
A Study of the Performance of Numerical Basis Sets in DFT Calculations on Sulfur-Containing Molecules

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ABSTRACT

The performance of numerical basis sets in relation to Gaussian basis sets is examined, by studying 20 small sulfur-containing molecules. The results of geometry optimization calculations are reported for each molecule using both density functional and Hartree-Fock methods. In comparison with experimental data, it is shown that the use of numerical bases tend to overestimate structural parameters, particularly bond lengths, and, in most cases, more than Gaussian basis sets. It is also shown that the use of a larger Gaussian basis set in DFT calculations has the effect of reducing bond lengths. © 1996 John Wiley & Sons, Inc.

Introduction

In recent years, there has been considerable interest in density functional theory (DFT) and its applications. The availability of a variety of functionals has enabled the release of specific DFT programs, such as DMol* [1]. In addition, some well-known ab initio programs, such as GAUSSIAN 92 [2] and CADPAC [3], have incorporated DFT codes as an added feature. At present, there are some differences in the type of functionals available in these packages. However, those that

* DMol is a trademark of Biosym Technologies Inc.

are commonly available are implemented using identical expressions; these include the Vosko-Wilk-Nusair (VWN) correlation functional [4], the gradient-corrected exchange functional of Becke (B88) [5], and the Lee-Yang-Parr correlation functional (LYP) [6], which includes both local and gradient-corrected terms.

An interesting feature of DMol is that it uses numerical bases for the calculations, whereas other ab initio programs use Gaussian basis sets. Numerical basis functions are values on an atomic-centered spherical-polar mesh. There are advantages associated with using such bases. First, bonds can undergo exact dissociation and thus the basis-set superposition error should be reduced; this is

expected to yield a good description of weak bonds. Moreover, the particular type of numerical basis selected for DMol was suggested [1] to be the most efficient for fast-convergent 3D numerical integrations.

The concept of an extended numerical basis set is slightly different from that of the Gaussians, mainly because of the generation procedure used. For example, in DMol, for first-row elements, this consists of a set being generated for the neutral atom and a second set for the corresponding +2 ion to form a double numerical (DN) basis. This DN basis is then augmented by generating hydrogenic *s*, *p*, and *d* orbitals for nuclei having empirically determined *Z*-values to obtain a double numerical with polarization (DNP) set. On the other hand, no augmentation is used for the creation of a DNP set for the second-row elements because it is claimed [7] that the generation procedure for the +2 ion automatically includes 3*d*- and 4*s*-type polarization functions.

The performance of these bases for sulfur and other second-row elements is not known because these were tested mainly for first-row elements [1]. Further, although a number of sulfur-containing small molecules were investigated previously by DFT methods [8–15], no systematic study of the performance of numerical bases has been attempted. The present work examines this performance regarding structural parameters of sulfur-containing molecules, in relation to Gaussian bases as well as to experiment.

Computational Details

A bench-mark of 20 small molecules was assembled with the criterion that it had to contain a sulfur atom which is bonded either to a first/second-row atom or to hydrogen. The geometries of these molecules were optimized at various levels of ab initio Hartree–Fock (HF) and DFT theory.

For the DFT work, combinations of the functionals used were as follows:

- (i) **S-VWN** comprising Dirac's $\rho^{4/3}$ exchange functional [16] and the VWN correlation functional. This is the local density approximation (LDA).
- (ii) **B-VWN** comprising Dirac's exchange functional and Becke's exchange correction (B88), together with the VWN correlation functional.

- (iii) **B-LYP** comprising Dirac's exchange functional and the B88 correction, together with the LYP correlation functional.

Two sets of DFT calculations were carried out: one set using double numerical with polarization (DNP) basis, available in the DMol program, and the other set employing Gaussian-type bases of 6-31G** quality, provided by the CADPAC program. Additional HF and DFT calculations were also carried out using a very large TZ2P Gaussian basis set supplemented with *f* functions on the sulfur and nonhydrogen atoms [17].

In the case of the DMol work, following a preliminary investigation [18], the integration mesh size was selected to be extra fine, in order to get the most accurate results. This mesh corresponds to 23,970 points for the sulfur atom, with some variations for the other atoms, since the radial points of the mesh depend on atomic number. CADPAC uses numerical quadrature to evaluate the DFT integrals, specifically Becke partitioning of space into atom-based polyhedra [19]. Inside each polyhedra, an Euler–Maclaurin-based radial grid [20] and a Gauss–Legendre angular grid is used. The quadrature scheme is defined by the number of points in each dimension. A medium quadrature scheme, found to be sufficient for geometry optimizations, was chosen for most molecules. The iterative procedure was performed at a lower quadrature to obtain an approximate density and the energy then evaluated at a higher quadrature. This means that 3840 quadrature points are generated around the sulfur atom at low quadrature, which increases to 30,720 points at high quadrature. Approximately 27,500 points are generated per atom at higher quadrature, giving an accuracy in the energy of five decimal places [21]. However, there will be variations in the number of points generated as the number of radial points depends on atomic number. Unfortunately, convergence problems can be experienced at low quadratures, and in the case of some molecules, particularly Cl₂S₂, ClSSH, HSOH, FSOH, and FSOH, a higher quadrature scheme was chosen for the iterative procedure.

Discussion of Results

The results are reported in tabular form, showing predicted geometries and total energies and displaying differences in the bond lengths, bond

angles, and total energies, for the various methods used. Experimentally determined geometries are listed where available. The experimental sources for the determination of this structure data are microwave, infrared, and ultraviolet spectroscopy

as well as electron diffraction. We have undertaken a careful search of the literature and the values in the tables are what we believe to be the best.

Tables I and II show bond distances and angles,

TABLE I
Bond lengths (in angstroms) obtained with functionals s-vwn and b-vwn.

Bond	Molecule	svwn(c)	svwn(d)	Δ_1	bvwn(c)	bvwn(d)	Δ_2	XPT
S—H	H ₂ S	1.359	1.364	0.005	1.355	1.360	0.005	1.336 r_e [22]
	HSOH	1.373	1.374	0.001	1.329	1.370	0.041	
	HSSH	1.368	1.371	0.003	1.361	1.366	0.005	1.327 r_s [23]
	HSF	1.369	1.373	0.004	1.363	1.369	0.006	
	CISSH	1.329	1.377	0.048	1.366	1.372	0.006	
S—O	F ₂ SO	1.450	1.454	0.004	1.468	1.474	0.006	1.413 r_0 [24]
	SO ₃	1.458	1.454	0.004	1.480	1.479	-0.001	1.420 r_0 [25]
	HSOH	1.677	1.689	0.012	1.653	1.742	0.089	
	FSOH	1.636	1.645	0.009	1.682	1.693	0.011	
	FSOF	1.509	1.499	-0.010	1.524	1.516	-0.008	
S—C	CS ₂	1.561	1.562	0.001	1.577	1.579	0.002	1.553 r_e [26]
	H ₂ CS	1.614	1.613	-0.001	1.634	1.634	0.000	1.611 r_s [27]
	OCS	1.568	1.564	-0.004	1.586	1.583	-0.003	1.561 r_e [28]
	C ₂ H ₆ S	1.801	1.810	0.009	1.856	1.900	0.044	1.802 r_s [29]
S—F	F ₂ SO	1.619	1.644	0.025	1.674	1.704	0.030	1.585 r_0 [24]
	F ₂ S	1.614	1.638	0.024	1.659	1.659	0.000	1.587 r_e [30]
	FSOH	1.636	1.664	0.028	1.685	1.715	0.030	
	FSOF	1.618	1.642	0.024	1.664	1.691	0.027	
	HSF	1.633	1.659	0.026	1.681	1.707	0.026	
S—Cl	Cl ₂ S	2.042	2.038	-0.004	2.107	2.101	-0.006	2.015 r_0 [31]
	Cl ₂ S ₂	2.110	2.105	-0.005	2.040	2.198	0.158	2.057 r_a [31]
	CISSH	2.045	2.088	0.043	2.173	2.172	-0.001	
S—S	HSSH	2.072	2.063	-0.009	2.135	2.128	-0.007	2.055 r_s [23]
	CISSH	2.034	2.011	-0.023	2.073	2.064	-0.009	
	Cl ₂ S ₂	1.950	1.937	-0.013	2.004	1.972	-0.032	1.931 r_a [31]
S—N	H ₃ NS	1.821	1.820	-0.001	1.900	1.893	-0.007	
S—P	H ₃ PS	1.947	1.939	-0.008	1.975	1.969	-0.006	
S—Li	Li ₂ S	2.093	2.071	-0.022	2.124	2.099	-0.025	
S—Na	Na ₂ S	2.408	2.414	0.006	2.474	2.491	0.017	
O—H	HSOH	0.978	0.989	0.011	0.948	0.986	0.038	
	FSOH	0.983	0.994	0.011	0.980	0.991	0.011	
C—H	H ₂ CS	1.104	1.105	0.001	1.096	1.096	0.000	1.093 r_a [27]
	C ₂ H ₆ S	1.104	1.103	-0.001	1.095	1.093	-0.002	1.091 r_s [29]
C—O	OCS	1.171	1.173	0.002	1.179	1.182	0.003	1.157 r_e [28]
F—O	FOSF	1.637	1.705	0.068	1.752	1.839	0.087	

Δ_1 is the bond length difference $svwn(d) - svwn(c)$, where $svwn(d)$ and $svwn(c)$ refers to results obtained using DMol with the DNP basis set and CADPAC with the 6-31G** basis set, respectively. Similarly, Δ_2 is the difference $bvwn(d) - bvwn(c)$. Definitions of experimental bond distances: r_e , distance between equilibrium nuclear positions; r_0 , distance between effective nuclear positions derived from rotational constants of zero-point vibrational levels; r_s , distance between effective nuclear positions derived from the isotopic differences in rotational constants; r_a , constant argument in molecular term measured by experimental electron gas diffraction.

TABLE II
Bond angles (in degrees) obtained from calculations with functionals s-vwn and b-vwn.

Angle	Molecule	svwn(c)	svwn(d)	Δ_1	bvwn(c)	bvwn(d)	Δ_2	XPT
HSH	H ₂ S	91.7	91.1	-0.6	92.4	92.3	-0.1	92.2 θ_0 [22]
FSH	HSF	97.4	95.4	-2.0	97.3	95.9	-1.4	
FSF	F ₂ SO	92.2	92.6	0.4	93.7	93.5	-0.2	92.8 θ_0 [24]
	F ₂ S	100.2	99.1	-1.1	101.2	98.8	-2.4	98.1 θ_0 [25]
HSO	HSOH	99.8	98.3	-1.5	98.8	98.2	-0.6	
SOH	HSOH	105.7	105.3	-0.4	108.9	104.9	-4.0	
	FSOH	108.2	107.3	-0.9	107.4	107.2	-0.2	
FSO	FSOH	102.7	101.8	-0.9	103.6	102.9	-0.7	
	F ₂ SO	106.9	106.8	-0.1	107.4	108.0	0.6	106.8 θ_0 [24]
	FSOF	108.1	108.6	0.5	109.1	109.8	0.7	
SSH	HSSH	99.1	98.2	-0.9	99.6	98.1	-1.5	91.3 θ_s [23]
	CISSH	99.3	99.4	0.1	100.2	99.7	-0.5	
SSCI	Cl ₂ S ₂	111.2	110.8	-0.4	105.9	112.1	6.2	108.2 θ_s [31]
	CISSH	105.1	107.0	1.9	108.4	108.1	-0.3	
CSC	C ₂ H ₆ S	97.1	102.2	5.1	98.8	102.1	3.3	98.9 θ_s [29]
HCS	C ₂ H ₆ S	110.2	110.4	0.2	109.7	110.0	0.3	110.8 θ_s [29]
CISCI	Cl ₂ S	105.1	104.2	-0.9	105.8	106.4	0.6	102.7 θ_0 [31]
SCH	H ₂ CS	122.2	121.9	-0.3	122.4	122.2	-0.2	121.6 θ_s [27]
LiSLi	Li ₂ S	121.3	125.9	4.6	122.9	125.0	-2.1	
NaSNa	Na ₂ S	113.6	115.6	2.0	116.7	113.8	-2.9	
SNH	H ₃ NS	111.2	110.8	0.6	110.9	110.6	-0.3	
HNH	H ₃ NS	107.6	108.2	0.6	108.0	108.4	0.4	
SPH	H ₃ PS	118.5	118.3	-0.2	118.3	118.1	-0.2	
HPH	H ₃ PS	99.1	99.3	0.2	99.4	98.9	-0.5	

Δ_1 is the difference in bond angles $svwn(d) - svwn(c)$, where $svwn(d)$ and $svwn(c)$ refer to results obtained using DMol with the DNP basis set and CADPAC with the 6-31G** basis set, respectively. Similarly, Δ_2 is the difference $bvwn(d) - bvwn(c)$. For bond angle definitions as for bond distances, see Table I.

respectively, obtained using functionals s-vwn and b-vwn with the DNP and 6-31G** bases. The tables list the differences in the parameters due to the different basis sets used for each functional. Similarly, Tables III and IV show the predicted structures from DFT calculations using the functional B-LYP and from HF calculations, with basis sets 6-31G** and TZ2P.

For the functional s-vwn, column Δ_1 of Table I lists, for each molecule, the difference in bond length $svwn(d)-svwn(c)$, where $svwn(d)$ and $svwn(c)$ refer to results obtained using DMol with a DNP basis set and CADPAC with a 6-31G** basis set, respectively. The column highlights the extreme discrepancy of the F—O bond in FOSF, the

magnitude of the difference being 0.068 Å. It is noteworthy that the S—F bonds are approximately 0.025 Å longer with DMol than with CADPAC, and the bonds S—Cl and S—H in CISSH are too long by 0.043 and 0.048 Å, respectively. The remaining bonds, however, show good agreement between DMol and CADPAC for this functional. Column Δ_1 of Table II shows similar results for bond angles where there are two notable discrepancies, specifically angles CSC in C₂H₆S and LiSLi in Li₂S. The remaining angles are indistinguishable between DMol and CADPAC.

The bond length and bond angle differences for the functional b-vwn, $bvwn(d)-bvwn(c)$, are listed under column Δ_2 of Tables I and II, respectively.

TABLE III

Bond lengths (in angstroms) obtained from DFT calculations using the functional B-LYP and from Hartree-Fock scf calculations, using CADPAC.

Bond	Molecule	BLYP1	BLYP2	Δ_1	HF1	HF2	Δ_2	XPT
S—H	H ₂ S	1.359	1.352	0.007	1.327	1.327	0.000	1.336 r_e
	HSOH	1.372			1.329			
	HSSH	1.366	1.359	0.007	1.328	1.328	0.000	1.327 r_s
	HSF	1.369	1.360	0.009	1.327	1.328	-0.001	
	CISSH	1.371			1.329			
S—O	F ₂ SO	1.468	1.444	0.024	1.409	1.392	0.017	1.413 r_0
	SO ₃	1.480	1.451	0.029	1.405	1.385	0.020	1.420 r_0
	HSOH	1.725			1.653			
	FSOH	1.677			1.610			
	FSOF	1.526			1.599			
S—C	CS ₂	1.578	1.567	0.011	1.544	1.538	0.006	1.553 r_e
	H ₂ CS	1.634	1.622	0.012	1.597	1.590	0.007	1.611 r_s
	OCS	1.586	1.574	0.012	1.572	1.563	0.009	1.561 r_e
	C ₂ H ₆ S	1.848	1.837	0.011	1.809	1.837	-0.028	1.802 r_s
S—F	F ₂ SO	1.663	1.651	0.012	1.571	1.541	0.030	1.585 r_0
	F ₂ S	1.652	1.638	0.014	1.586	1.560	0.026	1.587 r_e
	FSOH	1.677			1.605			
	FSOF	1.657			1.591			
	HSF	1.674	1.664	0.010	1.612	1.587	0.025	
S—Cl	Cl ₂ S	2.099	2.071	0.028	2.020	2.009	0.011	2.015 r_0
	Cl ₂ S ₂	2.185	2.155	0.030	2.040	2.033	0.007	2.057 r_a
	CISSH	2.162			2.045			
S—S	HSSH	2.129	2.101	0.028	2.064	2.054	0.010	2.055 r_s
	CISSH	2.069			2.035			
	Cl ₂ S ₂	1.982	1.954	0.028	2.004	1.982	0.022	1.931 r_a
S—N	H ₃ NS	1.887			1.859			
S—P	H ₃ PS	1.975			1.955			
S—Li	Li ₂ S	2.118			2.108			
S—Na	Na ₂ S	2.461			2.426			
O—H	HSOH	0.980			0.945			
	FSOH	0.984			0.947			
C—H	H ₂ CS	1.100	1.094	0.006	1.079	1.077	0.002	1.093 r_s
	C ₂ H ₆ S	1.100	1.095	0.005	1.083	1.095	-0.012	1.091 r_s
C—O	OCS	1.180	1.170	0.010	1.131	1.124	0.007	1.157 r_e
F—O	FOSF	1.718			1.391			

Δ_1 is the difference in bond lengths BLYP1 - BLYP2, where BLYP1 and BLYP2 refer to bond lengths obtained using basis sets 6-31G** and TZ2P + f, respectively. Similarly, Δ_2 refers to the difference HF1 - HF2. For experimental references, see Table I.

The bond length differences are very similar to those for s-VWN. There are minor exceptions such as the bond S—Cl in Cl₂S₂ which is longer by 0.158 Å using DMol, and the S—O bond in HSOH, which shows a discrepancy of 0.089 Å. Similarly,

for the bond angles in Table II, the most extreme difference is the SSCl angle in Cl₂S₂.

The final column of Tables I–IV, headed xPT, lists experimentally determined data for some of the molecules. Comparison of experimental bond

TABLE IV
Bond angles (in degrees) obtained from DFT calculations with functional B-LYP and from Hartree-Fock scf calculations, using CADPAC.

Angle	Molecule	BLYP1	BLYP2	Δ_1	HF1	HF2	Δ_2	XPT
HSH	H ₂ S	92.2	92.1	0.1	94.4	94.1	0.3	92.2 θ_e
FSH	HSF	97.4	95.8	1.6	96.4	95.5	0.9	
FSF	F ₂ SO	93.3	93.6	-0.3	92.4	93.1	-0.7	92.8 θ_o
	F ₂ S	101.0	99.6	1.4	98.0	97.4	0.6	98.1 θ_e
HSO	HSOH	99.5			98.8			
SOH	HSOH	104.8			108.9			
	FSOH	107.4			110.8			
FSO	FSOH	103.5			100.5			
	F ₂ SO	107.3	106.6	0.7	106.8	106.4	0.4	106.8 θ_o
	FSOF	108.8			110.1			
SSH	HSSH	98.7	98.5	0.2	99.1	98.9	0.2	91.3 θ_s
	CSSH	100.3			99.3			
SSCI	Cl ₂ S ₂	111.7	111.0	0.7	105.9	106.1	-0.2	108.2 θ_a
	CSSH	108.3			105.1			
CSC	C ₂ H ₆ S	98.2	98.5	-0.3	98.0	98.5	-0.5	98.9 θ_s
HCS	C ₂ H ₆ S	109.7	109.7	0.0	109.9	109.7	0.2	110.8 θ_s
CISCI	Cl ₂ S	105.7	105.0	0.7	102.8	102.6	0.2	102.7 θ_o
SCH	H ₂ CS	122.3	122.3	0.0	122.2	122.2	0.0	121.6 θ_s
LiLi	Li ₂ S	121.4			143.9			
NaSNa	Na ₂ S	114.6			162.2			
SNH	H ₃ NS	110.9			110.3			
HNH	H ₃ NS	108.0			108.6			
SPH	H ₃ PS	118.3			116.9			
HPH	H ₃ PS	99.3			101.1			

Δ_1 is the difference in bond angles BLYP1 - BLYP2, where BLYP1 and BLYP2 refer to results using basis sets 6-31G** and TZ2P + f respectively. Similarly, Δ_2 is the difference HF1 - HF2. For experimental references, see Table II.

lengths with the corresponding predicted bonds listed in column *svwn(c)* in Table I shows that the greatest discrepancy is S—Cl in Cl₂S₂, which is overestimated by 0.053 Å. Also, a number of other bond lengths appear to be too long by around 0.03 Å. Making the same comparison in Table II shows a gross distortion of the bond angle SSH in HSSH, which is too large by 7.8°. Tables III and IV show the effect of introducing gradient terms into the functional, keeping the basis constant. Detailed observation of the results in Tables I and III reveals that bonds from LDA computations correspond somewhat closer to the experimental values than do those from computations using B-LYP. A

similar comparison for bond angles from Tables II and IV shows that there is little difference between the predictions of LDA and B-LYP. From the examination of column BLYP2 of Table III, it is clear that bond lengths have been reduced as a result of increasing the size of basis set and this improves significantly the agreement between B-LYP and experiment.

The deviations from experiment of bond distances, as predicted by the HF theory, the LDA approach, and the BLYP functional, are illustrated in Figures 1, 2, and 3, respectively. One immediate observation is that the HF theory underestimates bonds slightly. However, even when this is taken

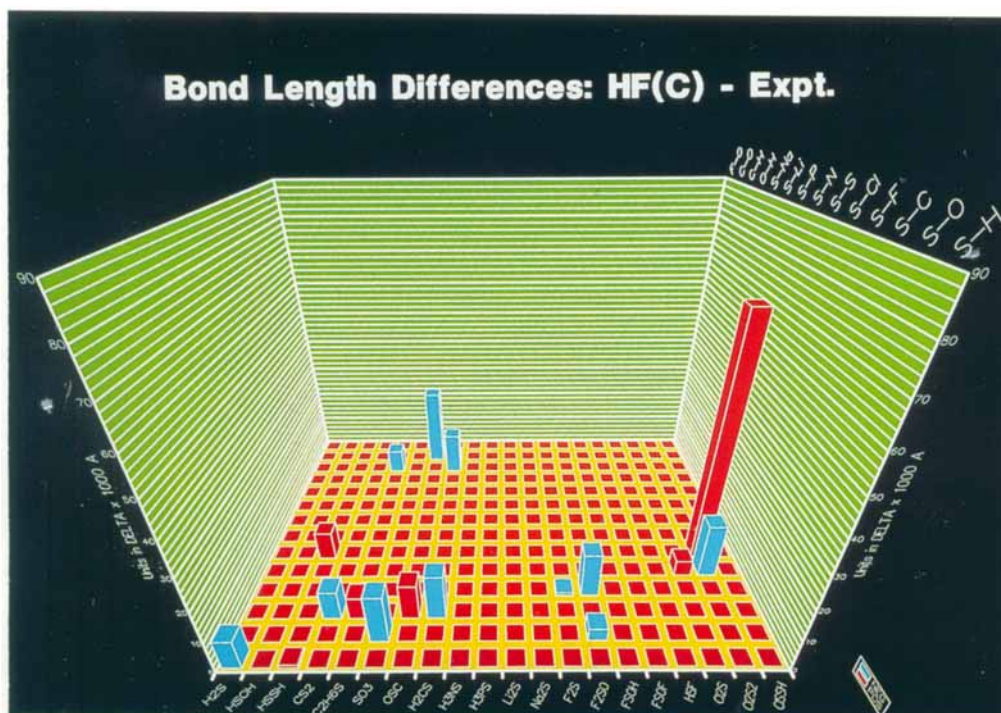


FIGURE 1. Three-dimensional representation of bond length differences between predictions of the HF theory with a 6-31G** basis and experimental observations. The molecules are on the X-axis facing the observer; bonds, on the Y-axis, and the scaled differences, on the Z-axis. A red bar indicates a positive value, and a blue bar, a negative value.

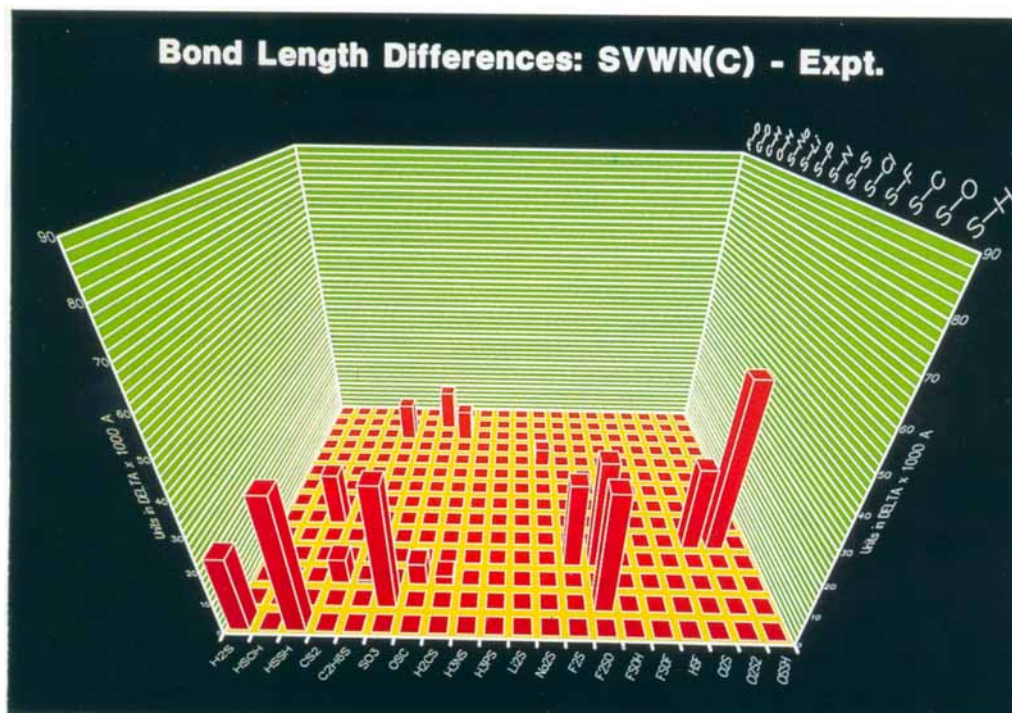


FIGURE 2. Bond length differences between the predictions of the LDA approach of DFT with a 6-31G** basis and experimental values. Designations of axes and colors are as in Figure 1.

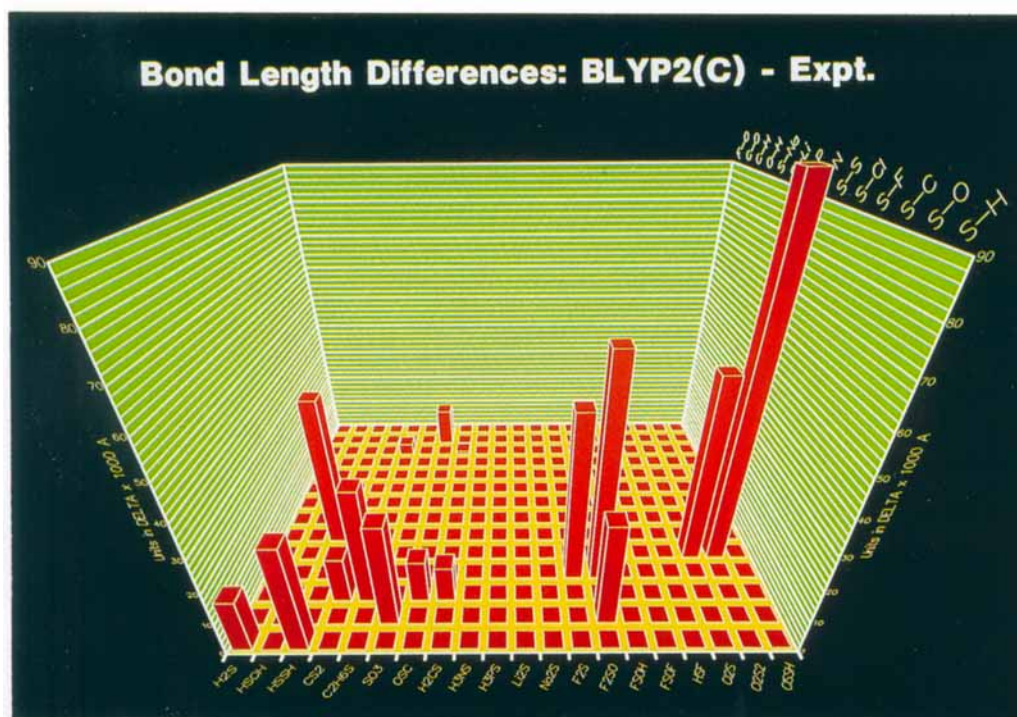


FIGURE 3. Bond length differences between the predictions of the BLYP functional of DFT with a TZ2P + *f* basis and experimental values. Designations of axes and colors are as in Figure 1.

into account, it is apparent that the predictions by the HF theory for this class of molecules are better than either of the DFT methods shown. Our previous observation regarding the LDA approach as being a better predictor of bonds than is the BLYP methodology at the basis-set level of 6-31G** quality can now be reexamined here by comparing LDA with BLYP methodology at a very large TZ2P basis level. We find that the LDA is still the better predictor of bonds. This is somewhat surprising given that the BLYP functional was shown [32] to perform very well for the G2 bench-mark, especially when such a large basis is used. Therefore, it may be that the present behavior is specific to the systems used for this investigation.

Finally, Table V shows the total energies obtained with functionals S-VWN and B-VWN for the DNP and 6-31G** bases, together with the HF energies. In the case of all molecules, DMol predicts lower energies than does CADPAC. This will be due to a number of reasons, in particular, the difference between numerical and analytical basis sets and the different treatment of the Coulomb potential.

Conclusions

According to our results, we conclude the following:

1. With some exceptions, DMol and CADPAC predict similar geometrical parameters, using DNP and 6-31G** basis sets, respectively.[†]
2. For this class of molecules, the bond lengths are better predicted by HF than they are by any of the functionals with a medium or large basis.
3. Whereas HF bonds tend to be too short, DFT predictions are all too long.
4. Increase in the size of the Gaussian basis set reduces the bond lengths for the functionals used in this study: S-VWN, B-VWN, and B-LYP.
5. Particular bonds which are poorly predicted are S—F and S—O in F₂SO, S—S, and S—Cl

[†] Since DMol uses numerical basis sets optimized for DFT, this indicates that reoptimization for DFT of the 6-31G** basis set would only be expected to further improve the correspondence of the parameters to those of DMol.

TABLE V

Total energies obtained from DFT calculations with functionals s-vwn and b-vwn, as well as from Hartree – Fock SCF calculations.

Molecule	HF	SVWN(C)	SVWN(D)	Δ_1	BVWN(C)	BVWN(D)	Δ_2
H ₂ S	-398.67503	-397.97483	-398.02091	28.92	-400.00428	-400.04552	25.88
HSOH	-473.50000	-472.64027	-472.72824	55.21	-475.43071	-475.53382	64.70
HSSH	-796.18207	-794.78906	-794.88652	61.16	-798.76067	-798.85497	59.17
CS ₂	-832.88418	-831.38932	-831.48971	62.99	-835.82016	-835.91478	59.37
C ₂ H ₆ S	-476.74454	-475.85568	-475.91458	36.96	-479.06328	-479.11573	32.91
SO ₃	-621.98157	-620.83509	-621.01186	100.92	-625.13024	-625.29978	106.38
OCS	-510.13656	-509.28571	-509.37729	57.47	-512.55830	-512.64618	55.15
H ₂ CS	-436.50995	-435.70024	-435.75511	19.52	-438.25994	-438.31092	32.00
H ₃ NS	-453.67116	-452.84734	-452.91367	41.62	-455.55394	-455.61412	37.76
H ₃ PS	-739.96978	-738.64340	-738.73874	59.83	-742.49679	-742.58856	57.59
Li ₂ S	-412.48024	-411.63668	-411.69313	35.42	-414.05785	-414.17870	75.83
Na ₂ S	-721.24957	-719.73907	-719.83306	58.98	-724.14283	-724.26563	77.06
F ₂ S	-596.31220	-595.16355	-595.32825	103.35	-598.98642	-599.14677	100.62
F ₂ SO	-671.18352	-669.90386	-670.10992	129.30	-674.49657	-674.69607	125.19
FSOH	-572.33271	-571.25413	-571.39982	91.42	-574.95986	-575.09960	87.69
FSOF	-671.04537	-669.78651	-669.99415	130.30	-674.39687	-674.59915	126.93
HFS	-497.48341	-496.55818	-496.66253	65.48	-499.48196	-499.58656	65.64
Cl ₂ S	-1316.43524	-1314.19113	-1314.34990	99.65	-1320.35814	-1320.50396	91.49
Cl ₂ S ₂	-1713.94967	-1711.03075	-1711.24194	132.53	-1719.08574	-1719.33370	155.62
ClSSH	-1255.06643	-1252.86704	-1253.06153	122.05	-1258.94673	-1259.09172	90.99

Δ_1 is the energy difference (in kcal / mol) SVWN(D) – SVWN(C), where SVWN(D) and SVWN(C) are the total energies obtained using DMol and CADPAC, respectively. Similarly, Δ_2 is the energy difference BVWN(D) – BVWN(C) (in kcal / mol).

in Cl₂S₂, S—S, and S—H in HSSH and S—O in SO₃. Poorly predicted angles are SSH in HSSH, FSF in F₂S, SSCL in Cl₂S₂, and ClSCL in Cl₂S.

Comparison with experimental data shows that DFT tends to overestimate bonds and angles, whereas HF underestimates bonds. However, in general, HF predicts more reliable structural parameters for this set of molecules.

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