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How many shades of grey? On the proximity of density functional approximation to *ab initio* method via calculations of electric multipole moments

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Abstract. The wide spreading of the application of Density Functional Approximation via its representatives, i.e. the Density Functionals (DFs), in almost all the fields of computational chemistry is globally witnessed. Therefore, it is believed that an evaluation of their performance in tedious calculations will offer useful insights to both users and developers. As such calculations we chose the prediction of electric multipole moments of first to fourth order, namely dipole (μ_α/ea_0), quadrupole ($\Theta_{\alpha\beta}/ea_0^2$), octupole ($\Omega_{\alpha\beta\gamma}/ea_0^3$) and hexadecapole ($\Phi_{\alpha\beta\gamma\delta}/ea_0^4$). Values at both *ab initio* up to the highly accurate couple cluster with singles and doubles (reference values) as well as different flavors of DFs: hybrid, GGA, double hybrid, long range corrected, including dispersion correction, both hybrid and long range corrected and some from the Minnesota family. The target set is a group of 10 molecules of C_{2v} symmetry. The results were further analyzed with the root mean square deviation (RMSD) method as to find the method that is the most proximal to reference CCSD. The functionals PBE1PBE, CAM-B3LYP and B2PLYP seem to survive the proximity test, whereas B97D, M05, M06 and M08 provide results that are the least proximal to CCSD ones.

1. Introduction

In processes that involve or not gaseous molecules dipole, quadrupole and hexadecapole moments are of certain importance at that fundamental level as its their occurrence. Such chemical and physical phenomena take place in liquids [1, 2] and fluids [3], inbetween surfaces [4, 5] and crystalline insulators [6], to name a few.

For most of the molecules dipole or at the most quadrupole moments can be estimated experimentally. Therefore a quantum-mechanical calculation is a demand as to deliver the values of the desired properties. These calculations can be performed at *ab initio*, as well as at the Density Functional Theory (DFT) levels of theory.



Since the pioneering work of Becke [7] started the flourish of the (DFT) as it expressed in all recent quantum chemistry codes, lots of attempts have been made as to both concrete the grounds of it, as well as to improve its reliability. Though the vast number of researchers working on the field there are still more to be done as both Yang et al [8] and Jones [9] have pointed out.

In the present study we are testing its predictive capability on the electric moments (namely dipole (μ), quadrupole ($\Theta_{\alpha\beta}$), octupole ($\Omega_{\alpha\beta\gamma}$) and hexadecapole ($\Phi_{\alpha\beta\gamma\delta}$)) of molecules of the type of XY_2 where X=H, F, Cl, Br, Y=O,S and O_3 , SO_2 and S_3 . These moieties have been chosen not only because of their crucial role in a plethora of chemical processes but also their characteristic bonding profile .

The employed methods span the fields of *ab initio* such as Hartree-Fock (HF) [10], second order Møller-Plesset (MP2) [11] and MP3 [12] and MP4(SDQ) [13], and coupled cluster with double (CCD) as well as with singles and doubles (CCSD) [14] (insights on these one could find in the book of Rode et al [15]), as well as that of the infinite DFT pool, such as B-[16] and B3-{LYP,P86,PW91} [17, 18, 19, 20], PBE1PBE [21], CAM-B3LYP [22], LC- ω PBE [23], M05 [24], M06 [25], M08 [26], B97D [27] and B2PLYP [28] functionals in the form they have been formulated in Gaussian 16 [29]. The applied functionals have been chosen since each one of them is characterizing a certain era of the Density Functional Theory (DFT) evolution as it is explained in an elucidative review by Burke et al [30] and a more recent article by Su et al [31].

2. Computational Protocol

The calculated properties are dipole (μ_z/ea_0), quadrupole ($\Theta_{\alpha\beta}/ea_0^2$), octupole ($\Omega_{\alpha\beta\gamma}/ea_0^3$) and hexadecapole ($\Phi_{\alpha\beta\gamma\delta}/ea_0^4$) moments. For molecules belonging to the C_{2v} symmetry group the number of independent components that should be used as to proper describe the last three tensors are two, two and three for $\Theta_{\alpha\beta}$, $\Omega_{\alpha\beta\gamma}$ and $\Phi_{\alpha\beta\gamma\delta}$ (when α , β and γ run over x , y and z) [32].

The density values have been used as to obtain electric moments estimates via the formulation provided by Buckingham [32]. Electron densities and charges have been computed with Gaussian 16 by requesting a full natural bond orbital (NBO) analysis [33]. In the cases of MP n , CCD, CCSD and B2PLYP all electrons were correlated.

The geometries of the molecules have been obtained from the NIST Computational Chemistry Comparison and Benchmark Database [34]. The 6-311G(p,d) basis set has been used in all calculation.

3. Statistical Analysis

The obtained results have been further analyzed with the aid of a powerful statistical tool that is root mean square distance (RMSD). We will use a slightly modified version of the common formula of RMSD (see Eq. 1), since we are targeting in gaining information on the proximity of methods towards the reference CCSD, furthermore we have been using properties of both different units and order of magnitude, as well. The modified RMSD has been given the name *distance* or $D_{method, CCSD}$ and is defined as: Let $\alpha \in (Methods)$, $i \in (components\ of\ properties)$ and the property $C \in (Properties)$, then the *distance* of a given method α towards the reference method could be defined as:

$$D_{(\alpha,reference)} = \sqrt{\sum_{i=1}^{10} \frac{(C_{i,\alpha} - C_{i,reference})^2}{\max_{\alpha}\{(C_{i,\alpha} - C_{i,reference})^2\}}} \quad (1)$$

The denominator ensures that the produced differences are both plain numbers (or dimensionless) and that the values of $D_{(\alpha,reference)} \in [0,1]$. The obtained values could also be explained as: The lower the value the higher the proximity.

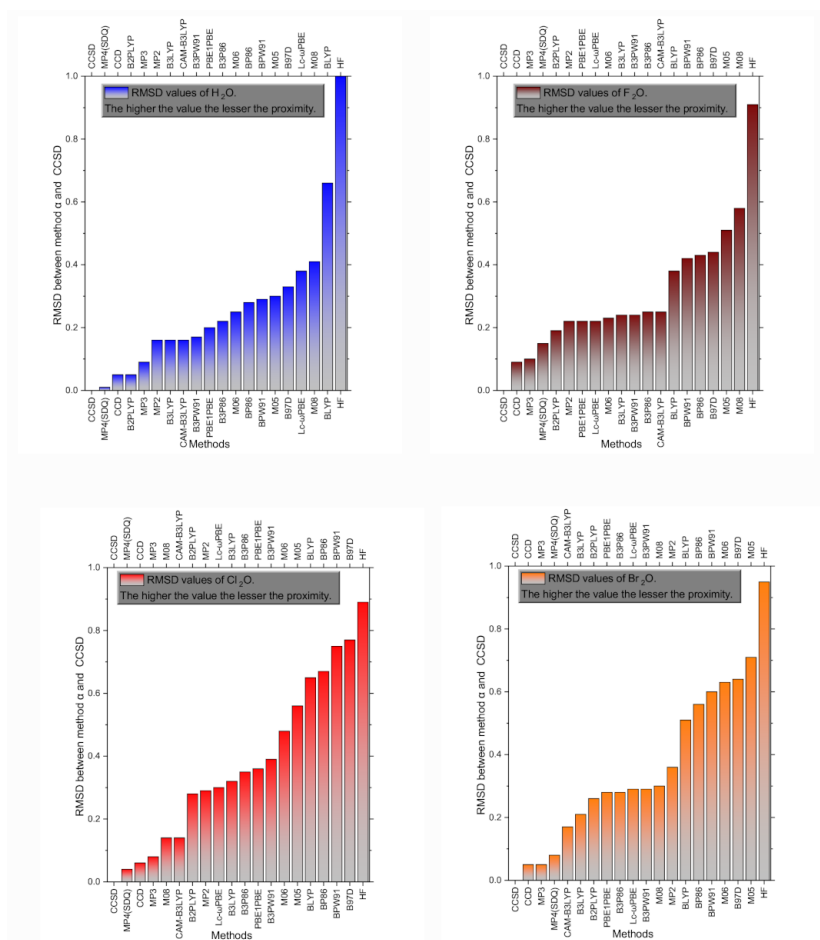


Figure 1. Distance ($D_{(\alpha,CCSD)}$) values of X_2O ($X=H, F, Cl, Br$).

4. Results and Discussion

After studying the obtained values which have been statistically analyzed (see Eq. 1) we came up to the conclusion that the performance of DFs heavily fluctuates. This is happening to that extend that someone can hardly find a DF that is steadily on the top or the bottom of the distance the ranking.

We have grouped the molecules in such a way as rational of possible substitutions leads to one from each other. In the first set (X_2O , $X=H, F, Cl, Br$), the inadequacy of HF method is more than clear (see Fig. 1). The MP4(SDQ) and CCD, with the latter to be still not feasible for larger systems, are always ranked at the top. The DFs that seem to survive are B2PLYP, PBE1PBE, CAM-B3LYP and LC- ω PBE that they manage to be in the near vicinity of the top ones. The electron correlation that introduces the first surpass the almost equivalent MP2. The characteristics of the other three, in particular the gradient approximation on the description of the density, the more sophisticated treatment of the primitive B3LYP and the corrections that brings into the game the latter DF seem to anticipate the overall unstable performance of the rest DFs.

Another group has been formed from X_2S ($X=H, F, Cl$) molecules and results have been collected in Tables 1, 2, 3. The outcomes from the observation of these tables can be summarized to the following. The HF method performs much better than most of the DFs. The pure B{LYP,P86,PW91} DFs seem inadequate for calculations of this type.

Table 1. Electric multipole moments of H₂S obtained at various levels of theory and the respective $D_{(\alpha,CCSD)}$ values.

Method	μ_z	Θ_{xx}	Θ_{yy}	Θ_{zz}	Ω_{xxz}	Ω_{yyz}	Ω_{zzz}	Φ_{xxxx}	Φ_{yyyy}	Φ_{zzzz}	$D_{(\alpha,CCSD)}$
HF	-0.5305	-2.94	2.27	0.67	0.26	-1.36	1.10	6.67	-5.62	-6.51	0.63
MP2	-0.5115	-2.88	2.21	0.68	0.23	-1.35	1.13	6.25	-5.15	-6.08	0.35
MP3	-0.4893	-2.83	2.16	0.67	0.15	-1.21	1.06	5.97	-4.91	-5.77	0.09
MP4(SDQ)	-0.4835	-2.81	2.15	0.66	0.12	-1.15	1.03	5.88	-4.83	-5.67	0.01
CCD	-0.4836	-2.81	2.15	0.66	0.12	-1.15	1.03	5.88	-4.82	-5.66	0.02
CCSD	-0.4831	-2.81	2.15	0.66	0.11	-1.14	1.03	5.86	-4.81	-5.64	0.00
BLYP	-0.5144	-2.93	2.22	0.70	0.20	-1.38	1.17	6.18	-5.03	-5.99	0.48
BP86	-0.5394	-2.94	2.23	0.71	0.35	-1.64	1.28	6.50	-5.33	-6.39	0.71
BPW91	-0.5406	-2.92	2.21	0.71	0.38	-1.67	1.29	6.53	-5.36	-6.44	0.67
B3LYP	-0.5250	-2.93	2.23	0.70	0.27	-1.46	1.19	6.40	-5.26	-6.25	0.54
B3P86	-0.5443	-2.93	2.23	0.70	0.40	-1.69	1.29	6.67	-5.52	-6.59	0.73
B3PW91	-0.5462	-2.92	2.22	0.70	0.41	-1.70	1.29	6.68	-5.53	-6.60	0.72
CAM-B3LYP	-0.5410	-2.93	2.24	0.68	0.35	-1.54	1.19	6.58	-5.44	-6.44	0.62
PBE1PBE	-0.5550	-2.95	2.24	0.70	0.46	-1.77	1.31	6.83	-5.67	-6.77	0.84
Lc- ω PBE	-0.5752	-2.89	2.22	0.67	0.57	-1.85	1.28	7.00	-5.86	-6.97	0.85
M05	-0.5494	-2.94	2.23	0.71	0.54	-1.88	1.34	6.84	-5.69	-6.84	0.89
M06	-0.4991	-2.85	2.16	0.70	0.29	-1.46	1.17	6.21	-5.11	-6.11	0.38
M08	-0.5515	-2.90	2.22	0.68	0.34	-1.59	1.26	6.60	-5.49	-6.46	0.62
B2PLYP	-0.5202	-2.91	2.22	0.69	0.26	-1.42	1.16	6.37	-5.24	-6.20	0.48
B97D	-0.5321	-2.91	2.21	0.70	0.34	-1.60	1.26	6.45	-5.30	-6.34	0.59

It is also of interest to notice that no matter the exotic bonding environment in F₂S and Cl₂S (see Tables 2 and 3) it is in the case of H₂S that most of the DFs are far from the reference method. Furthermore it seems that neither the long range correction nor the better approximation that introduces the CAM-B3LYP could lead to values closer to CCSD. At that side are lying the B3- $\{LYP, P86, PW91\}$ functionals as well. This is also true for the B97D that includes dispersion and for the B2PLYP DF that is the analogue to MP2.

The last group consists of O₃, SO₂ and S₃. The diradical [35] character of the first molecule make it a tough case for all mono-determinantal wavefunction methods. That is most likely why there is an obvious divergence between the HF MP2 and CC methods for all three, molecules. On the other hand, the DF analogue seems to lie closer to the CC results. Nevertheless, to obtain a clear picture about the relative method performance a muticonfigurational approach should be applied, a task that is beyond the scope of this work.

Table 2. Electric multipole moments of F₂S obtained at various levels of theory and the respective $D_{(\alpha,CCSD)}$ values.

Method	μ_z	Θ_{xx}	Θ_{yy}	Θ_{zz}	Ω_{xxz}	Ω_{yyz}	Ω_{zzz}	Φ_{xxxx}	Φ_{yyyy}	Φ_{zzzz}	$D_{(\alpha,CCSD)}$
HF	0.7472	-0.40	-1.26	1.66	-7.62	9.27	-1.65	4.82	-21.36	1.57	0.69
MP2	0.6291	-0.66	-0.95	1.61	-6.99	7.65	-0.66	6.81	-19.04	1.12	0.24
MP3	0.6614	-0.54	-1.05	1.59	-7.04	8.10	-1.06	5.93	-19.68	0.91	0.07
MP4(SDQ)	0.6465	-0.57	-1.03	1.60	-6.97	7.89	-0.93	6.18	-19.28	1.07	0.06
CCD	0.6678	-0.51	-1.08	1.60	-7.01	8.11	-1.09	5.87	-19.68	0.91	0.09
CCSD	0.6540	-0.54	-1.05	1.59	-6.98	7.99	-1.01	6.05	-19.41	1.02	0.00
BLYP	0.5087	-0.91	-0.63	1.54	-6.76	6.75	0.01	7.86	-17.20	1.77	0.86
BP86	0.5006	-0.89	-0.61	1.50	-6.55	6.59	-0.04	7.94	-16.80	1.43	0.90
BPW91	0.4995	-0.86	-0.62	1.48	-6.48	6.58	-0.09	7.88	-16.73	1.34	0.91
B3LYP	0.5777	-0.76	-0.81	1.57	-6.90	7.32	-0.42	7.03	-18.24	1.51	0.49
B3P86	0.5757	-0.72	-0.81	1.54	-6.70	7.19	-0.49	7.05	-17.89	1.19	0.50
B3PW91	0.5679	-0.73	-0.79	1.52	-6.69	7.17	-0.48	7.08	-17.86	1.17	0.53
CAM-B3LYP	0.6049	-0.70	-0.88	1.58	-6.96	7.57	-0.61	6.70	-18.58	1.46	0.35
PBE1PBE	0.5676	-0.75	-0.78	1.53	-6.75	7.20	-0.45	7.12	-18.01	1.18	0.52
Lc- ω PBE	0.5923	-0.61	-0.88	1.49	-6.64	7.48	-0.84	6.61	-18.06	0.98	0.44
M05	0.5988	-0.75	-0.85	1.60	-6.75	7.23	-0.48	7.00	-18.14	1.02	0.43
M06	0.6382	-0.66	-0.97	1.63	-6.79	7.44	-0.65	6.73	-18.48	0.99	0.29
M08	0.6134	-0.61	-0.93	1.54	-7.01	7.87	-0.85	6.00	-19.09	1.46	0.29
B2PLYP	0.5988	-0.72	-0.87	1.59	-6.95	7.46	-0.51	6.93	-18.55	1.41	0.39
B97D	0.5181	-0.84	-0.67	1.51	-6.56	6.71	-0.15	7.72	-16.99	1.37	0.81

Table 3. Electric multipole moments of Cl₂S obtained at various levels of theory and the respective $D_{(\alpha,CCSD)}$ values.

Method	μ_z	Θ_{xx}	Θ_{yy}	Θ_{zz}	Ω_{xxz}	Ω_{yyz}	Ω_{zzz}	Φ_{xxxx}	Φ_{yyyy}	Φ_{zzzz}	$D_{(\alpha,CCSD)}$
HF	0.2860	-1.53	0.06	1.47	-2.49	-5.86	8.35	70.60	-14.25	-32.25	0.47
MP2	0.2308	-1.65	0.19	1.46	-2.59	-6.08	8.67	69.88	-10.61	-27.88	0.26
MP3	0.2405	-1.58	0.14	1.43	-2.48	-5.97	8.45	68.88	-11.62	-28.93	0.04
MP4(SDQ)	0.2362	-1.58	0.16	1.43	-2.48	-5.97	8.45	68.96	-11.53	-28.87	0.02
CCD	0.2425	-1.56	0.13	1.43	-2.47	-5.90	8.38	68.60	-12.17	-29.31	0.09
CCSD	0.2362	-1.58	0.16	1.43	-2.47	-5.98	8.44	68.93	-11.63	-28.98	0.00
BLYP	0.1911	-1.80	0.32	1.49	-2.68	-6.05	8.73	71.70	-6.21	-24.35	0.73
BP86	0.1834	-1.84	0.39	1.45	-2.49	-6.35	8.84	71.55	-4.98	-24.36	0.80
BPW91	0.1805	-1.83	0.40	1.43	-2.41	-6.30	8.71	70.84	-4.82	-24.42	0.76
B3LYP	0.2195	-1.73	0.24	1.49	-2.56	-6.19	8.75	71.01	-8.08	-26.37	0.48
B3P86	0.2149	-1.76	0.30	1.46	-2.38	-6.46	8.84	70.65	-6.95	-26.33	0.56
B3PW91	0.2097	-1.76	0.32	1.44	-2.36	-6.38	8.74	70.39	-6.95	-26.37	0.53
CAM-B3LYP	0.2383	-1.66	0.19	1.47	-2.49	-6.09	8.58	70.33	-9.75	-28.04	0.26
PBE1PBE	0.2081	-1.77	0.34	1.43	-2.36	-6.46	8.83	70.74	-6.98	-26.55	0.59
Lc- ω PBE	0.2333	-1.59	0.23	1.36	-2.16	-6.01	8.17	68.10	-9.77	-29.19	0.41
M05	0.2140	-1.81	0.31	1.49	-2.46	-6.33	8.78	69.60	-5.26	-24.39	0.63
M06	0.2540	-1.77	0.20	1.57	-2.34	-6.71	9.05	70.64	-7.27	-26.76	0.70
M08	0.2031	-1.68	0.36	1.32	-2.23	-6.51	8.74	70.65	-9.44	-28.98	0.60
B2PLYP	0.2257	-1.71	0.23	1.48	-2.56	-6.21	8.77	70.75	-9.01	-27.09	0.41
B97D	0.1923	-1.80	0.34	1.46	-2.48	-6.20	8.68	70.45	-5.37	-24.37	0.66

5. Conclusion

After performing careful calculations of electric multipole moments in a series of relevant molecules we manage to gain deeper insights by performing a thorough analysis assisted by a modified tool (RMSD) of statistics. The CCSD has been set as the reference method and MP4(SDQ) and CCD were found to be the most proximal to it. The DFs used in this study, though they are representatives of a wide range of the flavours of Density Functional Approximation, does not seem to provide reliable results, since their behavior is changing from molecule to molecule even inside the same molecule. Thus, if the different distances from

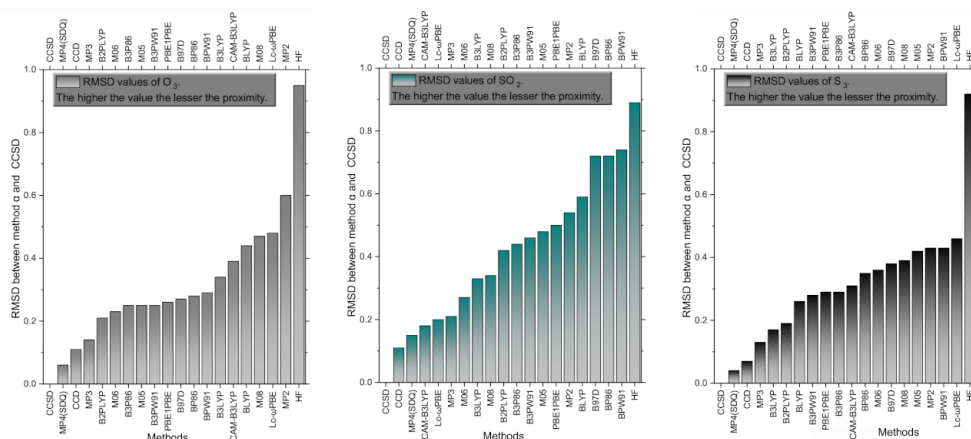


Figure 2. Distance ($D_{(\alpha,CCSD)}$) values of O_3 , SO_2 and S_3 .

the CCSD matched to different shades of gray, in most of the cases they are more than ten. However, among the tested DFs, the PBE1PBE, CAM-B3LYP and B2PLYP could be used in such calculations since they offer the better reliability and accuracy matching.

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