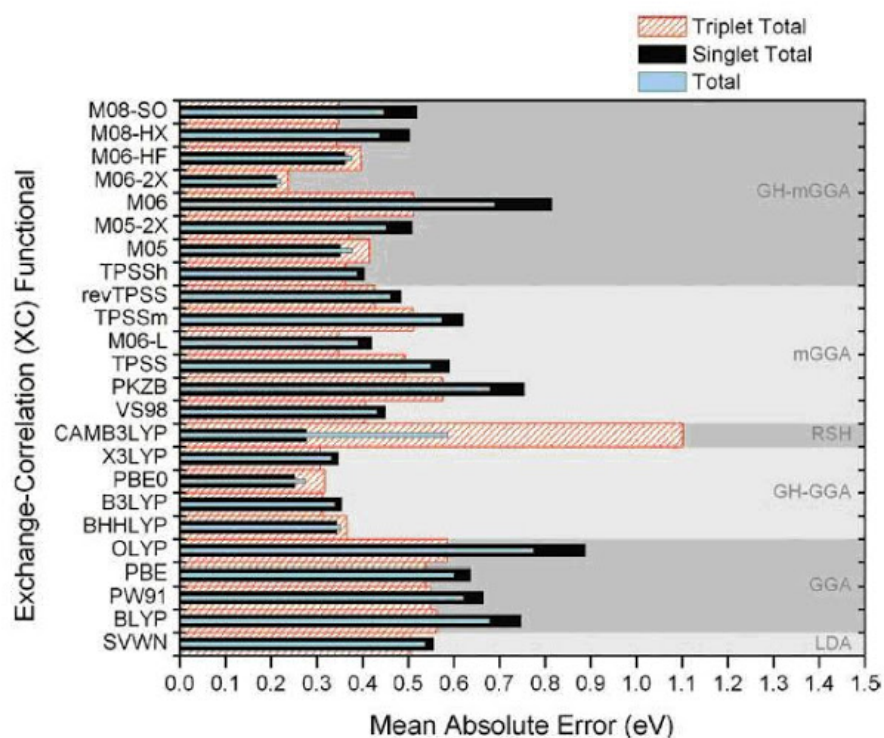


FIG. 1. Comparison of density functional mean absolute errors for singlet and triplet excited states.



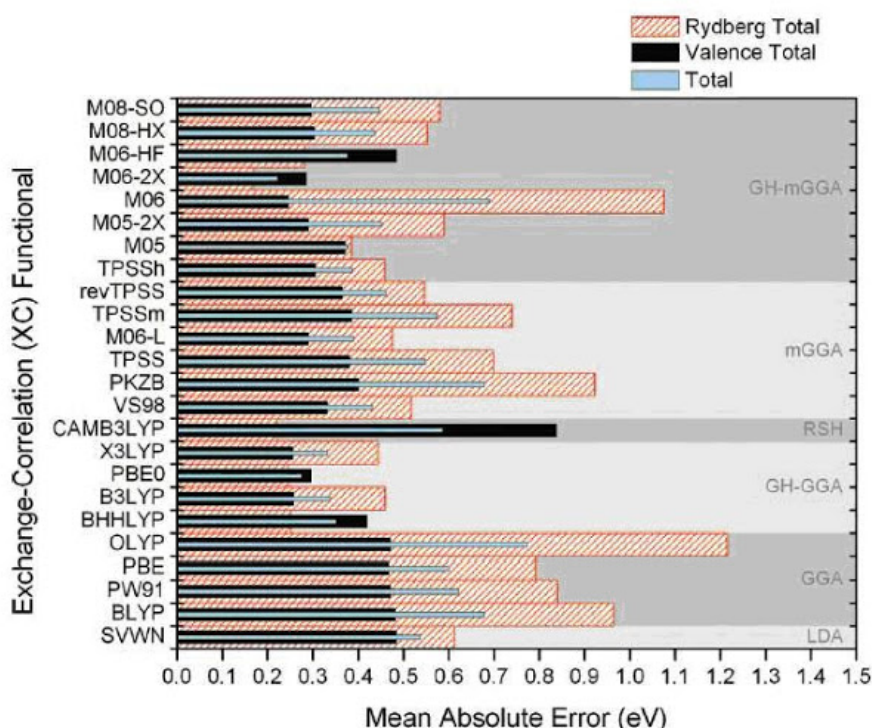


FIG. 2. Comparison of density functional mean absolute errors for valence and Rydberg excited states.

Ref. [4] reports that the CAM-B3LYP and BHandH functionals yield the best agreement between computed and experimental vertical absorption energies for a set of some simple organic molecules (involving first and second row atoms).

We have performed some benchmark NMR computations with different functionals. The  $^1\text{H}$  NMR spectra of 26 simple organic molecules (not containing internal hydrogen bonds) were computed at PCM wB97XD/6-31G(D,P), PCM B3LYP/6-31G(D,P), PCM B3LYP-D3/6-31G(D,P), PCM B3LYP-D3/aug-cc-pVTZ and some other levels, and the following conclusions were made:

- 1) The methods PCM wB97XD/6-31G(D,P) and PCM B3LYP-D3/6-31G(D,P) yield very similar standard deviations (SD) from the experiment of 0.1411 ppm and 0.13005 ppm, respectively; note that the signals of the protons not attached to carbons do not fit into common correlation). This, however, does not mean that these two functionals produce similar results (correlation of the values computed by them has an SD of 0.06849 ppm);
- 2) Switching from PCM B3LYP-D3/6-31G(D,P) to PCM B3LYP-D3/aug-cc-pVTZ does not improve the agreement with the experimental data: the SD is 0.13005 for the former and 0.13539 ppm for the latter. This is even rather strange for us, why the enlargement of the basis set does

not lead to the improvement of the agreement with experiment; maybe, the main source of disagreement is the experimental error or some fundamental problems of NMR computation algorithms.

Note that we have performed some benchmark IR spectra computations (mentioned in a previous post in this blog), and we found that switching from  $\omega$ B97XD/6-31G(D,P) to  $\omega$ B97XD/aug-cc-pVTZ method improves the agreement with the experiment approximately by a factor of 1.2;

3) It is of no real importance, whether to perform a full geometry optimization at PCM B3LYP-D3/aug-cc-pVTZ level of theory, or just perform the geometry optimization at PCM B3LYP-D3/6-31G(D,P) level and then do a single point with aug-cc-pVTZ basis set. The NMR shift values obtained by these two approaches correlate with  $SD=0.01442$  ppm;

4) Taking into account the solvation effects with PCM model improves the agreement with the experiment with an almost negligible increase in computational costs;

5) Switching from PCM B3LYP/6-31G(D,P) to PCM B3LYP-D3/6-31G(D,P) improves the agreement with the experiment by 0.4% only ( $SD$  changes from 0,13056 to 0,13005). This is because only such molecules as phenol, biphenyl, anthracene, hexane, etc. were computed. If we had computed such molecule as benzene dimer, the dispersion correction would become important. Besides that, for our molecules the energies differ rather significantly with the B3LYP and B3LYP-D3 methods.

6) Two NMR computation schemes – GIAO and CSGT – produce almost identical results ( $SD$  between them is 0.016 ppm).

The combination of these advices can confuse an inexperienced user. As for us, we decided that we should use PBE-D3 for inorganic molecules and  $\omega$ B97X-D or B3LYP-D3 for organic ones, since we deal with the Gaussian09A package. Such an advice should be useful only for “amateurs” who are unable to gather more information.

Anyway, it is better to use several functionals to ensure that they produce similar results. MP2 should not also be forgotten (SCS-MP2 seems to be better than conventional MP2, as written in the paper above; as far as we know, SOS-MP2 is better too).

Recently, the B3LYP/6-31G(D,P) method has been quite popular. We think that using this method for computing organic molecules (not containing d and f elements) is still rather adequate, but the snobs can interpret the use of this method as the sign of amateurishness (at least, if you don't employ different functionals and/or basis sets in the same study). See, for example, [this](#) and [this](#) posts on the CCL list.

The flaws of this famous B3LYP/6-31G\* model chemistry are discussed in Ref. [5]:

The authors write that the relatively good performance of B3LYP/6-31G\*, which made it so popular, is caused by a hidden error cancellation. The B3LYP-gCP-D3/6-31G\* method, according to the

B3LYP/6-31G\*      B3LYP-gCP-D3/6-31G\*

BSSE      Dispersion

BSSE      Dispersion

Here is a picture from Ref. [13] illustrating the availability of DFT functionals:



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following is stated:

"One of the primary reasons for the cc basis set family's lasting popularity is due to a series of empirical observations that as the cardinal number ( $n$  in cc-pVnZ) of the basis set is increased, energies and various properties converge smoothly toward the complete basis set (CBS) limit."

The so-called complete basis set (CBS) limit means that you first compute with cc-pVDZ, then cc-pVTZ, then cc-pVQZ, then cc-pV5Z, etc., and the energy should converge to a hypothetical "complete" basis set limit. At the same time, there are more than 10 extrapolation schemes which give nearly the same result after performing only 2-3 computations (however, these extrapolation schemes are empirical to some extent).

For heavy elements ( $Z > 29$ ), relativistic effects are strong and must be taken into account either using the methods like ZORA, DKH, or using effective core potentials (ECPs, PPs). The main relativistic effects include relativistic contraction and spin-orbit interaction. For many tasks, even such elements as Fe, Co, Ni do not require including relativistic effects in the computation (you will have a lot of problems besides relativism with these atoms).

The Ref. [6] provides an overview of the development of Gaussian basis sets for molecular calculations, with a focus on four popular families of modern bases ("Gaussian basis set" means any basis set with Gaussian (not Slater) functions, not a specific set for the GAUSSIAN program). The authors write about the cases when using ECPs is not advisable (in particular, electron paramagnetic resonance), and it is written that using the DFT-based ZORA or DKH models with segmented all-electron relativistic contracted (SARC) basis sets produce good agreement with experiment and higher level ab initio computations.

One interesting point is mentioned in Ref. [7]: the authors report that the computations with 6-311++G\*\* basis set gave better molecular geometries than the more costly aug-cc-pVDZ (the methods used were MP2 and CCSD). In addition, the smaller 6-311++G\*\* invariably leads to lower calculated total energies than aug-cc-pVDZ. So, it seems that the aug-cc-pVDZ can be worse than the 6-311++G\*\* set (nevertheless, we suppose that if you need an expensive basis set or CBS (complete basis set) extrapolation, you should use cc-pVTZ, cc-pVQZ, cc-pV5Z, etc).

Some people say that it is not actual to use basis sets larger than cc-pVTZ with DFT. However, in Ref. [14] the authors performed energy computations of 211 small first and second row compounds (mostly organic), and they concluded that the 5Z basis set (aug-cc-pV5Z) is required to get the MAE of atomization energies below 1 kcal/mol. See [this blog](#) for more information.

The same is written at this handbook "[Practical Advice for Quantum Chemistry Computations](#)":

## Choice of Basis Set

- STO-3G is too small
- 6-31G\* or 6-31G\*\* probably give reasonable results; they may be better than cc-pVDZ
- For higher accuracy, try cc-pVTZ. Better than 6-311G\*\*, etc.
- For benchmarks, probably want cc-pVQZ (but if you know enough to benchmark, you probably don't need my advice anymore...)
- For anions you must use diffuse functions (aug-, or +). Might also need them for excited states. Also need them for dispersion-bound complexes.
- Beyond Ne, you might want to try the cc-pV(X+d)Z basis sets
- For alkali or alkaline earth metals, you might want to correlate the (n-1) shell and use core-valence basis sets like cc-pCVXZ

For some small organic molecules, we have found that the basis sets 6-31++G(D,P) and AUG-cc-pVDZ give almost identical results (protonation energies of 16 amide-containing molecules computed with wB97XD/6-31++G(D,P) and wB97XD/AUG-cc-pVDZ methods correlate with  $R = 0.99966$ ; this difference is almost negligible for our applied tasks). In contrast to the results reported in the aforementioned paper, the total energies computed with wB97XD/AUG-cc-pVDZ method are 3-30 kJ/mol lower than the energies computed with wB97XD/6-31++G(D,P).

At the same time, with the basis set AUG- cc-pVDZ the computation time was 3-6 times higher than with the 6-31++G(D,P) basis set. So, the 6-31++G\*\* basis set should be still considered good enough.

It is usually considered that the computation of anions or significantly electronegative atoms (which show big negative Mulliken charge) requires the use of diffuse functions ("++" for 6-31G or "aug" for cc-pVnZ). However, in the paper [8] this conclusion is criticized to a significant extent. The authors write:

"We conclude that the use of diffuse functions for calculating geometrical parameters for PAH anions in general is unnecessary and does not improve the calculated results significantly. Energy calculations are affected in much the same way."

As the authors write, the only case when the diffuse functions are important are the computations of absolute values of chemical shifts; however, in most cases, when the experimental data are available, it is no necessary to obtain their absolute values as the correlations between the computed and experimental values can be built instead.

On the other hand, D. Truhlar who investigated the use of diffuse

functions writes [here](#):

"How should one add diffuse functions to the basis set? Diffuse functions are known to be critical in describing the electron distribution of anions (as discussed in my book), but they are also quite important in describing weak interactions, like hydrogen bonds, and can be critical in evaluating activation barriers and other properties."

The Truhlar group recommends using the "jun-" basis sets (see below).

One more source of information is the review "[Basis sets in quantum chemistry](#)" by C. David. Sherill. The author writes in this review about the diffuse functions:

### Diffuse Functions

- Diffuse functions have small  $\zeta$  exponents; this means the electron is held far away from the nucleus
- Necessary for anions, Rydberg states, very electronegative atoms (fluorine) with a lot of electron density
- Necessary for accurate polarizabilities or binding energies of van der Waals complexes (bound by dispersion)
- It is **very bad** to do computations on anions without using diffuse functions; your results could change completely!

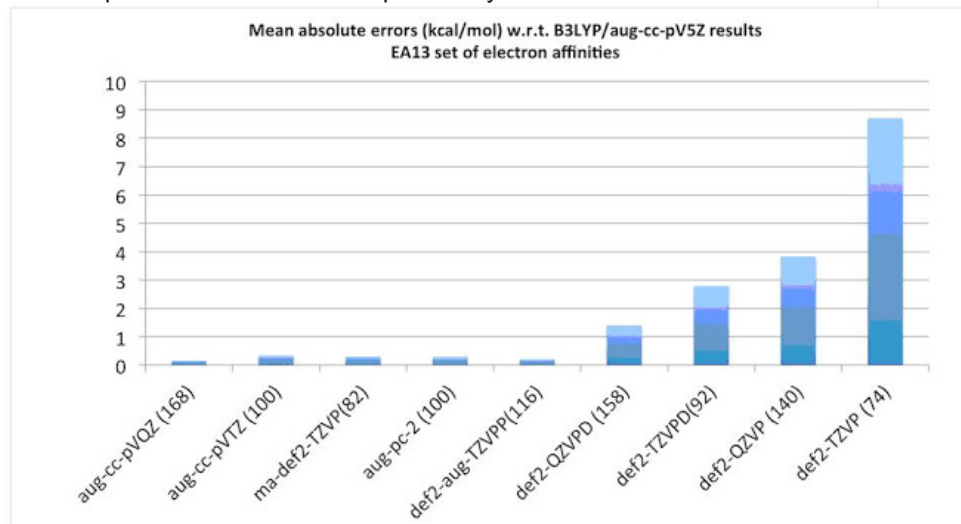
Our knowledge of the subject and our personal experience says that the diffuse functions indeed should be used when calculating anions. We have computed the energies of deprotonation of 12 carbon acids (with PCM solvation model), both with diffuse functions and without them (wB97XD/6-31++G(D,P) method and the wB97XD/6-31G(D,P) method), and the values calculated by the first method correlate much better with experimental PKa values than the values computed without diffuse function (the correlation coefficients R are correspondingly 0,99522 for wB97XD/6-31++G(D,P) and 0,98884 for wB97XD/6-31G(D,P)).

Some recommendations concerning the choice of basis sets can be found on [Orca input library](#):. These recommendations are:

- Rule of thumb: Energies and geometries are usually fairly converged at the DFT level when using a balanced polarized triple-zeta basis set (such as def2-TZVP) while MP2 and other post-HF methods converge slower w.r.t. the basis set. Ab initio methods are much more basis set sensitive than DFT methods

- Stick with one family of basis sets that is available for all the elements of your system. Mixing and matching basis sets from different families can lead to problems.
- Calculations on heavy elements can either be performed using an all-electron approach or effective core potentials (ECPs).

Here is a picture from the Orca input library:



So, it seems that diffuse functions are really important for computing electron affinities.

As far as we know, usually it is not needed to use a larger basis set than cc-pVTZ with DFT: further increasing basis set size will not improve the accuracy of the computation. In contrast, this is not true for ab initio computations, which will benefit from using larger basis sets, such as cc-pVQZ, cc-pV5Z, etc.

Some papers, in which the results of DFT computations are compared to those of ab initio methods and to the experimental data, conclude that DFT performs not worse (or even slightly better) [10, 11, 12]. This is caused by employing modest basis sets (not larger than cc-pVTZ) in these papers.

So, the choice between DFT or ab initio methods depends on which properties are calculated and what accuracy is required.

The larger the basis set, the more difficult the SCF convergence is (especially if diffuse-augmented basis sets are used). We recommend to always specify SCF=XQC in GAUSSIAN input files. With this keyword, the scf is firstly converged using the default DIIS algorithm, and if the convergence is not achieved, Gaussian switches to more reliable and costly quadratically convergent SCF procedure.

Ref. [9] describes the role of diffuse functions in computations. It is known, that for many tasks using the diffuse functions will not lead to significant increase of computational accuracy, but will increase the cost of the calculation; besides that, using the diffuse functions can lead to SCF convergence problems and can increase the basis set

superposition error (BSSE). The authors write: “We conclude that much current practice includes more diffuse functions than are needed. Often, better accuracy could be achieved if the additional cost were invested in higher- $\zeta$  basis set or more polarization functions.”

The popular basis set family cc-pVnZ (of Dunning and co-workers) comprises the diffuse functions, if “aug-” prefix is used. The authors notice that chemists usually utilize “fully augmented” basis sets, and this may not be optimal for large molecules. For example, the cc-pVTZ basis set for methane has s, p, d, and f functions on C and s, p, and d functions on H; aug-cc-pVTZ contains diffuse s, p, d, and f functions on C and diffuse s, p, and d functions on H atoms.

In contrast, the earlier “plus” basis sets originally systematized by Pople and co-workers contained only diffuse s and p functions on non-hydrogen atoms and no diffuse functions on hydrogen atoms. In Ref. [9] this is called “minimal augmentation”. The maug-cc-pVTZ basis set retains the diffuse s and p functions on carbon with the exponential parameters optimized for the aug case but deletes all other diffuse functions.

So, the authors (Truhlar et al.) conclude that using the minimal augmentation is usually more optimal than using the full augmentation (particularly with DFT). The authors recommend the so-called “calendar” basis sets, in particular the “jun” level of augmentation – for example, the jun-cc-pVTZ set is recommended in comparison to aug-cc-pVDZ or cc-pVTZ. When increasing the zeta number in Dunning basis sets (i.e. switching from cc-pVDZ to cc-pVTZ, then to cc-pVQZ, etc), augmentation becomes less important, and using the “calendar” basis sets provides a more efficient sequence of basis sets (than unaugmented, minimally augmented, or fully augmented sets) for basis set extrapolation to the complete basis set limit. We know, however, that many researchers have criticized the approach proposed by the authors.

### 3. DFT quackery

Anyway, density functional theory is a “black box”. Look at this picture from Ref. [13]:



:(	no simple rule for reliability	♡
:(	no systematic route to improvement	♡
:(	decades between each generation	♡
:(	full of arcane insider jargon	♡
:(	too many approximations to choose from	♡
:(	can only be learned from a DFT guru	♡

TABLE I. List of things users despise about DFT calculations. Please rank in order of induced frustration. The extreme left column indicates the users response to these 'features', the right denotes that of developers.

Our comment on this picture:

First and second points: In contrast to ab initio methods, DFT is not hierarchical. Ab initio (non-empirical) methods are hierarchical: this means that if we increase basis set size, level of taking into account the electronic correlation (excitation rank), and possibly the level of taking into account the relativistic effects (for heavy elements), we approach the exact solution (within the Born–Oppenheimer approximation). More specifically, if we go, e.g., through CCSD/cc-pVDZ → CCSDT/cc-pVDZ → CCSDTQ/cc-pVDZ → CCSDTQ5/cc-pVDZ, etc., the results of the computation systematically approach some limit; if we go through CCSD/cc-pVDZ → CCSD/cc-pVTZ → CCSD/cc-pVQZ → CCSD/cc-pV5Z → CCSD/cc-pV6Z, etc., the results systematically approach the complete basis set (CBS) limit. For the first row, the improvement can be non-monotonic, while for the second case the improvement seems to be always monotonic.

So, we can verify the accuracy of an ab initio method by comparing its results with the results of a higher level computation. For DFT, this possibility is much less available.

The points mentioned below are mostly our private opinion, maybe not fully right.

As far as we know, DFT is often used to “confirm” an experiment. This means that if the experiment and a DFT computation lead to similar conclusions, this increases the reliability of the investigation. On the contrary, if the experiment and the DFT calculation give different results, this can be either a discovery or a failure (inaccuracy of the computation, or maybe the experiment).

Speaking of “confirming” an experiment, it should be noted that this approach is only good with an independent experiment. We know some cases when the experiment was “adjusted” for better agreement with the computation (both at DFT and ab initio levels).

As mentioned above, it is a good practice to perform the computation with several different DFT functionals, to ensure that they all give the same results. And as far as we know, some researchers, being not

honest enough, meaningly avoid using more than one functional, because if different functionals give contradictory results in their work, this makes this whole work less "publishable".

Here you can read an ironical essay "[Obituary : Density Functional Theory. 1927-1993](#)":

The author claims that the density functional theory in current implementation is not a mathematically correct approach:

"The Hohenberg-Kohn argument is what mathematicians call an existence proof, as opposed to a constructive proof. That is, although we now know that, *in theory*, DFT can extract as much information from  $r(r)$  as her brother can from  $Y(r_1, r_2, \dots, r_n)$ , no-one knew how to dress her so that she could achieve this *in practice*. All quantum mechanical theories are created equal, but some are more equal than others."

The hybrid functionals, which appeared in 1993, are even more unreliable and not correct from the theoretical point of view; in other words, using such functionals may be a kind of "shamanism", or maybe even "scientific charlatanism". The author thinks that the density functional theory finally died (we should add, it died as a well-grounded scientific theory) in 1993, after the spreading of hybrid functionals.

On the other hand, in Ref. [13] the author states the following:

"I believe that a fundamental principle underlies the success of DFT, which is that local approximations are a peculiar type of *semiclassical* approximation to the many-electron problem. For the last 6 years, with both my group and many collaborators, I have been trying to uncover this connection, and make use of it. The underlying math is very challenging, and some must be invented."

The "DFT shamanism" can exist in the following form: if different functionals are applied to the same object, the user may select any results consistent with experimental data (even the latter are invalid or erroneous) and explain them. We suggest calling such practice "DFT quackery".

In Ref. [13] the following is proposed: "Users should stick to the standard functionals (as most do, according to Fig. 1), or explain very carefully why not."

## 4. DFT future

Here is a picture from Ref. [13]:

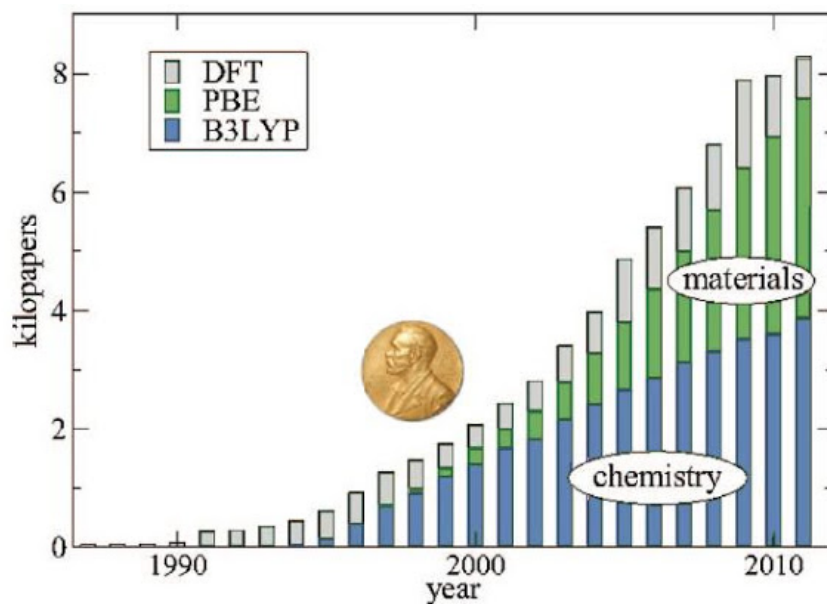


FIG. 1. Numbers of papers when DFT is searched as a topic in Web of Knowledge (grey), B3LYP citations (blue), and PBE citations (green, on top of blue).

A fragment of the paper [13]:

## "XII. THE FUTURE

So, where does this leave us? It is clearly both the best and worst of times for DFT. More calculations, both good and bad, are being performed than ever. One of the most frequently asked questions of developers of traditional approaches to electronic structure is: "When will DFT go away?." Judging from Fig. 1, the answer is clearly no time soon. Although based on exact theorems, as shown in Fig. 2, these theorems give no simple prescription for constructing approximations. This leads to the many frustrations of the now manifold users listed in Table I. Without such guidance, the swarm of available approximations of Fig. 3 will continue to evolve and reproduce, perhaps ultimately undermining the entire field. But I expect that some of the many excellent ideas being developed by the DFT community will come to fruition, i.e., produce new and more general standard approximations, well before that happens."

## References

[1]

<http://pubs.rsc.org/en/Content/ArticleLanding/2011/CP/c1cp20834a#!divAbstract>

[2]

<http://pubs.rsc.org/en/Content/ArticleLanding/2011/CP/c0cp02984j#!div>

## Abstract

[3] S.S.Leang, F.Zahariev, M.S.Gordon, J.Chem.Phys., 136, 104101 (2012)

[4] G.García, C.Adamo, I.Ciofini, Phys. Chem. Chem. Phys., 2013, 15, 20210--20219

[5] <http://pubs.acs.org/doi/abs/10.1021/jo302156p>

[6]

[https://www.researchgate.net/publication/263680088\\_Gaussian\\_basis\\_sets\\_for\\_molecular\\_applications\\_Int\\_J\\_Quant\\_Chem](https://www.researchgate.net/publication/263680088_Gaussian_basis_sets_for_molecular_applications_Int_J_Quant_Chem)

[7] <http://onlinelibrary.wiley.com/doi/10.1002/jcc.20058/abstract>

[8] Calculations of PAH anions: When are diffuse functions necessary? Noach Treitel<sup>1</sup>, Roy Shenhar, Ivan Aprahamian, Tuvia Sheradsky and Mordecai Rabinovitz. Phys. Chem. Chem. Phys., 2004, 6, 1113 – 1121

[9] <http://pubs.acs.org/doi/abs/10.1021/ct200106a>

[10] Do Practical Standard Coupled Cluster Calculations Agree Better than Kohn–Sham Calculations with Currently Available Functionals When Compared to the Best Available Experimental Da...

Article in Journal of Chemical Theory and Computation · May 2015  
Impact Factor: 5.5 · DOI: 10.1021/acs.jctc.5b00081

[11] On the dissociation energy of Ti(OH)<sub>2</sub><sup>+</sup>.

An MCSCF, CCSD(T), and DFT study

A. Irigoras, J.M. Ugalde, X. Lopez, and C. Sarasola

Can. J. Chem. 74: 1824-1829 (1996). Printed in Canada / Imprimé au Canada

[12]

[https://www.researchgate.net/post/What\\_do\\_you\\_think\\_about\\_recent\\_JCTC\\_paper\\_of\\_Truhlar\\_et\\_al\\_about\\_benchmarking\\_DFT\\_against\\_CC\\_for\\_TM\\_complexes](https://www.researchgate.net/post/What_do_you_think_about_recent_JCTC_paper_of_Truhlar_et_al_about_benchmarking_DFT_against_CC_for_TM_complexes)

[13] J. Chem. Phys. 136, 150901 (2012). Perspective on density functional theory. Kieron Burke.

[14]

Jensen, Stig Rune; Saha, Santanu; Flores-Livas, José Abdenago; Huhn, William; Blum, Volker; Goedecker, Stefan; Frediani, Luca, 2017, "GGA-PBE and hybrid-PBE0 energies and dipole moments with MRChem, FHI-aims, NWChem and ELK", doi:10.18710/OEM0EL, UiT Open Research Data Dataverse, V3

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