

Evaluation of the performance of the HCTH exchange-correlation functional using a benchmark of sulfur compounds

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The performance of the exchange-correlation density functional HCTH has been assessed using a benchmark of sulfur-containing molecules. Optimised structural parameters, harmonic frequencies and atomisation energies are presented and compared with calculations using the BLYP density functional, the MP2 methodology and appropriate experimental results. It is shown that, for sulfur compounds that do not contain halogens, the HCTH functional predicts geometries that are comparable to both the MP2 method and experiment, and harmonic frequencies are in much closer agreement with experiment than either the BLYP or MP2 methods; the atomisation energies are predicted within a few kcal mol⁻¹ of the calculated MP2 results. The performance regarding sulfur-halogen compounds needs to be improved by the inclusion of F₂S and Cl₂S into the training set of future HCTH functionals.

1. Introduction

In recent years there has been considerable theoretical interest in density functional theory (DFT) and its applications. A number of benchmarks have been carried out to examine the performance of the method under various conditions.^{1–3} Our own experience from an early benchmark study⁴ of sulfur-containing small molecules has been to find that the bond lengths of these compounds were severely overestimated, especially when sulfur was bonded to electronegative elements, such as F or Cl. Subsequently we found that, by using the hybrid functional B3P86, we could improve the structural parameters considerably to a level comparable to MP2 results and that the computed harmonic frequencies were closer to experiment than those predicted by both Hartree Fock and MP2 methodologies.⁵

We now extend our investigation to assess the latest member of a new class of generalised gradient approximation (GGA) functionals, called HCTH, developed recently by Hamprecht and co-workers.⁶ The HCTH functional has the form introduced by Becke.⁷ It is a GGA functional with 15 terms, the coefficients of which were determined by a least square minimisation to atomic and molecular data of a training set containing 93 atoms and molecules. The training set contains first and second row atoms and in particular includes S⁺, S₂, S₂⁺, CS, SO, SO₂ and CH₃SH. We therefore anticipate that general sulfur chemistry is well predicted. The specific details of the HCTH functional are given in ref. 6. We present structural parameters, harmonic frequencies and atomisation energies computed for our previous benchmark and compare these with predictions of the BLYP and MP2 methodologies† and with experiment.

† We selected BLYP because it is the most commonly used GGA functional and MP2 because it is the most commonly used *ab initio* functional.

2. Computational methods

The new HCTH functional was implemented into the Gaussian 94 package.⁸ Geometries of the twenty small molecules in our benchmark were optimised using the BLYP and the HCTH functionals and tight convergence criteria. The calculations employed a quadrature size of 99 radial shells and 770 angular points per shell, giving a total of 76 230 integration points per atom, which should give an accuracy in the energy of better than five decimal places. The basis set used was correlation consistent triple ζ with polarization functions (cc-pVTZ), attributed to Dunning.^{9,10} Analytic second derivatives and atomisation energies were also computed at the above level of theory. The MP2 data from our previous benchmark⁵ was used which employs the frozen core approximation.

3. Results and discussion

Our results obtained from DFT and conventional *ab initio* calculations for structural parameters, harmonic frequencies and atomisation energies are presented in Tables 1–4.

3.1. Molecular geometries

Tables 1 and 2 contain the predicted bond distances and bond angles, respectively, obtained from calculations using BLYP, HCTH and MP2 methods. The differences in these values, designated as Δ_n where $n = 1, 2, 3$, denote the bond length/angle difference $r_{\text{CALC}}/\alpha_{\text{CALC}} - r_{\text{XPT}}/\alpha_{\text{XPT}}$ between the calculated and experimental value for the above three methods, respectively, are also shown in the tables and the highest values highlighted by boldface. It is apparent from the data in Table 1 that all three methods predict bond distances that are longer to various extent than the reported experimental value, and that the bond distances predicted by BLYP are far worse than those predicted by HCTH. This is illustrated in Figs. 1 and 2 by depicting for this benchmark differences in bond

Table 1 Bond lengths (in Å) of molecules of the benchmark computed using the BLYP and HCTH density functionals and the MP2 method^a

Bond	Molecule	Bond length/Å							[ref.]
		r_{BLYP}	Δ_1	r_{HCTH}	Δ_2	r_{MP2}	Δ_3	r_{XPT}	
S–H	H ₂ S	1.354	0.018	1.346	0.010	1.335	–0.001	1.336 r_e	[14]
	HSOH	1.366		1.358		1.342			
	H ₂ S ₂	1.361	0.019	1.353	0.011	1.339	–0.003	1.342 r_s	[15]
	HSF	1.363		1.354		1.339			
	ClS ₂ H	1.366		1.358		1.343			
S–O	F ₂ SO	1.453	0.040	1.439	0.026	1.433	0.020	1.413 r_o	[16]
	SO ₃	1.464	0.044	1.445	0.025	1.442	0.022	1.420 r_o	[17]
	HSOH	1.713		1.682		1.676			
	FSOH	1.662		1.636		1.625			
	FSOF	1.496		1.477		1.449			
S–C	CS ₂	1.571	0.018	1.559	0.006	1.562	0.009	1.553 r_e	[18]
	H ₂ CS	1.625	0.014	1.611	0.000	1.614	0.003	1.611 r_s	[19]
	OCS	1.578	0.017	1.565	0.004	1.566	0.005	1.561 r_e	[20]
	C ₂ H ₆ S	1.840	0.038	1.812	0.010	1.806	0.004	1.802 r_s	[21]
	F ₂ SO	1.660	0.075	1.630	0.045	1.602	0.017	1.585 r_o	[16]
S–F	F ₂ S	1.643	0.056	1.617	0.030	1.601	0.014	1.587 r_e	[22]
	FSOH	1.673		1.645		1.627			
	FSOF	1.648		1.618		1.595			
	HSF	1.668		1.639		1.628			
	F ₂ S ₂	1.701		1.670		1.641			
S–Cl	Cl ₂ S	2.081	0.066	2.036	0.021	2.024	0.009	2.015 r_o	[23]
	Cl ₂ S ₂	2.166	0.109	2.110	0.053	2.063	0.006	2.057 r_a	[23]
	ClS ₂ H	2.141		2.089		2.058			
S–S	H ₂ S ₂	2.112	0.057	2.066	0.011	2.065	0.010	2.055 r_s	[15]
	F ₂ S ₂	1.933		1.902		1.906			
	Cl ₂ S ₂	1.966	0.035	1.939	0.008	1.964	0.033	1.931 r_a	[23]
ClS ₂ H	2.053		2.015		2.023				
S–N	H ₂ NS	1.873		1.830		1.826			
S–P	H ₃ PS	1.963		1.938		1.938			
O–H	HSOH	0.975		0.964		0.963			
	FSOH	0.978		0.968		0.966			
C–H	H ₂ CS	1.095	0.002	1.093	0.000	1.086	–0.007	1.093 r_a	[19]
	C ₂ H ₆ S	1.096	0.005	1.093	0.002	1.087	–0.004	1.091 r_s	[21]
C–O	OCS	1.171	0.014	1.164	0.007	1.168	0.011	1.157 r_e	[20]
F–O	FSOF	1.787		1.777		1.841			

^a See Table 2 for the definition of bond lengths. The values Δ_n , where $n = 1, 2, 3$, denote the bond length difference $r_{\text{CALC}} - r_{\text{XPT}}$ between the calculated value and experiment (where available).

Table 2 Bond angles (in degrees) of molecules of the benchmark computed using the BLYP and HCTH density functionals and the MP2 method^a

Angle	Molecule	Bond angle/degrees							[ref.]
		α_{BLYP}	Δ_1	α_{HCTH}	Δ_2	α_{MP2}	Δ_3	α_{XPT}	
HSH	H ₂ S	92.1	0.1	92.0	0.2	92.2	0.0	92.2 α_e	[14]
FSH	HSF	95.9		96.2		96.1			
FSF	F ₂ SO	93.5	0.7	93.7	0.9	92.7	–0.1	92.8 α_o	[16]
	F ₂ S	99.6	1.5	99.7	1.6	98.7	0.6	98.1 α_e	[22]
HSO	HSOH	98.6		98.9		98.4			
SOH	HSOH	105.8		105.9		105.8			
	FSOH	108.1		108.1		107.8			
	FSOH	102.1		102.2		101.3			
FSO	F ₂ SO	106.6	–0.2	106.6	–0.2	106.7	–0.1	106.8 α_o	[16]
	FSOF	108.4		108.6		109.6			
SOF	FSOF	110.7		111.5		107.2			
SSH	H ₂ S ₂	98.3	0.4	98.7	0.8	97.8	–0.1	97.9 α_s	[15]
	ClS ₂ H	99.7		100.0		98.5			
SSCl	Cl ₂ S ₂	110.8	2.6	111.0	2.8	107.1	–1.1	108.2 α_a	[23]
	ClS ₂ H	107.6		108.0		105.3			
SSF	F ₂ S ₂	109.3		109.8		108.0			
HCS	C ₂ H ₆ S	106.7	0.1	106.6	0.0	107.5	0.8	106.6 α_s	[21]
	C ₂ H ₆ S	111.0	0.8	111.5	0.7	110.8	0.0	110.8 α_s	[24]
CSC	C ₂ H ₆ S	98.4	–0.5	99.2	0.3	96.9	–2.0	98.9 α_s	[21]
ClSCl	Cl ₂ S	104.9	2.2	105.1	2.4	102.7	0.0	102.7 α_o	[23]
SCH	H ₂ CS	122.2	0.6	122.3	0.7	121.8	0.2	121.6 α_s	[19]
SNH	H ₃ NS	110.5		110.9		110.5			
HNH	H ₃ NS	108.5		108.1		108.4			
SPH	H ₃ PS	118.1		118.1		117.7			
HPH	H ₃ PS	99.6		99.6		100.2			

^a Definitions of experimental bond distances/angles: r_e/α_e , distance/angle between equilibrium nuclear positions; r_o/α_o , distance/angle between effective nuclear positions derived from rotational constants of zero-point vibrational levels; r_s/α_s , distance/angle between effective nuclear positions derived from the isotopic differences in rotational constants; and r_a/α_a , distance/angle between effective nuclear positions derived from constant argument in molecular term measured by experimental electron gas diffraction. The values Δ_n , where $n = 1, 2, 3$, denote the bond angle difference $\alpha_{\text{CALC}} - \alpha_{\text{XPT}}$ between the calculated and the experimental value (where available).

Table 3 Harmonic vibrational frequencies ω (cm^{-1}) calculated using BLYP and HCTH density functionals and MP2 method. The computed intensities I (km mol^{-1}) of the vibrations are also presented (in parentheses) for each molecule^a

Molecule and state	ω_{BLYP}	I	A_1	ω_{HCTH}	I	A_2	ω_{MP2}	I	A_3	ω_{XPT}	[ref.]
H ₂ S											
A ₁	2596	(2)	-4.8	2670	(5)	-2.1	2780	(0.1)	1.9	2727	[12]
	1176	(0.6)	-0.6	1181	(5)	-0.2	1211	(0.7)	2.4	1183	[12]
B ₂	2611	(1)	-4.7	2688	(6)	-1.9	2799	(0.1)	2.2	2739	[12]
OCS											
Σ^+	2031	(576)	-1.5	2098	(588)	1.7	2100	(586)	1.8	2062	[12]
	844	(5)	-1.7	874	(5)	1.7	890	(7)	3.6	859	[12]
Π	500	(2)	-3.8	513	(2)	-1.3	523	(2)	0.6	520	[12]
	500	(2)	-3.8	513	(2)	-1.3	523	(2)	0.6	520	[12]
CS ₂											
Σ_u	1508	(506)	-1.6	1565	(518)	2.1	1625	(518)	6.0	1533	[12]
Σ_g	647	(0)	-1.7	667	(0)	1.4	676	(0)	2.7	658	[12]
Π_u	389	(4)	-2.0	394	(2)	-0.8	402	(4)	1.3	397	[12]
	389	(4)	-2.0	394	(2)	-0.8	402	(4)	1.3	397	[12]
C ₂ H ₆ S											
A ₁	3046	(13)	-2.9	3098	(15)	-1.2	3186	(8)	1.6	3136	[25]
	2954	(36)	-3.6	2994	(36)	-2.3	3070	(27)	0.2	3064	[25]
	1453	(0.1)	0.4	1457	(0.1)	0.7	1503	(0.3)	3.8	1447	[25]
	1326	(1)	-0.8	1339	(0.5)	0.1	1372	(0.4)	2.6	1337	[25]
	1021	(10)	-0.9	1031	(10)	0.1	1057	(10)	2.5	1030	[25]
	642	(3)	-7.6	680	(3)	-2.2	726	(3)	4.3	695	[25]
	255	(0)	-8.9	275	(0)	-1.8	264	(0)	-5.7	280	[25]
B ₁	3047	(4)	-2.9	3098	(2)	-1.2	3187	(2)	1.6	3137	[25]
	2957	(32)	-3.3	2997	(31)	-2.0	3076	(24)	0.6	3058	[25]
	1446	(15)	0.3	1452	(14)	0.7	1495	(15)	3.6	1442	[25]
	1303	(8)	-0.9	1313	(8)	-0.2	1347	(5)	2.4	1315	[25]
	889	(0.2)	-1.6	900	(0.5)	-0.3	922	(0.3)	2.2	903	[25]
	689	(0)	-7.1	725	(0)	-2.3	779	(0)	5.0	742	[25]
A ₂	3024	(0)	-2.7	3084	(0)	-0.8	3171	(0)	2.0	3109	[25]
	1433	(0)	0.4	1438	(0)	0.8	1479	(0)	3.4	1427	[25]
	926	(0)	-2.1	945	(0)	-0.1	964	(0)	2.0	946	[25]
	183	(0)	4.6	176	(0)	0.0	181	(0)	3.4	175	[25]
B ₂	3016	(34)	-3.0	3075	(35)	-1.1	3162	(22)	1.7	3109	[25]
	1441	(12)	0.1	1449	(14)	0.7	1488	(14)	3.4	1439	[25]
	960	(5)	-1.3	976	(6)	0.3	999	(5)	2.7	973	[25]
	180	(1)	-1.6	225	(1)	23.0	193	(1)	5.5	183	[25]
F ₂ SO											
A'	1247	(126)	-6.4	1303	(134)	-2.2	1365	(139)	2.4	1333	[26]
	720	(153)	-10.9	756	(159)	-6.4	810	(190)	0.2	808	[26]
	458	(19)	-13.6	485	(19)	-8.5	520	(24)	-1.9	530	[26]
	310	(2)		331	(2)		368	(4)			
A''	657	(189)	-11.2	695	(194)	-6.1	749	(214)	1.2	740	[26]
	348	(2)	-10.8	367	(2)	-5.9	386	(4)	-1.0	390	[26]
Cl ₂ S											
A ₁	473	(8)	-8.7	506	(9)	-2.3	544	(11)	5.0	518	[27]
	183	(0.2)	-12.0	198	(0.3)	-4.8	209	(0.4)	0.5	208	[27]
B ₂	452	(81)	-14.1	490	(83)	-6.8	541	(68)	2.9	526	[27]
Cl ₂ S ₂											
A	538	(11)	-1.5	571	(11)	4.6	548	(5)	0.4	546	[27]
	388	(33)	-16.7	417	(36)	-10.5	493	(35)	5.8	466	[27]
	192	(1)	-5.0	205	(0.8)	1.5	208	(0.2)	3.0	202	[27]
	90	(0.1)	-2.2	97	(0.1)	5.4	95	(0.1)	3.3	92	[27]
B	373	(144)	-18.4	401	(152)	-12.2	482	(100)	5.5	457	[27]
	214	(9)	-10.8	229	(8)	-4.6	245	(5)	2.1	240	[27]
F ₂ S ₂											
A	627	(73)	-12.6	674	(82)	-6.0	745	(84)	3.9	717	[33]
	586	(1)	-4.7	628	(0.1)	2.1	621	(1)	1.0	615	[33]
	269	(2)	-15.9	285	(1)	-10.9	294	(1)	-8.1	320	[33]
	167	(2)	-8.7	176	(1)	-3.8	187	(2)	2.2	183	[33]
B	594	(219)	-12.8	637	(237)	-6.5	711	(215)	4.4	681	[33]
	285	(12)	-5.3	303	(12)	0.7	325	(14)	8.0	301	[33]
H ₂ S ₂											
A	2525	(4)	-3.7	2582	(3)	-1.5	2733	(0.1)	4.3	2621	[27] ^b
	850	(0)	-3.6	881	(0)	0.1	906	(0.3)	2.6	882	[27] ^b
	465	(0.1)	-8.6	503	(0.1)	-1.2	537	(0)	5.5	509	[27] ^b
	421	(12)		446	(13)		442	(14)			
B	2528	(9)	-5.3	2586	(9)	-3.1	2735	(1)	2.5	2669	[27] ^b
	852	(6)	-1.8	883	(6)	1.7	903	(5)	4.0	868	[27] ^c

Table 3 Continued

Molecule and state	ω_{BLYP}	I	Δ_1	ω_{HCTH}	I	Δ_2	ω_{MP2}	I	Δ_3	ω_{XPT}	[ref.]
SO ₃											
A ₁	966	(0)	-9.3	1024	(0)	-3.8	1049	(0)	-1.5	1065	[28]
	439	(24)	-11.8	465	(25)	-6.6	485	(29)	-2.6	498	[28]
E	1277	(153)	-8.2	1352	(167)	-2.8	1409	(152)	1.3	1391	[28]
	1277	(153)	-8.2	1352	(167)	-2.8	1409	(152)	1.3	1391	[28]
	478	(21)	-9.8	499	(27)	-5.8	514	(27)	-3.0	530	[28]
	478	(21)	-9.8	499	(27)	-5.8	514	(27)	-3.0	530	[28]
CH ₂ S											
A ₁	2975	(39)		3012	(43)		3113	(25)			
	1455	(6)		1462	(6)		1504	(3)			
	1041	(11)		1079	(13)		1100	(3)			
B ₁	990	(40)		999	(36)		1024	(42)			
B ₂	3048	(11)		3093	(14)		3209	(5)			
	981	(3)		987	(3)		1014	(2)			
F ₂ S											
A ₁	771	(58)	-8.1	806	(62)	-3.9	856	(73)	2.0	839	[34]
	310	(3)	-13.2	329	(3)	-7.8	351	(4)	-1.7	357	[34]
B ₂	744	(129)	-8.5	782	(133)	-3.8	832	(141)	2.3	813	[34]
H ₃ NS											
A'	3406	(60)		3477	(56)		3588	(80)			
	3326	(0.1)		3388	(1)		3469	(9)			
	1611	(32)		1634	(29)		1665	(33)			
	1266	(15)		1314	(11)		1338	(33)			
	790	(19)		839	(21)		858	(20)			
	561	(1)		608	(0.2)		656	(3)			
A''	3406	(60)		3477	(56)		3588	(80)			
	1611	(32)		1634	(29)		1665	(33)			
	790	(19)		839	(21)		858	(20)			
H ₃ PS											
A'	2308	(143)	-2.2	2342	(142)	-0.7	2499	(112)	5.9	2359	[29] ^d
	2286	(56)		2321	(54)		2488	(45)			
	1098	(187)	-11.5	1100	(172)	-11.3	1155	(216)	-6.9	1240	[29] ^d
	1072	(14)		1075	(13)		1147	(17)			
	686	(0.1)		701	(0.1)		741	(1)			
	631	(41)	-26.5	670	(46)	-21.9	693	(52)	-18.8	858	[29] ^d
A''	2286	(56)	-3.6	2321	(54)	-2.1	2488	(45)	4.9	2371	[29] ^d
	1072	(14)	-6.2	1075	(13)	-5.9	1148	(17)	0.4	1143	[29] ^d
	686	(0.1)	-38.4	701	(0.1)	-37.1	741	(1)	-33.5	1114	[29] ^d
HSF											
	2530	(9)	-3.7	2603	(8)	-0.9	2748	(3)	4.6	2628	[30]
	964	(4)	-5.8	994	(4)	-2.8	1043	(7)	2.0	1023	[31] ^e
	729	(59)	-7.5	769	(62)	-2.4	811	(65)	2.9	788	[31] ^e
HSOH											
	3634	(50)	3.1	3755	(57)	6.5	3830	(85)	8.7	3525	[32]
	2485	(26)		2556	(24)		2712	(11)			
	1170	(37)	-0.6	1196	(38)	1.6	1219	(39)	3.6	1177	[32]
	962	(0.5)		990	(1)		1035	(2)			
	700	(43)	-8.3	750	(50)	-1.7	788	(53)	3.3	763	[32]
	465	(70)	4.5	485	(71)	9.0	485	(76)	9.0	445	[32]
FSOH											
	3575	(53)		3692	(58)		3787	(98)			
	1167	(36)		1194	(36)		1219	(42)			
	767	(69)		843	(86)		867	(42)			
	697	(134)		738	(131)		793	(142)			
	557	(83)		573	(84)		574	(98)			
	311	(4)		327	(3)		351	(5)			
FSOF											
	1058	(28)		1118	(30)		1369	(48)			
	719	(140)		761	(151)		813	(193)			
	441	(109)		431	(87)		519	(89)			
	384	(8)		397	(28)		421	(8)			
	282	(12)		289	(18)		241	(5)			
	151	(2)		158	(2)		138	(1)			
ClSSH											
	2479	(7)		2545	(7)		2707	(0.4)			
	857	(5)		879	(5)		906	(4)			
	480	(9)		517	(10)		540	(11)			
	404	(52)		436	(74)		504	(52)			
	410	(28)		427	(7)		406	(15)			
	183	(3)		198	(3)		208	(2)			

^a The values Δ_n , where $n = 1, 2, 3$, are percentage differences between the calculated and experimental values. For definition of Δ_n please see the text. ^b Liquid state results. ^c Solid state results. ^d Experimental assignments for H₃PO. ^e These were the observed bands suggested for the isolated HSF, but the actual predictions were 1015 and 790 cm⁻¹.

and experiment as a percentage of the experimental value:

$$\Delta_n = \frac{\omega_{\text{CALC}} - \omega_{\text{XPT}}}{\omega_{\text{XPT}}} \times 100 \quad n = 1, 2, 3. \quad (1)$$

Examination of the data reveals that all the frequencies predicted by the GGA functionals are lower than the corresponding data arising from the MP2 method which is partly due to the structural parameters overestimated by the GGA methods.

For consistency, we compare our data with the same experimental results as used previously.^{5†} However, this time, for the high frequency modes (which involve H) the fundamentals ν_{XPT} have been corrected for anharmonicity (approximately) as follows. The symmetric and asymmetric S–H stretches were corrected by adding 112 cm^{-1} , this being the value published¹¹ for H_2S . Similarly, the C–H stretches were corrected by adding 139 cm^{-1} , as reported¹² for HCN. These corrected values, highlighted by boldface in the table, have been compared with the ω values for BLYP, HCTH and MP2. Since this constitutes the largest anharmonic correction for the benchmark, we designated the experimental column as ω_{XPT} . The differences shown in the table indicate that, for those molecules that do not contain halogen, the HCTH method predicts frequencies that match better with experiment than the other two methods. Especially noticeable are the errors associated with the predictions arising from the MP2 method which appear to be somewhat larger than expected, in comparison to the HCTH technique. The worst predictions are produced by BLYP, as was expected on the basis of the poor structural data.

Much larger errors are evident for the halogen-containing molecules, as highlighted in the table by boldface. This time, however these high errors are associated only with the GGA functionals, except for F_2S_2 , for which the bending mode at 320 cm^{-1} is severely underestimated by all three methods, suggesting that perhaps the other observed bending mode at 301 cm^{-1} should have been assigned the A symmetry. This reversal of the symmetry of the two bending modes would be in accord with the predictions of the MP2 theory and would also reduce the errors introduced by the predictions of the GGA methods. The problems associated with the assignments

† The exception is H_2S_2 for which we found a new value from the same authors.

Table 4 Atomisation energies calculated using BLYP and HCTH density functionals and the MP2 method^a

Molecule	Atomisation energy $E_{\text{at}}/\text{kcal mol}^{-1}$									
	$E_{\text{at}}(\text{HCTH})$	Δ_1	Δ_{BLYP}	$E_{\text{at}}(\text{BLYP})$	Δ_2	Δ_{HCTH}	$E_{\text{at}}(\text{MP2})$	Δ_3	$E_{\text{at}}(\text{XPT})$	[ref.]
H_2S	178.74	5.54	4.90	179.56	6.36	4.08	174.66	1.46	173.2	[13]
H ₃ SOH	262.09		7.05	266.57		2.57	259.52			
HSSH	233.00		5.53	235.42		3.11	229.89			
CS_2	281.25	7.75	-0.25	282.13	8.63	-1.13	282.38	8.88	273.8	[13]
$\text{C}_2\text{H}_6\text{S}$	756.24		5.42	756.09		5.56	750.67			
SO_3	334.64		-1.77	337.16		-4.29	338.93			
OCS	341.41	13.4	1.61	342.51	14.81	0.51	340.90	13.2	327.7	[13]
H_2CS	321.77	4.37	5.00	322.89	5.49	3.88	317.89	0.49	317.4	[13]
H_3NS	316.65		14.04	326.95		3.74	312.91			
H_3PS	295.12		10.83	300.14		5.81	289.30			
F_2S_2	248.41		13.83	253.57		8.67	239.74			
F_2S	175.98		7.32	180.50		2.80	173.18			
F_2SO	304.69		3.86	309.17		-0.62	305.31			
F ₃ SOH	271.49		8.31	277.65		2.15	269.34			
F ₃ OF	232.42		24.18	242.87		13.73	218.69			
HFS	169.48		6.62	172.52		3.58	165.90			
Cl_2S	123.85		3.10	127.75		-0.80	124.65			
Cl_2S_2	192.31		7.53	198.15		1.69	190.62			
ClSSH	211.16		5.68	215.29		1.55	209.61			

^a The values Δ_n where $n = 1, 2, 3$ are defined as the differences $E_{\text{at}}(\text{CALC}) - E_{\text{at}}(\text{XPT})$ for the HCTH, BLYP and MP2 methods, respectively. The values Δ_{method} correspond to the differences $E_{\text{at}}(\text{method}) - E_{\text{at}}(\text{MP2})$.

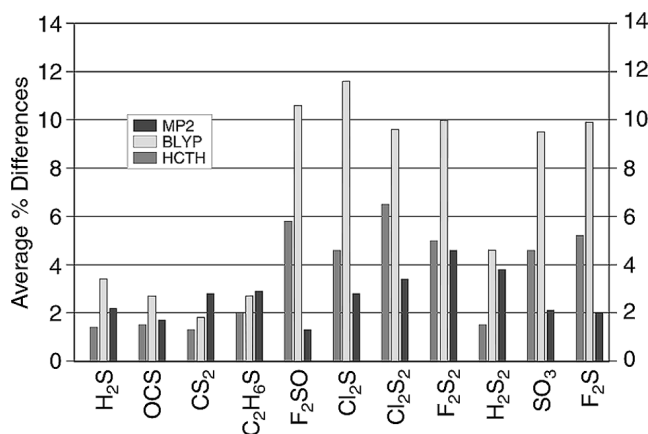


Fig. 3 Average of % frequency differences: $[F(i)\text{theoretical} - F(i)\text{experimental}]$.

of the fundamentals for the molecules H_3PS , HFS and HSOH have been discussed previously⁵ in detail and will not be discussed here, except to note that these molecules are not included in the graphical analysis below.

The percentage differences shown in Table 3 were averaged, by taking their absolute values, for each compound and these are illustrated in Fig. 3. The figure reflects our analysis above regarding the excellent performance of HCTH for sulfur compounds without halogens and highlights the problems associated with sulfur–halogen compounds. The calculated mean absolute errors for the molecules shown in Fig. 3 are 6.9, 3.6 and 2.7% for BLYP, HCTH and MP2, respectively. This is to be contrasted with the mean absolute errors associated exclusively with the sulfur–halogen compounds of 10.1, 5.9 and 2.9%, for BLYP, HCTH and MP2, respectively. Clearly, for the GGA functionals and especially for HCTH, the sulfur–halogen compounds are responsible for the bulk of the errors in predicting frequencies.

We believe that, just as in the case of the molecular structures, significant improvement could be achieved by including F_2S and Cl_2S into the training set for future HCTH functionals.

3.3. Atomisation energies

Table 4 gives a summary of the atomisation energies calculated for the benchmark using the three methods, together

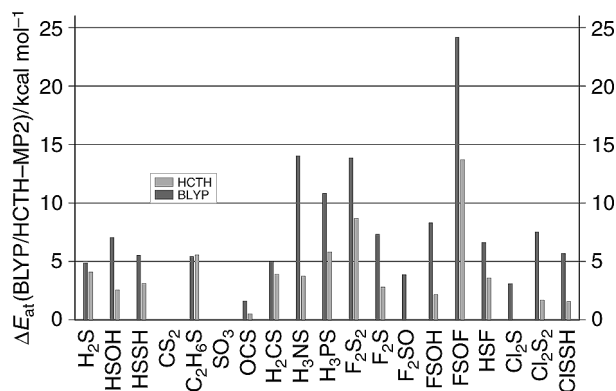


Fig. 4 $\Delta E_{\text{at}}(\text{BLYP}/\text{HCTH} - \text{MP2})$ for the benchmark.

with the deviations calculated relative to the MP2 values. With a few exceptions, indicated by boldface, the atomisation energies predicted by the HCTH method are higher than those obtained using the MP2 functional. Of the four values that are lower, three are within 1 kcal mol^{-1} of the MP2 value. It is also apparent from the table that, all but one of the energies predicted by the BLYP functional are higher than their HCTH equivalent. This is illustrated in Fig. 4 which depicts the deviations in the atomisation energies as predicted by the BLYP and the HCTH functionals, relative to the MP2 values for the benchmark. It can be seen from this figure that the largest deviations occur in the predictions for the sulfur-halogen compounds and in particular when the BLYP method is used.

Included in Table 4 are a few atomisation energies determined by experiment. A comparison of these with the predictions of the three methods studied reveals the following. First, that the MP2 method predicts excellent atomisation energies for H_2CS and H_2S , these being within 0.5 and $1.5 \text{ kcal mol}^{-1}$ of the experimental value, respectively. This is to be contrasted with the predictions for the same two molecules by HCTH of 4.4 and $5.5 \text{ kcal mol}^{-1}$, respectively. This we attribute to the fact that H_2S was not included into the training set for HCTH. Second, that the predictions arising by all three methods for CS_2 and OCS are very poor and not much different from each other. In fact, HCTH appears to do a better prediction for CS_2 than the other two methods. We don't know the reason for the bad performance involving these two molecules, but we wish to point out that the G2 theory had similar problems predicting the atomisation energy for H_2CS ($\sim 7.1 \text{ kcal mol}^{-1}$ error)¹³ which was predicted extremely well by MP2 in this study.

Based on the above we conclude that the atomisation energies predicted by the HCTH functional are a definite improvement over the predictions arising from BLYP, especially for sulfur compounds that do not contain halogens, but need to be further improved to compare better with the predictions of the MP2 methodology and experiment. We believe that this could be achieved by the inclusion of H_2S and F_2S to the training set of future HCTH functionals.

4. Conclusions

The results of these studies using our benchmark of sulfur-containing small molecules lead to the following conclusions.

(1) Structural predictions from the HCTH method are, on the whole, in good agreement with MP2 theory and a significant improvement over the BLYP methodology. There are a few sulfur bonds that appear to be problematic for the HCTH method, namely the S-F bond in F_2SO and in F_2S , and the S-Cl bond in Cl_2S and Cl_2S_2 .

(2) Harmonic frequencies are underestimated by both GGA methods. However, the mean absolute error involved in the

predictions by the HCTH functional for those molecules that do not contain halogens is lower (2.05%) than the corresponding value arising from the MP2 theory (2.6%). For sulfur-halogen compounds, the error for the HCTH method is much higher (5.9%) than the error from the MP2 theory (2.9%) but much lower than the error from the BLYP method (10.1%). Overall, the HCTH method predicts better frequencies than the BLYP method.

(3) The atomisation energies predicted by the HCTH are too high, as compared to the MP2 theory, by an average of a few kcal mol^{-1} and deviate from experiment[¶] by an average of 5 kcal mol^{-1} . This value, however, may not be representative for the benchmark because of the scarcity of available experimental values.

The energies predicted by the BLYP method are even higher than those predicted by the HCTH method. The largest deviations between the predictions of both GGA methods and the MP2 technique are associated with the sulfur-halogen compounds of the benchmark. Thus the atomisation energies predicted by the HCTH method correspond much better to the predictions of the MP2 theory as well as experiment than the BLYP results.

(4) It may be concluded that, overall, the performance of the HCTH functional constitutes a significant improvement over the BLYP functional. Further improvements for the prediction of the molecular properties of sulfur-halogen compounds can be achieved by including the molecules F_2S and Cl_2S into the training set of future HCTH functionals.

This study exemplifies the extent to which the reliability of parameterised functionals, such as HCTH, depend on the molecules included in their training sets.

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References

- 1 A. C. Scheiner, J. Baker and J. W. Andzelm, *J. Comput. Chem.*, 1997, **18**, 775.
- 2 M. W. Wong, *Chem. Phys. Lett.*, 1996, **256**, 391.
- 3 M. L. McKee, *J. Phys. Chem.*, 1996, **100**, 3473.
- 4 J. A. Altmann, N. C. Handy and V. E. Ingamells, *Int. J. Quantum Chem.*, 1996, **57**, 533.
- 5 J. A. Altmann, N. C. Handy and V. E. Ingamells, *Mol. Phys.*, 1997, **92**, 339.
- 6 F. A. Hamprecht, A. J. Cohen, D. J. Tozer and N. C. Handy, *J. Chem. Phys.*, 1998, **109**, 6264.
- 7 A. D. Becke, *J. Chem. Phys.*, 1997, **107**, 8554.
- 8 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrewski, J. V. Ortiz, J. B. Foresman, J. Ciolowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzales and J. A. Pople, Gaussian 94, Rev E3 (Pittsburgh, PA: Gaussian Inc.), 1995.
- 9 T. H. Dunning Jr., *J. Chem. Phys.*, 1989, **90**, 1007.
- 10 D. E. Woon and T. H. Dunning Jr., *J. Chem. Phys.*, 1993, **98**, 1358.
- 11 J. Senekowitsch, S. Carter, A. Zilch, H-J. Werner, N. C. Handy and P. Rosmus, *J. Chem. Phys.*, 1989, **90**, 783.
- 12 G. Herzberg, *Molecular Spectra and Molecular Structure, Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand, New York, 1945, vol. II.
- 13 L. A. Curtiss, K. Raghavachari, G. W. Trucks and J. A. Pople, *J. Chem. Phys.*, 1991, **94**, 7221.

¶ For two molecules only (see text).

- 14 T. H. Edwards, N. K. Moncur and L. E. Snyder, *J. Chem. Phys.*, 1967, **46**, 2139.
- 15 G. Winnewisser and K. M. T. Yamada, *Vib. Spectrosc.*, 1991, **1**, 263.
- 16 N. J. Lucas and J. G. Smith, *J. Mol. Spectrosc.*, 1972, **43**, 327.
- 17 A. Kaldor and A. G. Maki, *J. Mol. Spectrosc.*, 1973, **45**, 123.
- 18 G. Blanquet, J. Walrand and C. P. Courtroy, *Ann. Soc. Bruxelles*, 1974, **88**, 87.
- 19 D. R. Johnson F. J. Lovas and W. H. Kirchhoff, *J. Phys. Chem. Ref. Data*, 1972, **1**, 1001.
- 20 Y. Morino and C. Matsumuta, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 1095.
- 21 L. R. Pierce and M. Hayashi, *J. Chem. Phys.*, 1961, **35**, 479.
- 22 Y. Endo, S. Saito, E. Hirota and T. Chikaraishi, *J. Mol. Spectrosc.*, 1979, **77**, 222.
- 23 M. W. Chase, C. A. Davies, J. R. Downey, D. R. Frurip, R. A. Macdonald and N. Syverud, *JANAF Thermochemical Tables*, 3rd edn; *J. Phys. Chem. Ref. Data*, 1985, **14**, (Suppl. 1).
- 24 D. C. McKean and P. McQuillang, *J. Mol. Struct.*, 1978, **49**, 275.
- 25 J. E. Ellwood, D. Steele and D. Gerrard, *Spectrochim. Acta A*, 1994, **50**, 913.
- 26 S. D. Ross, *Inorganic and Raman Spectra*, McGraw-Hill, New York, 1972.
- 27 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1986.
- 28 *J. Phys. Chem. Ref. Data*, 1977, **6**, 1011.
- 29 W. B. Person, J. S. Kwiatkowski and R. J. Bartlett, *J. Mol. Struct.*, 1987, **157**, 237.
- 30 N. P. Machara and B. S. Ault, *J. Mol. Struct.*, 1988, **172**, 129.
- 31 L. Andrews, T. C. McInnis and Y. Hannachi, *J. Chem. Phys.*, 1992, **96**, 4248.
- 32 R. R. Smardzewski and M. C. Lin, *J. Chem. Phys.*, 1977, **66**, 3197.
- 33 R. D. Brown and G. P. Pez, *Spectrochim. Acta A*, 1970, **26**, 1375.
- 34 R. J. Glinski, C. D. Taylor and F. W. Kutzler, *J. Phys. Chem.*, 1990, **94**, 6196.

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