ELSEVIER

A comparison of the accuracy of different functionals

Charles W. Bauschlicher Jr.

NASA Ames Research Center. Moffett Field, CA 94035, USA

Received 11 September 1995

Abstract

The errors in the computed geometries, zero-point energies, and atomization energies of molecules containing only first and second row atoms are compared for several levels of theory, including Hartree–Fock, second-order Møller–Plesset perturbation theory (MP2), and density functional theory (DFT) using five different functionals, including two hybrid functionals. The 6-31G* and 6-311 + G(3df, 2p) basis sets are used. Overall, the B3LYP hybrid functional yields the best results.

1. Introduction

Density functional theory (DFT) is an area of current interest. It has been known for some time that DFT can yield reasonable vibrational frequencies and geometries [1]. Recently DFT methods have been implemented that include analytic second derivatives [2]; this greatly expands the number of systems for which vibrational frequencies can be computed. In addition, hybrid functionals [3], such as B3LYP [4], yield good atomization energies [3,5] as well as good geometries and frequencies.

We have found that B3LYP yields accurate results for many systems containing transition metal atoms [6]. However, we have also found [7,8] two cases where an older, non-hybrid, functional performs better than B3LYP. Before trying to establish which functional performs better for transition metal containing systems, it seemed worthwhile to compare two hybrid functionals with several older functionals using the same basis set, same grid, and the same program for systems containing only first and second row atoms. It is also of interest to consider the results for both a small and large sized basis set.

In this Letter we report on the calculation of geometries, zero-point energies, and atomization energies for molecules containing first and second row atoms using five different functionals. These DFT results are compared with those obtained using Hartree–Fock (HF) and second-order Møller–Plesset perturbation theory [9] (MP2). All calculations use the same basis sets and all DFT calculations use the same grid.

2. Methods

GAUSSIAN 92/DFT [2] is used for all calculations. In all DFT calculations the 'finegrid' option is used. The 6-31G* and 6-311 + G(3df, 2p) basis sets [10] are used, and the latter basis set is commonly referred to as the big set.

The five functionals [11–15] used are defined in Table 1. Note the functional denoted BP is somewhat

Table 1
Definition of the functionals used

Functional	Local		Gradient	
	exchange	correlation	exchange	correlation
BLYP	Slater	LYP [11]	Becke [12]	LYP
BP	Slater	VWN	Becke	Perdew86 [14]
BP86	Slater	Perdew81 [15]	Becke	Perdew86
B3LYP [a]	Slater + HF	LYP-VWN	Becke	LYP
B3P86 [a]	Slater + HF	VWN	Becke	Perdew86

[a] The coefficients weighting the different terms are taken from Becke [3].

non-standard in GAUSSIAN 92/DFT, as it is invoked using IOP(5/42), while the others are defined by a method keyword. The BP and BP86 functionals differ only in the choice of the local correlation functional. Because we are interested in atomization energies as well as geometries and vibrational frequencies, we only consider functionals that include a gradient correction for both exchange and correlation. The recently proposed [3] hybrid functionals differ from the older functionals in that some Hartree–Fock exchange is included. We consider two different hybrid functionals.

The results of the DFT calculations are compared to those obtained using the Hartree–Fock and second-order Møller–Plesset perturbation theory approaches. In the MP2 calculations, all electrons are correlated in the calculation of the geometries, but

only the valence electrons are correlated in the calculation of the atomization energies.

3. Results and discussion

We first consider the errors in the computed geometrical parameters. There are good experimental results for the 55 G2 molecules [16], except for SiH_3 and the $^3B_1$ state of SiH_2. This set of 53 molecules includes 71 bond lengths, 26 bond angles, but unfortunately only 2 dihedral angles. The geometry of the $^1A_1$ and $^3B_1$ states of CH_2 is taken from Jensen and Bunker [17], PH_2 from Herzberg [18], the diatomics from Huber and Herzberg [19], and the remainder from the tabulation of Hehre et al. [20]. (Note the

Table 2
Summary of the average absolute error and maximum error for the geometrical parameters. The bond lengths are in Å and the angles in deg. The system with the maximum error is given in parentheses

	Bonds		Angle		Dihedral	
	avg	max	avg	max	avg	max
HF	0.020	0.134(Li_2)	1.16	3.17($CH_2\ ^3B_1$)	1.92	3.14(H_2O_2)
MP2	0.015	0.100(Li_2)	0.67	2.32($CH_2\ ^3B_1$)	1.24	2.08(H_2O_2)
BLYP	0.026	0.090(Cl_2)	1.03	2.83($CH_2\ ^1A_1$)	0.89	1.45(H_2O_2)
BP	0.020	0.074(Li_2)	0.91	2.79($CH_2\ ^1A_1$)	0.27	0.27(H_2O_2)
BP86	0.022	0.090(Li_2)	0.96	2.90($CH_2\ ^1A_1$)	0.24	0.31(N_2H_4)
B3P86	0.010	0.067(Li_2)	0.62	1.65($CH_2\ ^1A_1$)	0.86	1.53(H_2O_2)
B3LYP	0.013	0.055(Cl_2)	0.62	1.69($CH_2\ ^1A_1$)	0.35	0.63(H_2O_2)
B3LYP(big [a])	0.008	0.039(Na_2)	0.61	1.85(N_2H_4)	3.66	6.61(H_2O_2)

[a] Indicates that the 6-311 + G(3df, 2p) basis set is used.

results for the inner and outer H atoms in N_2H_4 are reversed in Ref. [20] – see Kohata et al. [21].)

The average absolute deviation and maximum error are summarized in Table 2. For the calculation of bond lengths, the hybrid B3LYP and B3P86 functionals have the smallest average and maximum errors. Improving the basis set reduces the error for the B3LYP functional further. The average error for the HF and MP2 approaches is smaller than for several of the functionals, but the maximum errors are smaller for the DFT approaches. The bond angles show slightly different trends, but the hybrid functionals still have the smallest errors. Improving the basis set actually increases the maximum error at the B3LYP level of theory, however this error is still smaller than found for the HF, MP2, and non-hybrid functionals. As for the bond lengths, the B3LYP and B3P86 functionals in the 6-31G* basis set have the smallest errors. All of the functionals using the 6-31G* basis set yield small errors for the two dihedral angles. Unlike the bond lengths or bond angles, the hybrid approaches do not have the smallest errors. It is also unfortunate that improving the basis set increases the error for the B3LYP approach for the dihedral angle in H_2O_2. The potential is flat, so small errors in the energy can result in larger errors for the dihedral angles than for the bond lengths or bond angles. In addition, with only two dihedral angles, it is hard to draw any definitive conclusions about the reliability of these approaches for this geometrical property.

It appears that all of the functionals yield good geometries for these 53 known systems. However, we have previously found [22] that for cis-FONO the B3LYP approach yields a structure in much better agreement with the highest levels of theory than BLYP. Thus there may be more difference between the various functionals for systems that are less well described by a single reference.

We next consider the calculation of the zero-point energy. We use 41 molecules for which the experimental zero-point energy is well known. These include the 26 diatomic molecules from the G2 set of dissociation energies and the 15 additional molecules from Grev, Janssen and Schaefer [23]. The zero-point energies for the diatomics are computed using the ω_e and $\omega_e x_e$ values from Huber and Herzberg [19], while the zero-point energies for the remaining

Table 3
Summary of the average absolute error and maximum error, in kcal/mol. Both the atomization energies (for the 55 G2 molecules) and zero-point energies (for the 41 molecules described in the text) are given

	6-31G*					Big [a]	
	ZPE			atomization energy		atomization energy	
	scale	avg	max	avg	max	avg	max
HF	0.916	0.12	0.46	80.52	184.3	74.50	170.0
MP2 [b]	–	–	–	16.04	40.3	7.43	25.4
BP	1.012	0.09	0.42	8.21	25.8	11.81	28.9
BLYP	1.020	0.12	0.52	5.31	18.8	4.95	15.8
BP86	1.018	0.09	0.45	7.23	24.0	10.32	25.4
B3P86	0.977	0.06	0.22	5.87	22.6	7.82	22.7
B3LYP [c]	0.980	0.08	0.26	5.18	31.5	2.20	8.4

[a] Indicates that the 6-311 + G(3df, 2p) basis set is used.
[b] The geometry and scaled zero-point energies are taken from the B3LYP 6-31G* results.
[c] Using the 6-311 + G(3df, 2p) basis set yields average and maximum error, respectively, for the zero-point of 0.05 and 0.28 kcal/mol and 2.22 and 8.1 for the atomization energy. The scaling factor for the zero-point energy is 0.989.

molecules are taken from Grev, Janssen and Schaefer. We determine a single scaling factor for each level of theory to minimize the average error. These results are summarized in Table 3. (Note we do not consider the MP2 level of theory for this property as it can be prohibitively expensive for large molecules.) The average and maximum error are small for all levels of theory. As for the geometry, the hybrid functionals have smaller errors than the HF or non-hybrid functionals. Improving the basis set at the B3LYP level reduces the average error, but increases the maximum error slightly. We should note that Grev, Janssen and Schaefer [23] have previously recommended 0.91 for the HF scale factor.

The final property considered is the atomization energy. The 55 G2 molecules are used and the experimental values are those summarized by Pople and co-workers [16]. We note that the big basis set calculations are performed using the 6-31G* geometries, as optimizing the geometry in the big basis set is costly and does not significantly improve the results [5]. In addition, the MP2 calculations are performed at the B3LYP 6-31G* geometry, as these values were obtained as part of another study [5]. Considering the similarity of the MP2 and B3LYP

geometries and the poor quality of the MP2 results, it did not seem warranted to rerun the MP2 calculations at the MP2 6-31G* geometries.

The errors at the HF level are very large and improving the basis set makes only a small improvement. All of the remaining methods account for electron correlation and have significantly smaller errors. Using the 6-31G* basis set, the BLYP, B3P86, and B3LYP functionals would appear to be the methods of choice. However, when the basis set is improved the B3LYP method is clearly superior to the others, having the smallest average and maximum errors. It is interesting to note that improving the basis set improves the MP2, BLYP, and B3LYP results, but degrades the BP, BP86, and B3P86 results. The errors for the B3LYP approach in the large basis set are consistent with those reported by Becke [3] for his proposed hybrid functional, while the B3P86 results are significantly worse. Since Becke used a numerical basis set, his results should be compared with those obtained using the big basis set. Apparently, the Perdew and Wang gradient correction adopted by Becke works better than the older Perdew correction used in the B3P86 functional.

On the basis of this study, the B3LYP would appear to be the functional of choice for molecules containing first and second row atoms. However, for systems containing transition metal atoms the choice is not so obvious. We have found that for many systems the B3LYP works well. This includes cases such as $Fe(CO)_5^-$ where BLYP works very poorly [24]. For FeCO, $FeCO^+$, and FeCO, the B3LYP also appears to work better than BP for Fe-CO binding energies, but similarly for vibrational frequencies [24–26]. Unfortunately, this comparison is not definitive as different grids, different basis sets and different programs were used. In addition, we have shown [7] that for Cr_2 the hybrid functionals mix in too much exchange leading to only the 4s–4s well. This is even true of the B3P86 functional, which leads to over binding for 55 G2 molecules. However, BLYP, without the Hartree–Fock exchange, yields a reasonable bond length, but is over bound. More recently, we have found [8] that BP appears to give better vibrational frequencies than B3LYP for FeO_2. Schaefer and co-workers [27] have come to the same conclusion for other transition metal containing systems. Thus for the calculation of

vibrational frequencies of transition metal containing systems the choice of functional is not as straightforward as for the non-transition metal systems.

4. Conclusions

We have compared the errors in the geometry, zero-point energy, and atomization energy of molecules containing only first and second row atoms. Overall the B3LYP hybrid functional appears to perform the best. The geometry and zero-point energy are computed accurately using a 6-31G* basis set, while the atomization energy requires a larger basis set. The geometries and zero-point energies computed with the other functionals appear to be acceptable, however, for more difficult systems this might not be true. The results for the BP or BP86 functionals, which may yield better results for the vibrational frequencies of transition metal systems, suggest that they may suffer from an over binding problem for the metal systems as well. The B3P86 hybrid functional, which has errors similar to the B3LYP for geometry and zero-point energies, has a significantly larger error for the atomization energies.

References

[1] T. Ziegler, Chem. Rev. 91 (1991) 651.
[2] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.W. Wong, J.B. Foresman, M.A. Robb, M. Head-Gordon, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. DeFrees, J. Baker, J.J.P. Stewart and J.A. Pople, GAUSSIAN 92/DFT, Revision G.2 (Gaussian, Pittsburgh, 1993).
[3] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[4] P.J. Stevens, F.J. Devlin, C.F. Chablowski and M.J. Frisch, J. Phys. Chem. 98 (1994) 11623.
[5] C.W. Bauschlicher Jr. and H. Partridge, J. Chem. Phys. 103 (1995) 1788.
[6] A. Ricca and C.W. Bauschlicher Jr., J. Phys. Chem. 99 (1995) 9003.
[7] C.W. Bauschlicher Jr. and H. Partridge, Chem. Phys. Letters 231 (1994) 277.
[8] G.V. Chertihin, W. Saffel, J.T. Yustein, L. Andrews, M. Neurock, A. Ricca, and C.W. Bauschlicher Jr., to be published.

[9] J.A. Pople, J.S. Binkley and R. Seeger, Intern. J. Quantum Chem. Symp. 10 (1976) 1.

[10] M.J. Frisch, J.A. Pople and J.S. Binkley, J. Chem. Phys. 80 (1984) 3265, and references therein.

[11] C. Lee, W. Yang and R.G. Parr, Phys. Rev. B 37 (1988) 785.

[12] A.D. Becke, Phys. Rev. A 38 (1988) 3098.

[13] S.H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. 58 (1980) 1200.

[14] J.P. Perdew, Phys. Rev. B 33 (1986) 8822; 34 (1986) 7406(E).

[15] J.P. Perdew and A. Zunger, Phys. Rev. B 23 (1981) 5048.

[16] L.A. Curtiss, K. Raghavachari, G.W. Trucks and J.A. Pople, J. Chem. Phys. 94 (1991) 17221.

[17] P. Jensen and P.R. Bunker, J. Chem. Phys. 89 (1988) 1327.

[18] G. Herzberg, Molecular spectra and molecular structure, Vol. 3 (Van Nostrand Reinhold, New York, 1966).

[19] K.P. Huber and G. Herzberg, Constants of diatomic molecules (Van Nostrand Reinhold, New York, 1979).

[20] W.J. Hehre, L. Radom, P. von R. Schleyer and J.A. Pople, Ab initio molecular orbital theory (Wiley–Interscience, New York, 1986).

[21] K. Kohata, T. Fukuyama and K. Kuchitsu, J. Phys. Chem. 86 (1982) 602.

[22] T.J. Lee, C.W. Bauschlicher Jr., C.E. Dateo and J.E. Rice, Chem. Phys. Letters 228 (1994) 583.

[23] R.S. Grev, C.L. Janssen and H.F. Schaefer III, J. Chem. Phys. 95 (1991) 5128.

[24] A. Ricca and C.W. Bauschlicher Jr., J. Phys. Chem. 98 (1994) 12899.

[25] A. Ricca and C.W. Bauschlicher Jr., Theoret. Chim. Acta, in press.

[26] A. Ricca and C.W. Bauschlicher Jr., J. Phys. Chem. 99 (1995) 5922.

[27] H.F. Schaefer, private communication.