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Performance of recently developed kinetic energy density functionals for the calculation of hydrogen binding strengths and hydrogen-bonded structures

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Abstract. The accuracy of predicted hydrogen binding energies and equilibrium structures for a benchmark set of molecules is compared for some recently developed density functionals, Becke's three parameter hybrid method with the Lee, Yang, and Parr (LYP) correlation functional (B3LYP), Becke's half and half functional combined with the LYP correlation functional (BHLYP), Perdew, Burke and Ernzerhof functional (PBE), Van Voorhis, Scuseria exchange correlation functional (VSXC), the hybrid Perdew, Burke and Ernzerhof functional (PBE1PBE), and meta-generalized gradient approximation (meta-GGA). Overall, the hybrid functionals which contain a portion of Hartree–Fock exchange (B3LYP, BHLYP, and PBE1PBE) yield the most accurate results. The kinetic-energy-density-dependent functionals, VSXC and meta-GGA, are significantly less accurate.

Key words: Density functionals

1 Introduction

Accurate representation of hydrogen bonding is necessary in order to predict molecular properties of numerous biologically important molecules and other clusters. Second-order Møller–Plesset (MP2) and higher levels of theory treat hydrogen bonding accurately, but are computationally expensive. Less computationally expensive methods that treat hydrogen bonding sufficiently would be advantageous. One possibility is density functional theory (DFT) methods. DFT methods have been shown to describe reliably properties of numerous chemical systems and the computational cost is considerably lower than for MP2 and higher levels of theory.

In this article, we investigate the accuracy of four recently proposed DFT functionals, Van Voorhis, Scuseria exchange correlation functional (VSXC) [1], meta-generalized gradient approximation (meta-GGA) [2], Perdew, Burke, and Ernzerhof functional (PBE) [3], and the hybrid Perdew, Burke, and Ernzerhof functional (PBE1PBE) [4, 5] for predicting hydrogen-bonded structures and binding energies. We compare the accuracy of these DFT functionals to Becke's three parameter hybrid method with the Lee, Yang, and Parr (LYP) correlation functional (B3LYP) [6], which is considered to be one of the most accurate DFT methods [7–10], and Becke's half and half (BH) [11] functional combined with the LYP [12] correlation functional (BHLYP).

Previous studies have shown that DFT methods that contain Hartree–Fock (HF) exchange (hybrid functionals) obtain more accurate hydrogen-bonding data than nonhybrid functionals (DFT methods that do not contain HF exchange) [7–10, 13–16]. Hybrid functionals are computationally more expensive because of the evaluation of exact exchange. Thus, a nonhybrid functional that yields hydrogen-bonding with greater accuracy would be beneficial. In this article, we compare the results of three nonhybrid functionals (VSXC, meta-GGA, and PBE) and three hybrid functionals (PBE1PBE, BHLYP, and B3LYP) with experimental data and MP2 results. VSXC is a kinetic-energy-density-(τ)-dependent functional recently developed by our group[1]. Although VSXC does not contain HF exchange, its accuracy for describing thermochemical [1, 17] and molecular properties, such as proton-transfer barriers [18] and vibrational frequencies [19], is remarkable and is shown to be of a quality similar to that of hybrid methods [1, 17–19]. Meta-GGA is based on the GGA and also includes information from τ [2, 20]. The PBE and the PBE hybrid (PBE1PBE) functionals are also based on the GGA but contain no information from τ. The PBE hybrid combines PBE exchange and correlation with exact exchange using a nonempirical one-parameter equation [5]. PBE1PBE is also referred to in the literature as PBE0 [21].

A number of previous studies that use a variety of functionals have yielded promising results regarding the

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accuracy of DFT predictions on hydrogen-bonded systems [7–9, 13–16, 22–26]. Pudzianowski [8, 13] compared the 1988 Becke exchange functional (B) with the LYP correlation functional (BLYP) and B3LYP DFT functionals to MP2 for the calculation of the binding energies and geometries for ten binary ionic complexes. He found that B3LYP gave similar results to MP2 for these systems and that diffuse basis sets are needed in both DFT and MP2 methods to describe hydrogen-bonded systems, particularly for anionic hydrogen-bonded systems. Topol et al. [22] compared DFT methods to experimental data for a number of hydrogen-bonded systems and noted that for dipole moments, enthalpies, and entropies of dimerization, the DFT methods produced results with near chemical accuracy. Lundell and Latajka [9] focused on the H_2O/CO system employing numerous DFT methods, HF, MP2, and coupled-cluster single-double and perturbative triple excitation [CCSD(T)]. They found that local DFT methods are unreliable, overestimate intermolecular distances, and underestimate binding energies. On the other hand, the hybrid DFT functionals studied by these authors [9] showed promising results. Sodupe et al. [15] compared the Perdew 1986 gradient-corrected correlational functional with Becke's exchange functional (BP86) and the BLYP, B3LYP, and BHLYP functionals to MP2 and CCSD(T) for the calculation of the ground state of the $(H_2O)_2^+$ radical cation. They found that the BHLYP functional compared best with the MP2 and CCSD(T) methods. Sadlej et al. [16] studied the structure and energetics of the NH3/H_2O complex using HF, Becke's three parameter hybrid method with the Perdew-Wang 1991 gradient-corrected correlation functional (B3PW91), MP2, fourth-order Møller–Plesset, and CCSD(T). They concluded that DFT methods are not applicable to hydrogen-bonded systems in which the dispersion interactions are large in comparison to the classical electrostatic and induction effects.

These studies found hybrid and nonlocal DFT functionals, such as B3LYP, to be promising computational methods for larger hydrogen-bonded systems where high-level calculations such as CCSD(T) become computationally intensive. Previous studies, however, have not included the recently developed τ-dependent functionals, such as VSXC and meta-GGA, which generally yield results comparable to hybrid methods. In this article, we compare the accuracy of B3LYP, BHLYP, VSXC, meta-GGA, PBE, and hybrid PBE functionals to experimental and MP2 results for the calculation of the properties of hydrogen-bonded systems.

2 Computational details

All calculations were done using a developmental version of the Gaussian suite of programs [27]. The geometries of each test molecule were optimized for each functional using the 6-311++G(d,p) basis set. The zero-point energies and basis set superposition error (BSSE) were also calculated for every functional using this basis set. Previous research has shown this basis set to be sufficiently large to produce reliable hydrogen-bonding data [8, 10]. We utilize the counterpoise procedure (CP) to calculate the BSSE correction [28]. This is given by

$$E_{\mathrm{interaction}}^{\mathrm{CP}} = E_{\mathrm{super}} - \sum_{i=1}^{n} E_{\mathrm{m_{opt}}i} + \sum_{i=1}^{n} \left(E_{\mathrm{m_f}i} - E_{\mathrm{m_f}i*} \right) , \qquad (1)$$

where E_m denotes individual monomer energies, E_super is the energy of the hydrogen-bonded system, opt denotes the energy of the individually optimized monomers, f denotes the energy of a monomer frozen in its optimized dimer energy, and $*$ denotes the use of "ghost" atoms in the monomer calculation.

3 Results and discussion

We separate the data into two sets: ionic and nonionic systems. We studied five representative molecules of each type. For the ionic systems, our data is compared to the MP2/6-311++G(d,p) calculations, which were found to produce good results, normally within the error limits of experimental values [8]. For the statistical analysis, the mean value of multiple experimental data for the HF/HF, HCl/HCl, H_2O/H_2O, and HF/HCN systems is utilized as the experimental value. The B3LYP/6-311++G(d,p) optimized geometries for the ten molecules studied here are pictured in Fig. 1.

3.1 Hydrogen-bonded geometries

The calculated hydrogen-bond lengths, angles, and the statistical analysis are listed in Tables 1 and 2. Although VSXC does produce equilibrium geometries of covalently bonded polyatomic molecules with similar quality to B3LYP [19], VSXC does not predict hydrogen-bonded structures accurately for either the ionic or the

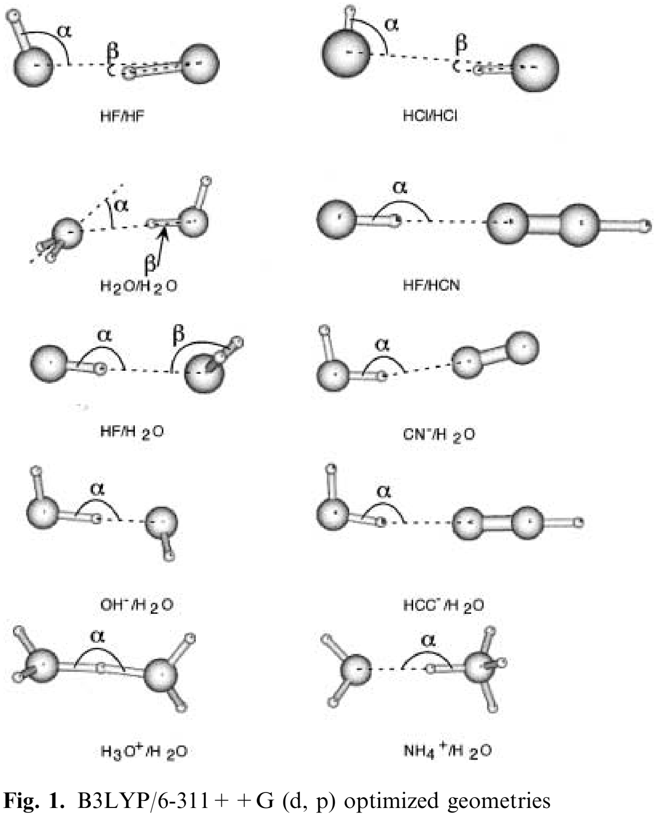

Fig. 1. B3LYP/6-311++G (d, p) optimized geometries

Table 1. Optimized hydrogen-bond lengths (Å), angles (degrees), and statistical analysis (with respect to experimental data). All calculations employed the 6-311+ +G(d,p) basis set. Experimental and second-order Møller–Plesset (MP2) results are listed for reference

Molecules	Bond/ angle type	B3LYP	VSXC	Meta-GGA	PBE1PBE	PBE	BHLYP	Expt.	MP2
HF/HF	F···F	2.745	2.842	3.008	2.729	2.738	2.719	2.73–2.74[a]	2.73[a]
	α	116.8	119.0	120.2	116.1	111.6	119.0	117 ± 6[a]	110.3[a]
	β	7.8	8.2	8.8	8.1	9.1	7.9	7.9[a]	6.4[a]
HCl/HCl	Cl···Cl	3.887	4.015	4.345	3.807	3.766	3.898	3.75–3.79[a]	3.89[c]
	α	95.9	95.6	93.6	95.4	94.2	95.0	100–110[a]	91.4[c]
	β	7.4	7.7	15.6	7.4	6.9	9.5	0–10[a]	6.06[c]
H_2O/H_2O	O···O	2.900	3.014	3.162	2.874	2.882	2.882	2.946/2.952[a]	2.91[a]
	α	65.6	63.4	63.9	66.1	68.1	65.3	57 ± 10[a]	57.3[a]
	β	3.4	1.7	1.5	3.7	4.4	3.1	<30[a]	5.7[a]
HF/HCN	N···H	1.836	1.963	2.062	1.815	1.796	1.844	1.827[b]	1.809[b]
	α	180.0	179.2	178.7	179.9	179.8	179.9	180.0[b]	180.0[b]
HF/H_2O	O···F	2.643	2.759	2.806	2.620	2.631	2.630	2.662[b]	2.652[b]
	α	177.4	176.7	176.7	177.7	177.9	176.8	182.5[b]	182.5[b]
	β	117.5	118.9	116.2	116.5	114.2	119.7	116.3[b]	116.3[b]
Bonds									
$\overline{\lvert x \rvert}$		0.05	0.12	0.28	0.04	0.03	0.06		
Root mean square		0.06	0.14	0.32	0.05	0.05	0.08		
Angles									
$\overline{\lvert x \rvert}$		3.4	3.7	5.0	3.4	4.7	4.3		
Root mean square		4.9	4.8	6.5	5.1	6.1	5.5		

[a] Ref. [10]
[b] Ref. [29]
[c] Ref. [32]

Table 2. Optimized hydrogen-bond lengths (Å), angles (degrees), and statistical analysis (with respect to MP2 data) for selected ionic compounds. All calculations employed the 6-311+ +G(d,p) basis set

Molecules	Bond/angle type	B3LYP	VSXC	Meta-GGA	PBE1PBE	PBE	BHLYP	MP2[a]
CN^-/H_2O	N···H	1.801	2.095	1.934	1.774	1.752	1.824	1.83
	α	169.9	179.9	166.4	169.8	171.0	168.5	168.4
OH^-/H_2O	O···H	1.357	1.559	1.382	1.218	1.233	1.423	1.38
	α	176.7	170.2	176.1	177.8	177.6	175.2	176.0
HCC^-/H_2O	C···H	1.848	1.998	1.938	1.818	1.769	1.895	1.87
	α	171.4	162.3	169.5	171.3	172.5	170.0	170.0
H_3O^+/H_2O	O···H	1.202	1.205	1.216	1.194	1.207	1.197	1.19
	α	175.0	174.3	173.3	174.8	173.9	176.1	174.2
NH_4^+/H_2O	O···H	1.636	1.719	1.728	1.607	1.597	1.650	1.65
	α	179.6	179.6	179.6	179.6	179.7	179.8	179.6
Bonds								
$\overline{\lvert x \rvert}$		0.02	0.13	0.06	0.06	0.08	0.02	
Root mean square		0.02	0.16	0.07	0.08	0.09	0.02	
Angles								
$\overline{\lvert x \rvert}$		0.9	5.0	0.7	1.0	1.4	0.6	
Root mean square		1.0	6.7	1.0	1.2	1.8	0.9	

[a] Ref. [8]

nonionic hydrogen-bonded systems considered here. The meta-GGA functional yields significantly poor hydrogen-bond geometries for the nonionic systems (mean absolute error of 0.28 Å) and performs somewhat better for the ionic systems considered in our study (mean absolute error of 0.06 Å). B3LYP and BHLYP produce hydrogen bonds for the ionic structures studied here with much better accuracy (mean absolute error of approximately 0.02 Å), 3 times better than any of the other DFT methods studied here. The B3LYP and BHLYP functionals are the most accurate at calculating hydrogen-bond lengths, whereas the PBE and hybrid PBE functionals are only slightly less accurate in describing the bond structures.

3.2 Binding energies

The calculated hydrogen binding energies and statistical analysis are listed in Tables 3 and 4. The BSSE corrections, which typically amount to 10% of the calculated binding energy with the 6-311+ +G(d,p) basis set, are listed in Table 5. The total statistical errors and maximum deviations for both the binding energies and geometries are listed in Table 6.

Meta-GGA underestimates most of the binding energies calculated here. This results in a larger underestimation of the binding energies when the zero-point corrections are added in. In particular, the meta-GGA functional most accurately predicts the binding energies

Table 3. Binding energies and statistical analysis for the zero-point vibrational energy (ZPVE) corrected energies with respect to experimental data (kcal/mol). The second entry for each molecule includes the ZPVE. All calculations employed the 6-311++G(d,p) basis set. Experimental and MP2 results are listed for reference

Molecules	B3LYP	VSXC	Meta-GGA	PBE1PBE	PBE	BHLYP	Expt.	MP2
HF/HF	−5.05	−5.04	−3.44	−5.24	−5.38	−5.45		
	−3.27	−3.41	−2.05	−3.47	−3.60	−3.65	−4.47–4.52[a]	−4.1[a]
HCl/HCl	−1.58	−2.38	−1.19	−2.09	−2.35	−1.69		
	−0.71	−1.61	−0.29	−1.19	−1.43	−0.83	−1.4–2.0[a]	−1.9[c]
H_2O/H_2O	−5.83	−5.72	−3.84	−6.26	−6.40	−6.17		
	−3.52	−3.67	−1.98	−3.93	−4.09	−3.83	−5.4 ± 0.2[a]	−4.9[d]
HF/HCN	−7.74	−7.17	−7.02	−8.06	−8.26	−8.05		
	−5.91	−5.57	−3.56	−6.23	−6.49	−6.16	−4.52 ± 0.26[b]	−4.45[b]
HF/H_2O	−10.11	−9.14	−6.93	−10.51	−10.75	−10.44		
	−7.35	−6.64	−4.50	−7.75	−7.99	−7.71	−6.2[b]	−5.40[b]
$\overline{\lvert x\rvert}$	1.3	0.9	2.0	1.3	1.3	1.3		
Root mean square	1.4	1.1	2.2	1.3	1.4	1.3		

[a] Ref. [10]
[b] Ref. [29]
[c] Ref. [32]
[d] Ref. [33]

Table 4. Binding energies and statistical analysis (kcal/mol) for selected ionic compounds. The second entry for each molecule includes the ZPVE. All calculations employed the 6-311++G(d,p) basis set

Molecules	B3LYP	VSXC	Meta-GGA	PBE1PBE	PBE	BHLYP	MP2[a]
CN^-/H_2O	−16.36	−13.63	−13.13	−17.09	−17.56	−16.43	
	−14.61	−12.19	−11.61	−15.35	−15.98	−14.56	−15.7
OH^-/H_2O	−29.39	−26.53	−25.58	−30.90	−32.14	−28.85	
	−28.77	−25.05	−25.40	−29.72	−32.11	−27.49	−28.3
H_3O^+/H_2O	−37.76	−32.86	−31.74	−38.99	−39.90	−37.18	
	−35.94	−32.53	−30.76	−36.96	−37.61	−35.88	−35.5
NH_4^+/H_2O	−22.00	−20.62	−18.18	−22.75	−22.95	−22.21	
	−20.17	−19.06	−16.55	−20.97	−21.32	−20.23	−21.6
HCC^-/H_2O	−19.06	−17.83	−15.72	−20.03	−21.13	−18.75	
	−16.65	−15.76	−13.64	−17.65	−19.22	−15.88	−18.4
$\overline{\lvert x\rvert}$	1.0	3.0	4.3	0.9	1.5	1.2	
Root mean square	1.2	3.0	4.4	1.0	2.0	1.4	

[a] Ref. [8]

Table 5. Basis set superposition error (*BSSE*) corrections to hydrogen binding energies (kcal/mol)

Molecules	B3LYP	VSXC	Meta-GGA	PBE1PBE	PBE	BHLYP
HF/HF	0.50	0.54	0.34	0.53	0.55	0.49
HCl/HCl	0.34	0.33	0.23	0.38	0.38	0.33
H_2O/H_2O	0.81	0.84	0.60	0.84	0.90	0.75
HF/HCN	0.37	0.36	0.34	0.41	0.43	0.36
HF/H_2O	1.13	1.04	1.03	1.17	1.26	1.03
CN^-/H_2O	0.33	0.27	0.43	0.37	0.42	0.29
OH^-/H_2O	1.61	2.30	2.64	1.59	2.33	1.13
HCC^-/H_2O	0.30	0.42	0.41	0.32	0.41	0.25
H_3O^+/H_2O	1.42	1.45	1.45	1.48	0.28	1.38
NH_4^+/H_2O	0.84	0.79	0.78	0.90	0.06	0.80

for the nonionic species when the zero-point vibrational energy is not included (mean absolute error of 1.3 kcal/mol), but this functional has the lowest accuracy when this correction is included (mean absolute error of 2.0 kcal/mol).

VSXC also underestimates the binding energies for the ionic systems. Although VSXC does not accurately render hydrogen-bonded structures (mean absolute errors for all complexes considered here of 0.15 Å and 4.4° for bond lengths and angles, respectively), this functional gives the best overall results for the energetics of the nonionic structures when the zero-point vibrational correction is added in (mean absolute error of 0.9 kcal/mol).

The PBE1PBE functional yields the best performance for predicting hydrogen binding energies, with a mean absolute error of 1.3 and 0.9 kcal/mol, for the nonionic and ionic molecules considered here, respectively. B3LYP and BHLYP give comparable results for both the nonionic and ionic molecules. As illustrated in Tables 3–6, the nonhybrid PBE functional also produces quality hydrogen binding energies (mean absolute errors of 1.3 and 1.5 kcal/mol for the nonionic and ionic systems listed here, respectively). When the BSSE correc-

Table 6. Statistical total errors (ionic + nonionic) of binding energies (kcal/mol) and geometries (Å and degrees)

	B3LYP	VSXC	Meta-GGA	PBE1PBE	PBE	BHLYP
Bonds						
$\overline{\lvert x\rvert}$	0.03	0.13	0.17	0.05	0.06	0.04
Root mean square	0.05	0.15	0.23	0.07	0.07	0.06
Max. dev. (+)	0.08	−0.01	−0.00	0.16	0.15	0.10
Max. dev. (−)	0.12	0.26	0.57	0.04	0.02	0.13
Angles						
$\overline{\lvert x\rvert}$	2.4	4.4	3.4	2.5	3.4	2.9
Root mean square	3.9	5.6	5.1	4.0	4.9	4.3
Max. dev. (+)	9.1	9.4	11.4	9.6	10.8	10.0
Max. dev. (−)	8.6	11.5	10.6	9.1	11.1	8.3
Binding energy including ZPVE						
$\overline{\lvert x\rvert}$	1.2	1.9	3.2	1.1	1.4	1.3
Root mean square	1.3	2.2	3.5	1.2	1.7	1.4
Max. dev. (+)	1.4	1.1	−1.0	1.7	3.8	1.6
Max. dev. (−)	1.9	3.5	5.1	1.5	1.3	2.5
Binding energy including ZPVE and BSSE						
$\overline{\lvert x\rvert}$	1.5	2.6	3.8	1.0	1.1	1.6
Root mean square	1.6	3.1	4.3	1.2	1.3	1.7
Max. dev. (+)	1.0	0.7	−1.3	1.3	1.8	1.3
Max. dev. (−)	2.7	5.3	6.2	2.3	2.2	2.8

tions are included, the PBE1PBE and PBE functionals yield the best overall binding energies (mean absolute errors of 1.0 and 1.1 kcal/mol, respectively, over the benchmark set), with B3LYP and BHLYP producing quality results (mean absolute errors of 1.5 and 1.6 kcal/mol, respectively). From our data it seems that, in general, the τ-dependent functionals (especially meta-GGA) do not adequately describe hydrogen binding energies.

4 Conclusion

We have assessed the accuracy of six DFT functionals (B3LYP, BHLYP, VSXC, meta-GGA, PBE, and PBE1PBE) for calculating hydrogen-bonded structures and binding energies. For a test set consisting of five ionic and five nonionic systems, the three hybrid functionals studied here, B3LYP, BHLYP, and PBE1PBE, yield the best results. The B3LYP and BHLYP functionals produce the most accurate hydrogen-bonded structures. Although the τ-dependent functionals studied here (VSXC and meta-GGA) yield good results for the binding energies of the nonionic systems, they do not give accurate results for the ionic systems. The τ-dependent functionals also do not accurately describe hydrogen-bonded system geometries for the nonionic systems. Meta-GGA does fairly well at predicting the geometries of ionic systems, unlike the VSXC functional. The accuracy of τ-dependent functionals for describing hydrogen-bonding properties had not been previously studied. Our results indicate that these types of functionals might not be the appropriate choice for a hydrogen-bonded system. Overall, the hybrid functionals studied here produce more accurate hydrogen-bond lengths and binding energies than the τ-dependent functionals.

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