News Item: Popularity Poll Density Functionals 2010

Marcel Swart,[a,b,*] F. Matthias Bickelhaupt[c] and Miquel Duran[a]

a) Institut de Química Computacional and Departament de Química, Universitat de Girona, Campus Montilivi, 17071 Girona, Spain

b) Institució Catalana de Recerca i Estudis Avançats (ICREA), Pg. Lluís Companys 23, 08010 Barcelona, Spain

c) Department of Theoretical Chemistry and Amsterdam Center for Multiscale Modeling, Scheikundig Laboratorium der Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

E-mail: marcel.swart@icrea.cat, **Fax**: +34-972418356

Abstract. We have recently held the first of an annual online poll for favorite density functionals in order to obtain a popularity adapted consensus object (PACO). This "consensus" PACO functional may serve as a measure of how well the computational chemistry community is doing if compared to state-of-the-art reference data. It will change over time and hopefully will result in gradual improvements. To track the performance of the PACO functionals, it is checked for a variety of diverse interactions: atomization energies of six representative molecules (AE6), barrier heights of hydrogen-transfer reactions (BH6), π-π stacking of anti-parallel cytosine dimer, spin-state splittings of FeFHOH and Ni(EDT)$_2^{2-}$, excitation energies (singlet, triplet) of CO, and hydrogen-bonding in four dimers (ammonia, water, formic acid, formamide). These small systems are studied using basis sets close to the basis set limit, and compared to either coupled cluster results or experimental data. A surprising result from the poll was that the widely-used B3LYP is in fact not the most popular density functional, but came only second after PBE0 (also known as PBE1PBE).

Introduction. Following a presentation by Prof. 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 an online poll (see e.g. www.marcelswart.eu/dft-poll) where people could indicate their preferences for a number of density functionals. The poll was announced on the CCL mailing list (twice), on Facebook, Twitter, blogs, etc. in order to get the maximum number of participants. The aims of this poll were: (i) to probe the "performance 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.

Scheme 1. List of functionals included in the poll

Initial 20 choices:

B2PLYP,[1] B3LYP,[2] B3LYP*,[3] B3PW91,[4] B97-D,[5] BHandH,[6] BLYP,[7,8] BP86,[7,9] CAM-B3LYP,[10] LDA[11-14] (SVWN[5], PW92[13]), mPW1K,[15] M06-2X,[16] M06-L,[17] PBE,[18] PBE0[19] (PBE1PBE), OLYP,[8,20] revTPSS-D,[21] SAOP,[22] SSB-D,[23] TPSSh[24,25]

Additional suggestions:

LB94,[26] revTPSS,[21] τ-HCTH,[27] M05-2X,[28] LC-wPBE,[29,30] HSE,[31] XLYP,[32] X3LYP,[32] M05,[33] PW91[34]

A list of rules was set up for how to deal with the setup and outcome of the poll, which are listed below:

1) Points are given similar to football, i.e. a 'like' gives +3 points, 'neutral' +1 points, no answer at all ('Vot en blanc','None Of The Above') 0 points, 'hate' -1 points. A ranking of the functionals will be made by taking into account these points.

2) In case there are two or more functionals with the same number of points, the ordering will be decided by the following criteria: (i) most number of 'like's, (ii) least number of 'hate's, (iii) results from previous years (for future editions), (iv) year of publication of the functional (the younger, the better), (v) decision by organizers.

3) There will be a Primera Divisió with the 20 most popular functionals. At the end of each year, the 5 least popular of the Primera Divisió will relegate to the Segona Divisió.
Each year, only the 20 most popular functionals of the Segona Divisió will be kept. The five most popular ones of the Segona will be promoted to the Primera, while the 15 next will form the Segona for the next year together with the 5 relegated from the Primera.
The other functionals will not take part in the poll for the year after (unless suggested again). There is a maximum of 10 additional suggestions for each year, which are added chronologically (after being suggested by mail to M. Swart).
For the 2011 edition of next year, the 20 most popular functionals of 2010 will form the Primera, the other 10 the Segona Divisió. There will be 20 places left in the Segona Divisió of 2011 for additional suggestions.

4) A new PACO functional will be constructed each year, by taking a weighted linear combination of the 20 functionals in the Primera Divisió. For those functionals that do not have an energy expression (e.g. SAOP, LB94), a weight of zero (except for the excitation energies) will be used for the construction of PACO20xx. In particular, the following energy expressions are obtained:
   The weight of each functional is given by its number of points, divided by the total number of points of the 20 functionals in the Primera Divisió (using a value of 0 for those without an energy expression, see above). The sum of the weights is therefore one.
Note that with these PACO functionals we do not wish to ridicule the development of density functionals, which is hard and painstaking work, and often underestimated. Neither do we intend to mix different functionals for the sake of mixing, in the hope of reducing discrepancies. However, we do wish to help the community by getting a consensus current opinion on the many functionals, which may help the reader choose a functional for his/her own study on chemistry. As mentioned in the introduction, it can also be enlightening to compare the consensus current opinion with the actual performance.

5) The PACO20xx functionals will be applied to a small number of typical chemical systems:
   - the AE6 set for six atomization energies (SiH$_4$, SiO, S$_2$, propyne, glyoxal, cyclobutane)
   - the BH6 set for six barrier heights (forward and reverse reaction of OH+CH$_4$, H+OH, H+H$_2$S)
   - the π-π stacking energy of anti-parallel cytosine dimer
   - spin-state splitting of FeFHOH and Ni(EDT)$_2^{2-}$
   - excitation energies (singlet, triplet) of CO
   - the hydrogen-bonding energies of four dimers (ammonia, water, formic acid, formamide)
   For all of these coupled cluster CCSD(T) or experimental (reference) data are available.

6) Each year, a new popularity poll will be held between June 1 and October 1, and will be announced on www.marcelswart.eu/dft-poll, on the CCL list, etc. and a short news item such as the current one about it will be published.

Table 1. Polling results for the density functionals, ordered according to ranking

	functional	year	cites[a]	like	neutral	hate	empty	points	W_{energy}[b]	W_{TD-DFT}[c]
	Primera Divisió									
1	PBE0	1996	583	72	33	5	51	**244**	0.1022	0.0984
2	B3LYP	1994	20869	81	30	32	18	**241**	0.1010	0.0972
3	PBE	1996	1221	64	41	8	48	**225**	0.0943	0.0907
4	BP86	1988	732	45	47	16	53	**166**	0.0695	0.0669
5	M06-2X	2008	100	48	34	32	47	**146**	0.0612	0.0589
6	B2PLYP	2006	35	33	52	17	59	**134**	0.0561	0.0540
7	B3PW91	1993	1026	29	57	15	60	**129**	0.0540	0.0520
8	B97-D	2006	23	27	55	12	67	**124**	0.0519	0.0500
9	M06-L	2006	58	39	37	33	52	**121**	0.0507	0.0488
10	CAM-B3LYP	2004	82	29	50	16	66	**121**	0.0507	0.0488
11	TPSSh	2003	42	26	52	14	69	**116**	0.0486	0.0468
12	OLYP	2001	82	19	55	18	69	**94**	0.0394	0.0379
13	mPW1K	2000	152	17	60	17	67	**94**	0.0394	0.0379
14	SAOP	2000	62	17	56	14	74	**93**	0.0000[d]	0.0375
15	SSB-D	2009	2	16	56	13	76	**91**	0.0381	0.0367
16	BLYP	1988	1161	25	47	33	56	**89**	0.0373	0.0359
17	LDA	1980	9496	27	42	38	54	**85**	0.0356	0.0343
18	revTPSS-D	2009	0	13	59	13	76	**85**	0.0000[d]	0.0000[d]
19	M05-2X	2006	140	26	29	23	83	**84**	0.0352	0.0339
20	B3LYP*	2001	36	24	46	35	56	**83**	0.0348	0.0335
	Segona Divisió									
21	BHandH	1993	47	15	57	25	64	**77**		
22	revTPSS	2009	0	11	50	14	86	**69**		
23	LB94	1994	28	10	51	14	86	**67**		
24	LC-wPBE	2006	2	11	31	5	114	**59**		
25	τ-HCTH	2002	4	9	42	17	93	**52**		
26	HSE	2003	13	5	35	5	116	**45**		
27	M05	2005	200	13	17	13	118	**43**		
28	X3LYP	2004	45	7	27	14	113	**34**		
29	XLYP	2004	4	3	29	12	117	**26**		
30	PW91	1992	429	4	4	3	118	**13**		

a) obtained by searching for density functional names as Topic in Web of Science (accessed Nov. 2010); b) weight for normal energies; c) weight for TD-DFT excitation energies; d) no energy expression, therefore not taken into account for PACO2010 energies

Computational details. Almost all of the calculations for checking the performance of PACO2010 were performed with either Gaussian09[35] or NWChem 5.1.1[36] (*locally modified to include SSB-D*[23]). Large correlation-consistent basis sets[37,38] have been used (*aug-cc-pVTZ, except for the spin-state splittings which used cc-pVTZ*), with accurate integration of the density (*ultrafine grid in g09, xfine in NWChem*). The only exception was the SAOP data which were obtained with the ADF program[39,40] (version 2009.01) with the ET-QZ+5P basis set[41] and accurate integration (accint = 9.0).

Results. A total number of 162 responses have been obtained in the popularity poll, which should be sufficient to give a reasonable estimate of the popularity of the different density functionals. The only exceptions are the functionals that were suggested at halfway (M05) or almost the end of the polling period (PW91). However, they will be present from the start in next year's edition (in the Segona Divisió), so could be promoted to the Primera Divisió the year after. Moreover, M05 was present as suggestion for almost half of the responses, so in principle it could have reached a total number of points of over 200 (but did obtain 43). Therefore, the only really disadvantaged was PW91 that was present only in the last polling period, in which fifteen responses (i.e. less than 10% of the total) were given.

The most popular functional from this year's edition is PBE0, before B3LYP and PBE (see Table 1). In a sense, this is surprising since the number of articles (according to Web of Science) corresponding to the "topic" PBE0 or PBE1PBE is orders of magnitude smaller than for B3LYP. Although B3LYP has more 'like's than PBE0 (81 vs. 72), it also has a substantial amount of 'hate's (32) compared to PBE0 (with 5 'hate's). Moreover, the amount of empty responses ('None of the Above', 'vot en blanc') was three times as low for B3LYP as for PBE0. Therefore, the B3LYP functional is quite well-known and almost everyone has an opinion about it, which is quite diverse. In contrast, PBE0 seems to be less well-known, but those that do know it, like it better.

Interestingly, the choice between pure and hybrid functionals is not decided yet. Of the 20 functionals in the Primera Divisió there are 10 pure (GGA, meta-GGA) functionals, and 10 hybrids. The (hybrid) meta-GGA functionals (M06-L, M06-2X, TPSSh, etc.) are not yet among the most popular ones, despite the many recent studies that show their usually good behavior.

The application of PACO2010 to chemical systems exhibits the general trends shown for many of the current density functionals [see Table 2]. Given in the Table are not only the reference data and the PACO2010 results, but also those of the most popular functional (PBE0), and for each of the items the results of the best and worst functional (*except for the spin-states for which no accurate reference data are available yet to compare with*). The trends for PACO2010 indicate that there are improvements needed for atomization energies, barrier heights, π-π stacking energies and perhaps spin-state splittings. The stacking may now be adequately handled[42] by including a portion of an empirical dispersion correction[5] (even though from a purist's point of view it would be better if such an *ad-hoc* adjustment would not be needed). The situation for the barrier heights in Table 2 may be exaggerated because the BH6 set contains only hydrogen-radical transfer reactions, which are difficult on its own (possibly related to self-interaction errors). For more normal organic chemistry reactions, many of the density functionals perform in fact much better.[43-46] Therefore, the performance for the BH6 set might be judged as a worst-case scenario. The spin-state splittings remain a difficult property for many density functionals,[47] especially the hybrid ones (see Appendix). Fortunately, PACO2010 gives the correct spin ground-state for the two transition-metal complexes studied here. Especially noteworthy is the M06-2X functional that is the best for the AE6, BH6, and H-bonding sets, but fails for the spin-states.

Conclusions. We have held the first edition of an annually returning popularity poll of density functionals, whose results have been used to construct a popularity adapted functional (PACO2010). The ranking of the functionals showed that PBE0 (and not B3LYP) is the most popular density functional currently available. We hope that this poll will contribute to monitoring weaknesses of currently applied DFT approaches and provide hints for shifting preferences towards better performing alternatives.

Table 2. Application of PACO2010 to chemical systems[a] with mean absolute deviations (MAD)[b]

	reference	PACO2010	PBE0	best	worst
<u>AE6</u>	*Ref. [48]*			*M06-2X*	*LDA [SVWN5]*
SiH₄	322.83	320.29	313.49	320.50	344.49
SiO	192.74	187.35	180.07	188.60	219.96
S₂	102.79	105.88	104.42	102.65	132.52
propyne	705.06	711.32	707.06	703.86	800.27
glyoxal	633.99	642.00	634.21	632.21	751.15
cyclobutane	1149.37	1158.05	1155.40	1146.74	1302.09
MAD		*5.66*	*5.32*	*2.04*	*73.95*
<u>BH6</u>[c]	*Ref. [48]*			*M06-2X*	*LDA [SVWN5]*
OH+CH₄ (fw)	6.54	0.21	1.97	5.17	-16.89
OH+CH₄ (rv)	19.61	12.78	13.94	17.64	2.19
H+OH (fw)	10.45	4.55	6.98	9.67	-2.04
H+OH (rv)	12.90	4.76	5.71	11.35	-13.04
H+H₂S (fw)	3.55	-0.13	0.96	4.23	-6.97
H+H₂S (rv)	17.27	13.88	12.63	18.30	-0.31
MAD		*5.71*	*4.69*	*1.23*	*17.90*
<u>Excited states CO</u>	*Refs. [22,50]*			*SAOP*	*B2PLYP*
*¹Π, σ → π**	8.51[d,e]	8.37[d,e]	8.44[d,e]	8.55[d,e]	8.59[d,e]
*¹Σ⁻, π → π**	9.88[d,e]	9.67[d,e]	9.79[d,e]	10.03[d,e]	9.58[d,e]
*¹Δ, π → π**	10.23[d,e]	10.05[d,e]	10.19[d,e]	10.46[d,e]	9.99[d,e]
*³Π, σ → π**	6.32[d,f]	5.87[d,f]	5.73[d,f]	6.28[d,f]	5.70[d,f]
*³Σ⁺, π → π**	8.51[d,f]	7.98[d,f]	7.85[d,f]	8.64[d,f]	7.41[d,f]
*³Δ, π → π**	9.36[d,f]	8.74[d,f]	8.60[d,f]	9.36[d,f]	8.33[d,f]
MAD		*0.35[d]*	*0.37[d]*	*0.10[d]*	*0.56[d]*
<u>π-π stacking</u>[g]	*Ref. [51]*			*SSB-D*	*OLYP*
Cyt₂	-9.93	-3.66	-3.14	-9.69	+4.99
MAD		*6.27*	*6.79*	*0.24*	*14.92*
<u>Spin-states</u>	*Ref. [49]*				
FeFHOH	5.4[h] ??	11.42	10.00	??	??
Ni(EDT)₂²⁻	>0	3.49	-0.45	??	??
MAD		*??*	*??*	*??*	*??*
<u>H-bonding</u>	*Refs. [22,50]*			*M06-2X*	*OLYP*
ammonia	-3.17	-2.61	-2.76	-3.17	-0.56
water	-5.02	-4.74	-4.95	-5.13	-2.40
formic acid	-18.61	-18.44	-19.17	-19.52	-11.40
formamide	-15.96	-14.93	-15.47	-16.01	-8.66
MAD		*0.51*	*0.38*	*0.27*	*4.93*

a) all values in kcal·mol⁻¹, reference data from refs. 22, 48-53; b) mean absolute deviation from reference data; c) indicated are the forward (fw) and reverse (rv) reaction barrier for reactions: i) OH+CH₄ → H₂O+CH₃, ii) H+OH → O + H₂, iii) H+H₂S → H₂ + HS; d) value in eV; e) singlet-singlet splitting; f) singlet-triplet splitting; g) interaction energy between two anti-parallel π-π stacked cytosines; h) current work

References

1. Grimme, S. J Chem Phys 2006, 124.
2. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. J Phys Chem 1994, 45, 11623-11627.
3. Reiher, M.; Salomon, O.; Hess, B. A. Theor Chem Acc 2001, 107, 48-55.
4. Becke, A. D. J Chem Phys 1993, 98, 5648-5652.
5. Grimme, S. J Comput Chem 2006, 27, 1787-1799.
6. Becke, A. D. J Chem Phys 1993, 98, 1372-1377.
7. Becke, A. D. Phys Rev A 1988, 38, 3098-3100.
8. Lee, C.; Yang, W.; Parr, R. G. Phys Rev B 1988, 37, 785-789.
9. Perdew, J. P. Phys Rev B 1986, 33, 8822-8824.
10. Yanai, T.; Tew, D. P.; Handy, N. C. Chem Phys Lett 2004, 393, 51-57.
11. Dirac, P. A. M. Proc Roy Soc London Ser A 1929, 123, 714-733.
12. Slater, J. C. Phys Rev 1951, 81, 385-390.
13. Perdew, J. P.; Wang, Y. Phys Rev B 1992, 45, 13244-13249.
14. Vosko, S. H.; Wilk, L.; Nusair, M. Can J Phys 1980, 58, 1200-1211.
15. Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. J Phys Chem A 2000, 104, 4811-4815.
16. Zhao, Y.; Truhlar, D. G. Theor Chem Acc 2008, 120, 215-241.
17. Zhao, Y.; Truhlar, D. G. J Chem Phys 2006, 125, 194101.
18. Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys Rev Lett 1996, 77, 3865-3868.
19. Perdew, J. P.; Ernzerhof, M.; Burke, K. J Chem Phys 1996, 105, 9982-9985.
20. Handy, N. C.; Cohen, A. J. Molec Phys 2001, 99, 403-412.
21. Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Constantin, L. A.; Sun, J. W. Phys Rev Lett 2009, 103.
22. Schipper, P. R. T.; Gritsenko, O. V.; van Gisbergen, S. J. A.; Baerends, E. J. J Chem Phys 2000, 112, 1344-1352.
23. Swart, M.; Solà, M.; Bickelhaupt, F. M. J Chem Phys 2009, 131, 094103.
24. Tao, J. M.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Phys Rev Lett 2003, 91, 146401.
25. Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. J Chem Phys 2003, 119, 12129-12137.
26. van Leeuwen, R.; Baerends, E. J. Phys Rev A 1994, 49, 2421-2431.
27. Boese, A. D.; Handy, N. C. J Chem Phys 2002, 116, 9559-9569.
28. Zhao, Y.; Schultz, N. E.; Truhlar, D. G. J Chem Theory Comp 2006, 2, 364-382.
29. Tawada, Y.; Tsuneda, T.; Yanagisawa, S.; Yanai, T.; Hirao, K. J Chem Phys 2004, 120, 8425-8433.
30. Vydrov, O. A.; Scuseria, G. E. J Chem Phys 2006, 125.
31. Heyd, J.; Scuseria, G. E.; Ernzerhof, M. J Chem Phys 2003, 118, 8207-8215.
32. Xu, X.; Goddard III, W. A. Proc Natl Acad Sci USA 2004, 101, 2673-2677.
33. Zhao, Y.; Schultz, N. E.; Truhlar, D. G. J Chem Phys 2005, 123.
34. Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Phys Rev B 1992, 46, 6671-6687.
35. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision A.02, Gaussian Inc., Wallingford CT, 2009.
36. Bylaska, E. J.; de Jong, W. A.; Kowalski, K.; Straatsma, T. P.; Valiev, M.; Wang, D.; Apra, E.; Windus, T. L.; Hirata, S.; Hackler, M. T.; Zhao, Y.; Fan, P.-D.; Harrison, R. J.; Dupuis, M.; Smith, D. M. A.; Nieplocha, J.; Tipparaju, V.; Krishnan, M.; Auer, A. A.; Nooijen, M.; Brown, E.; Cisneros, G.; Fann, G. I.; Fruchtl, H.; Garza, J.; Hirao, K.; Kendall, R.; Nichols, J. A.; Tsemekhman, K.; Wolinski, K.; Anchell, J.; Bernholdt, D.; Borowski, P.; Clark, T.; Clerc, D.; Dachsel, H.; Deegan, M.; Dyall, K.; Elwood, D.; Glendening, E.; Gutowski, M.; Hess, A.; Jaffe, J.; Johnson, B.; Ju, J.; Kobayashi, R.; Kutteh, R.; Lin, Z.; Littlefield, R.; Long, X.; Meng, B.; Nakajima, T.; Niu, S.; Pollack, L.; Rosing, M.; Sandrone, G.; Stave, M.; Taylor, H.; Thomas, G.; van Lenthe, J.; Wong, A.; Z.

Zhang. NWChem, A Computational Chemistry Package for Parallel Computers, Pacific Northwest National Laboratory, Richland, Washington, 2006.

37. Dunning Jr., T. H. J Chem Phys 1989, 90, 1007-1023.

38. Dunning Jr. , T. H.; Peterson, K. A.; Wilson, A. K. J Chem Phys 2001, 114, 9244-9253.

39. te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. J Comput Chem 2001, 22, 931-967.

40. Baerends, E. J.; Autschbach, J.; Bashford, D.; Berger, J. A.; Bérces, A.; Bickelhaupt, F. M.; Bo, C.; de Boeij, P. L.; Boerrigter, P. M.; Cavallo, L.; Chong, D. P.; Deng, L.; Dickson, R. M.; Ellis, D. E.; van Faassen, M.; Fan, L.; Fischer, T. H.; Fonseca Guerra, C.; Giammona, A.; Ghysels, A.; van Gisbergen, S. J. A.; Götz, A. W.; Groeneveld, J. A.; Gritsenko, O. V.; Grüning, M.; Harris, F. E.; van den Hoek, P.; Jacob, C. R.; Jacobsen, H.; Jensen, L.; Kadantsev, E. S.; van Kessel, G.; Klooster, R.; Kootstra, F.; Krykunov, M. V.; van Lenthe, E.; Louwen, J. N.; McCormack, D. A.; Michalak, A.; Mitoraj, M.; Neugebauer, J.; Nicu, V. P.; Noodleman, L.; Osinga, V. P.; Patchkovskii, S.; Philipsen, P. H. T.; Post, D.; Pye, C. C.; Ravenek, W.; Rodríguez, J. I.; Romaniello, P.; Ros, P.; Schipper, P. R. T.; Schreckenbach, G.; Seth, M.; Snijders, J. G.; Solà, M.; Swart, M.; Swerhone, D.; te Velde, G.; Vernooijs, P.; Versluis, L.; Visscher, L.; Visser, O.; Wang, F.; Wesolowski, T. A.; van Wezenbeek, E. M.; Wiesenekker, G.; Wolff, S. K.; Woo, T. K.; Yakovlev, A. L.; Ziegler, T. ADF 2009.01, SCM, Amsterdam, The Netherlands, 2009.

41. Chong, D. P.; van Lenthe, E.; van Gisbergen, S. J. A.; Baerends, E. J. J Comput Chem 2004, 25, 1030-1036.

42. Swart, M.; Solà, M.; Bickelhaupt, F. M. J Comput Chem 2011, online, DOI: 10.1002/jcc.21693.

43. Swart, M.; Solà, M.; Bickelhaupt, F. M. J Comput Chem 2007, 28, 1551-1560.

44. Bento, A. P.; Solà, M.; Bickelhaupt, F. M. J Chem Theory Comp 2008, 4, 929-940.

45. Swart, M.; Solà, M.; Bickelhaupt, F. M. J Chem Theory Comp 2010, 6, 3145-3152.

46. Zhao, Y.; Truhlar, D. G. J Chem Theory Comp 2010, 6, 1104-1108.

47. Swart, M. J Chem Theory Comp 2008, 4, 2057-2066.

48. Lynch, B. J.; Truhlar, D. G. J Phys Chem A 2003, 107, 8996-8999.

49. Jurecka, P.; Sponer, J.; Cerny, J.; Hobza, P. Phys Chem Chem Phys 2006, 8, 1985-1993.

50. Grüning, M.; Gritsenko, O. V.; van Gisbergen, S. J. A.; Baerends, E. J. J Chem Phys 2001, 114, 652-660.

51. Jurecka, P.; Sponer, J.; Hobza, P. J Phys Chem B 2004, 108, 5466-5471.

52. Bruschi, M.; De Gioia, L.; Zampella, G.; Reiher, M.; Fantucci, P.; Stein, M. J Biol Inorg Chem 2004, 9, 873-884.

53. Güell, M.; Luis, J. M.; Solà, M.; Swart, M. J Phys Chem A 2008, 112, 6384-6391.
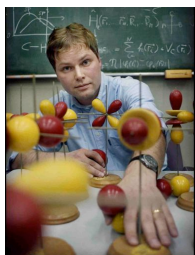
M. Swart   F.M. Bickelhaupt   M. Duran

Appendix A. Description of chemical systems

AE6-BH6 set

This set was devised by Lynch and Truhlar[48] as the minimal representation of the much larger G2-set for atomization energies and likewise for a set of barrier heights. It contains the following molecules in the AE6 set:

- SiH$_4$ D$_e$ = 322.83 kcal·mol^{-1}
- SiO   D$_e$ = 192.74 kcal·mol^{-1}
- S$_2$ D$_e$ = 102.79 kcal·mol^{-1}
- propyne (C$_3$H$_4$)   D$_e$ = 705.06 kcal·mol^{-1}
- glyoxal (C$_2$H$_2$O$_2$)   D$_e$ = 633.99 kcal·mol^{-1}
- cyclobutane (C$_4$H$_8$)   D$_e$ = 1149.37 kcal·mol^{-1}

The BH6 set consists of the forward and reverse barriers of the following reactions:

- OH+CH$_4$ → H$_2$O + CH$_3$ E$_w$‡ = 6.54 kcal·mol^{-1} E$_r$‡ = 19.61 kcal·mol^{-1}
- H+OH → OH + H   E$_w$‡ = 10.45 kcal·mol^{-1} E$_r$‡ = 12.90 kcal·mol^{-1}
- H+H$_2$S → H$_2$ + HS   E$_w$‡ = 3.55 kcal·mol^{-1} E$_r$‡ = 17.27 kcal·mol^{-1}

Note that we have taken the electronic energy data, and not the ZPE-corrected ones that were reported in the paper. See: t1.chem.umn.edu/misc/database_group/database_therm_bh

Stacking energy

Hobza and co-workers[50] used cytosine dimer in different orientations as benchmark system to study π-π stacking energies, and obtained CCSD(T) data with large basis sets. For the anti-parallel cytosine dimer, a reference value of -9.93 kcal·mol^{-1} is then obtained for the interaction energy between the two cytosines.

Excitation energies of CO

The experimental values for the excitation energies were taken from ref. [22], and correspond to the three lowest singlet-singlet excitations:

- 8.51 eV
- 9.88 eV
- 10.23 eV

and the three lowest singlet-triplet excitations:

- 6.32 eV
- 8.51 eV
- 9.36 eV

Hydrogen-bonding of four dimers

Hobza and co-workers[49] reported in 2006 the S22 set, of which the four first systems are the dimers studied here for hydrogen-bonding:

- ammonia   ΔE = -3.17 kcal·mol^{-1}
- water   ΔE = -5.02 kcal·mol^{-1}
- formic acid   ΔE = -18.61 kcal·mol^{-1}
- formamide   ΔE = -15.96 kcal·mol^{-1}

Spin-state splittings

The spin-state splittings of the two transition-metal complexes studied here should both be positive, i.e. for FeFHOH the quartet state should be lower than the sextet,[52] while for Ni(EDT)$_2$$^{2-}$ the singlet should be lower than the triplet.[53] A preliminary study with CCSD(T) showed that for the first system a value of ca. +5.5 kcal·mol^{-1} is observed, but this is likely to change by increasing the basis set size and inclusion of core-electrons. Therefore, no reliable reference values are available yet, but for next year's edition we hope to have these.

Appendix B. Results of the 20 density functionals for the chemical systems

All data in kcal·mol^{-1}, except the excitation energies of CO [eV]

	reference	PACO2010	PBE0
AE1	322.83	320.29	313.49
AE2	192.74	187.35	180.07
AE3	102.79	105.88	104.42
AE4	705.06	711.32	707.06
AE5	633.99	642.00	634.21
AE6	1149.37	1158.05	1155.40
BH1	6.54	0.21	1.97
BH2	19.61	12.78	13.94
BH3	10.45	4.55	6.98
BH4	12.90	4.76	5.71
BH5	3.55	-0.13	0.96
BH6	17.27	13.88	12.63
π-π Cyt₂	-9.93	-3.66	-3.14
FeFHOH	5.40	11.42	10.00
Ni(EDT)₂²⁻		3.49	-0.45
HB1	-3.17	-2.61	-2.76
HB2	-5.02	-4.74	-4.95
HB3	-18.61	-18.44	-19.17
HB4	-15.96	-14.93	-15.47
CO-Sing1	8.51	8.37	8.44
CO-Sing2	9.88	9.67	9.79
CO-Sing3	10.23	10.05	10.19
CO-Trip1	6.32	5.67	5.73
CO-Trip2	8.51	7.98	7.85
CO-Trip3	9.36	8.74	8.60

	B3LYP	PBE	BP86
AE1	321.79	311.63	324.54
AE2	184.90	193.43	194.48
AE3	100.69	112.53	111.35
AE4	701.92	720.09	724.91
AE5	629.57	661.73	661.50
AE6	1140.75	1166.09	1176.98
BH1	2.25	-5.32	-4.47
BH2	13.89	8.90	9.70
BH3	3.96	3.57	0.94
BH4	6.08	-1.62	-0.36
BH5	-0.70	-1.31	-3.44
BH6	16.12	9.65	11.80
π-π Cyt2	-0.99	-2.64	-0.19
FeFHOH	13.25	17.68	19.21
Ni(EDT)22-	1.22	11.84	11.70
HB1	-2.20	-2.83	-1.89
HB2	-4.51	-4.98	-4.16
HB3	-17.58	-18.40	-17.38
HB4	-14.17	-14.90	-13.77
CO-Sing1	8.40	8.25	8.27
CO-Sing2	9.73	9.66	9.83
CO-Sing3	10.04	9.86	9.87
CO-Trip1	5.86	5.74	5.96
CO-Trip2	7.95	8.12	8.29
CO-Trip3	8.64	8.73	8.81

Appendix B. Results of the 20 density functionals for the chemical systems (contd.)

	M06-2X	B2PLYP	B3PW91
AE1	320.50	319.41	316.89
AE2	188.60	188.35	181.95
AE3	102.65	100.13	103.69
AE4	703.86	701.00	705.39
AE5	632.21	629.91	632.89
AE6	1146.74	1139.12	1150.34
BH1	5.17	4.27	2.16
BH2	17.64	16.77	14.48
BH3	9.67	7.83	5.78
BH4	11.35	9.81	6.31
BH5	4.23	1.76	0.41
BH6	18.30	16.84	14.40
π-π Cyt2	-9.61	-5.54	-0.10
FeFHOH	0.24	9.01	12.12
Ni(EDT)22-	-15.83	12.71	2.58
HB1	-3.17	-2.66	-1.75
HB2	-5.13	-4.83	-3.99
HB3	-19.52	-18.28	-17.32
HB4	-16.01	-15.10	-13.64
CO-Sing1	8.20	8.59	8.42
CO-Sing2	9.14	9.58	9.83
CO-Sing3	10.20	9.99	10.19
CO-Trip1	6.24	5.70	5.83
CO-Trip2	8.12	7.41	8.00
CO-Trip3	9.14	8.33	8.69

	B97-D	CAM-B3LYP	M06-L
AE1	321.89	323.41	326.87
AE2	186.68	185.66	186.60
AE3	101.77	97.87	108.24
AE4	702.55	704.37	707.82
AE5	632.66	633.14	635.77
AE6	1141.90	1149.39	1149.55
BH1	-2.59	3.23	3.02
BH2	10.87	15.27	11.86
BH3	1.60	5.59	6.58
BH4	6.27	6.43	6.46
BH5	-0.04	0.48	3.42
BH6	18.02	16.13	13.16
π-π Cyt₂	-8.93	-3.32	-8.97
FeFHOH	11.36	7.44	3.16
Ni(EDT)₂²⁻	7.02	0.37	3.18
HB1	-3.15	-2.79	-2.78
HB2	-4.37	-5.20	-4.74
HB3	-17.83	-19.57	-19.25
HB4	-14.83	-15.76	-15.91
CO-Sing1	8.32	8.47	8.61
CO-Sing2	9.79	9.72	9.87
CO-Sing3	9.90	10.09	10.32
CO-Trip1	5.92	5.90	6.16
CO-Trip2	7.84	7.95	8.11
CO-Trip3	8.81	8.67	8.94

	TPSSh	mPW1K	OLYP
AE1	332.20	315.87	317.34
AE2	179.87	170.32	185.27
AE3	103.71	97.61	106.24
AE4	703.89	694.26	703.35
AE5	624.70	610.55	636.86
AE6	1153.26	1141.81	1143.50
BH1	1.64	7.32	0.11
BH2	11.75	17.54	13.88
BH3	-0.27	8.93	1.65
BH4	6.84	11.41	4.81
BH5	-3.85	2.46	-1.31
BH6	13.82	15.56	15.60
π-π Cyt2	-1.33	-2.47	4.99
FeFHOH	15.36	4.29	10.53
Ni(EDT)22-	5.20	-13.47	8.41
HB1	-2.27	-2.41	-0.56
HB2	-4.52	-4.68	-2.40
HB3	-18.17	-19.24	-11.40
HB4	-14.39	-15.31	-8.66
CO-Sing1	8.51	8.55	8.26
CO-Sing2	10.02	9.72	9.18
CO-Sing3	10.17	10.17	9.88
CO-Trip1	5.78	5.71	5.84
CO-Trip2	7.90	7.64	7.97
CO-Trip3	8.60	8.48	8.84

	SAOP	SSB-D	BLYP
AE1		317.93	315.90
AE2		183.98	192.34
AE3		115.00	104.59
AE4		735.68	700.82
AE5		663.80	639.23
AE6		1206.78	1129.73
BH1		-2.14	-2.43
BH2		10.21	10.54
BH3		3.86	1.41
BH4		3.54	1.24
BH5		-0.61	-2.31
BH6		11.03	14.56
π-π Cyt2		-9.69	0.82
FeFHOH		8.55	18.76
Ni(EDT)22-		7.48	8.60
HB1		-3.94	-1.79
HB2		-5.27	-4.05
HB3		-18.74	-15.78
HB4		-16.27	-12.66
CO-Sing1	8.55	8.33	8.23
CO-Sing2	10.03	9.74	9.51
CO-Sing3	10.46	9.98	9.78
CO-Trip1	6.28	5.79	5.82
CO-Trip2	8.64	7.97	8.10
CO-Trip3	9.36	8.84	8.68

	LDA	M05-2X	B3LYP*
AE1	344.49	315.73	319.52
AE2	219.96	189.55	189.17
AE3	132.52	106.39	104.57
AE4	800.27	703.24	708.04
AE5	751.15	629.31	640.99
AE6	1302.09	1148.41	1148.75
BH1	-16.89	4.71	-0.74
BH2	2.19	17.48	11.82
BH3	-2.04	10.13	3.11
BH4	-13.04	11.23	2.74
BH5	-6.97	5.27	-1.49
BH6	-0.31	18.49	13.39
π-π Cyt2	-9.15	-8.13	-1.97
FeFHOH	21.16	3.92	14.67
Ni(EDT)22-	21.25	-15.31	4.98
HB1	-5.10	-3.16	-2.59
HB2	-7.89	-5.20	-4.98
HB3	-27.17	-19.93	-18.71
HB4	-22.04	-16.26	-15.13
CO-Sing1	8.18	8.28	8.34
CO-Sing2	9.81	9.15	9.74
CO-Sing3	9.88	10.33	10.05
CO-Trip1	5.96	6.05	5.83
CO-Trip2	8.42	7.97	7.99
CO-Trip3	9.19	9.11	8.68