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Behavior of Density Functionals with Respect to Basis Set. 3. Basis Set Superposition Error†

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The impact of basis set superposition error (BSSE) upon molecular properties determined using the density functionals B3LYP, B3PW91, B3P86, BLYP, BPW91, and BP86 in combination with the correlation consistent basis sets [cc-pVnZ, where n = D(2), T(3), Q(4), and 5] for a set of first-row closed-shell molecules has been examined. Correcting for BSSE enables the irregular convergence behavior in molecular properties such as dissociation energies with respect to increasing basis set size, noted in earlier studies, to be improved. However, for some molecules and functional combinations, BSSE correction alone does not improve the irregular convergence behavior.

I. Introduction

The correlation consistent basis sets[1−9] provide an effective means to gauge the performance of ab initio methods. This is due to the systematic construction of the sets, which enables the complete basis set (CBS) limit to be ascertained. At the CBS limit, no further modification to the basis set will result in a change in the total energy; thus, any remaining error—the intrinsic error—is isolated from possible basis set errors and can be attributed to the choice of approximate method alone. This has also led to a greater understanding of apparent errors—errors arising from the choice of both basis set and ab initio method. As a result, a now well-established hierarchy of ab initio methods has emerged. A key characteristic of the correlation consistent basis sets is that the CBS limit for many molecular properties can be estimated quite simply, using schemes such as those introduced by Feller[10] and Halkier et al.,[11] albeit the use of the larger correlation consistent basis sets in combination with ab initio methods such as CCSD(T) quickly becomes prohibitive in terms of computational cost.

Density functional theory has provided a cost-effective approach for treating larger molecules as compared with high-level ab initio methods. Due to significant advances in density functional methodology (i.e., improved density functionals and hybrid methods such as B3LYP[12]), the methods are also known for their favorable prediction of properties ranging from geometries to reaction energies. The methodology continues to evolve, and the development of new functionals is a highly active area of research.[13−17] Thus, with both existing functionals and new functionals, there is a need for a general means to evaluate functional reliability. Such a means would help to establish a hierarchy of functional performance.

A simple means to assess the performance of density functionals is needed, as it could aid in the emergence of a hierarchy of functionals and lead to a greater understanding of the interplay of functional and basis set. The correlation consistent basis sets have provided such as means for ab initio methods. However, it is not clear whether this means could be applied to density functional theory, as the correlation consistent basis sets were developed using configuration interaction with single and double excitations (CISD). Thus, the performance of density functionals with respect to increasing correlation consistent basis set size has been investigated.[18−20]

In a previous study,[19] irregular convergence behavior for dissociation energies with respect to increasing correlation consistent basis set size was noted for several density functionals. A second study of a similar systematic series of basis sets, the polarization consistent basis sets, developed by Jensen[21] explicitly for density functional theory, also reported irregular convergence of energetic properties with respect to increasing basis set size.[20] As occasional irregularity in molecular properties (i.e., bond lengths) with respect to increasing basis set size has been observed for methods such as coupled cluster with single, double, and quasiperturbative triple excitations (CCSD(T)) and has been resolved by accounting for basis set superposition error,[22] we investigate the impact of basis set superposition error upon the convergence of energetics determined using DFT.

Basis set superposition error (BSSE) arises from the overdescription of a molecule or complex relative to the atoms or molecular fragments of the molecule or complex.[23] To illustrate a simple case, the supermolecule approach can be used to define the interaction energy, ΔE, as the energy of supermolecule AB minus the energies of the separated fragments A and B as shown below:

$$\Delta E(R) = E_{AB}(R) - E_A - E_B \qquad (1)$$

where R represents the distance between A and B. When $R = \infty$, E_A and E_B are the energies of the separate fragments, and for a size-consistent quantum mechanical method, $E_{AB}(R)$ is equal to the sum of the energies of A and B. For smaller distances, R, and finite basis sets, fragment A within complex AB can attempt to compensate for its own basis set deficiencies by utilizing the basis set on B, and fragment B can make use of the basis set on A. This results in an artificial lowering of the energy of the complex, as fragment energies, E_A and E_B, do not benefit from the use of additional basis functions (i.e., E_A does not benefit from B's basis functions).[24] This is basis set superposition error. At the complete basis set (CBS) limit—the limit at which no further enhancement to the basis set will change the results—there is no BSSE, as each fragment within the complex receives no gain from the use of additional functions from the other fragment.

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Though there have been a number of approaches suggested to account for BSSE,[25−32] the most widely used approach is the counterpoise approach of Boys and Bernardi,[33] where the energies of the separate fragments are allowed to benefit from the basis set upon the other fragments, e.g., the separate fragment A also utilizes the basis set of B. For example, the interaction energy defined in eq 1 now becomes the counterpoise corrected interaction energy

$$\Delta E^{\mathrm{CP}}(R) = E_{\mathrm{AB}}(R) - E_{\mathrm{A}}^{\{\mathrm{AB}\}} - E_{\mathrm{B}}^{\{\mathrm{AB}\}} \qquad (2)$$

where $E_{\mathrm{A}}^{\{\mathrm{AB}\}}$ represents the energy of fragment A, in the presence of both A's and B's basis sets, and similarly for fragment B. This correction has played a particularly important role in accounting for BSSE in weakly bound systems, where BSSE is widely known to be significant. (For recent examples, see refs 34−36.)

As mentioned earlier, accounting for BSSE can be important in the improvement of the convergence of molecular properties with respect to increasing correlation consistent basis set size. A number of studies of weakly bound systems have demonstrated that energies which have been corrected for BSSE and those that have not will converge to the same CBS limit; however, the corrected energies will converge more quickly.[10,37−42] The largest BSSE occurs for the double-ζ basis set and, overall, systematically decreases with respect to increasing correlation consistent basis set size until the CBS limit for the molecular property is reached. Interestingly, previous work has shown that irregularities in the convergence of molecular properties (i.e., geometries) with respect to increasing basis set size can be remedied.[10,37−42] Much of this previous work has utilized correlated ab initio methods such as MP2 and CCSD(T). There have been fewer studies of the impact of BSSE in DFT calculations (due largely to known deficiencies in the treatment of weakly bound systems by common DFT methods). One noteworthy investigation is that by Rappe and Bernstein, where binding energies for several nonbonded systems determined using HF, MP2, CCSD(T), and B3LYP in combination with correlation consistent and Pople basis sets were reported.[43] Though the energetic predictions by B3LYP of the nonbonded systems were inadequate, correcting for BSSE did improve the convergent behavior of the energies with respect to increasing size of the correlation consistent basis sets.

While there has been much focus upon the effect of BSSE upon weakly bound systems, the impact of BSSE upon strongly bound systems also can be significant. Dunning, et al. have investigated the effect of BSSE on strongly bound systems using correlated ab initio methods with correlation consistent basis sets.[4,22,39,44] These studies have demonstrated that the effect of BSSE on strongly bound systems is not insignificant, especially for low-level basis sets.

In this study, the effect of BSSE on the convergence behavior of atomization energies computed using several combinations of density functionals with standard and augmented correlation consistent basis sets is examined. The objective is to determine whether BSSE correction enables the irregular convergence with respect to increasing basis set size, noted in early work, to be remedied.

II. Computational Details

The BSSE was corrected using the counterpoise method, as implemented in the Gaussian 98 package suite.[45] BSSE-corrected energies, geometries, and frequencies were determined for each combination of density functional (B3LYP,[12,46] B3PW91,[47] and B3P86,[48] and BLYP,[49] and BPW91, and BP86) and basis set [cc-pV*n*Z and aug-cc-pV*n*Z (n = D(2), T(3), Q(4), and 5)]. Uncorrected results were obtained from previous calculations.[19] BSSE-corrected and uncorrected zero-point energies were obtained from the corresponding frequency calculations and have been included in the determination of the BSSE-corrected and uncorrected atomization energies, respectively.

III. Results and Discussion

A. The Effect of BSSE on Structures. Prior studies on the impact of BSSE on the geometries of weakly bound systems have indicated that the effect of BSSE on geometries is smaller for density functional methods than for ab initio methods such as MP2.[50] As well, generally, it is believed that the stronger the interaction is, the smaller the effect of BSSE on geometries, frequencies, and energies. In this study, all molecules studied are strongly bound systems. Thus, it is expected that the impact of BSSE on the geometries and frequencies will be quite small.

The uncorrected and BSSE-corrected geometries, provided in Table S1, were determined using the six density functionals with the cc-pV*n*Z and aug-cc-pV*n*Z basis sets. From our earlier study, three molecules, CO, N_2, and HOF, were chosen as representative examples of the test systems in our earlier study. As expected, overall, for these systems, the effect of BSSE on geometries is small, even at the double-ζ basis set level. The impact of BSSE upon bond length is less than 0.001 Å and upon bond angle is less than 0.2°. With increasing basis set size, both uncorrected and BSSE-corrected geometries converge to the same basis set limit.

Though molecular properties, such as geometries and frequencies, do not necessarily converge toward a basis set limit as basis set size is increased,[22] in this work, the bond lengths and angles do converge toward the basis set limit as basis set size is increased. This convergence toward the Kohn−Sham limit, however, is not likely best described by the Feller exponential extrapolation scheme,[10] though the scheme is commonly used to determine CBS limits of molecular properties that have been calculated using ab initio methods in combination with a series of correlation consistent basis sets of increasing size. The effect of BSSE upon frequencies was also examined, and the impact was trivial.

B. The Effect of BSSE on Atomization Energies. A common assumption is that, for strongly bound molecules, the effect of BSSE on energy is minimal. However, earlier work by Wilson et al. has found that, for advanced correlated ab initio methods used in combination with small basis sets, BSSE is not insignificant in calculating the energy of strongly bound systems.[4] For example, a BSSE of 5 kcal/mol for the N_2 binding energy at the CCSD(T)/cc-pVDZ level was observed. Though the impact for DFT approaches is expected to be smaller than for ab initio methods, it is important to understand the impact of BSSE for DFT upon strongly bound systems, particularly upon the irregular convergence behavior of atomization energies noted in earlier work.

As shown in Table 1, the largest BSSE was observed at the double-ζ level, and the BSSE decreases with increasing basis set size. For example, with BLYP/cc-pVDZ, the BSSE of CO_2 is 7.11kcal/mol, and it rapidly drops to 2.25 kcal/mol at the triple-ζ level, 1.36 kcal/mol at the quadruple-ζ level, and finally to 0.28 kcal/mol at the quintuple-ζ level. The impact upon N_2 is much smaller (1.54 kcal/mol) at the double-ζ level, significantly less than the ∼5 kcal/mol noted for CCSD(T)/cc-pVDZ in earlier work, and quickly decreases to 0.38, 0.33, and 0.09 at the triple-, quadruple-, and quintuple-ζ levels, respectively.

TABLE 1: Basis Set Superposition Error in the Atomization Energies Calculated Using DFT in Combination with the Correlation Consistent Basis Sets[a]

molecules	basis sets	B3LYP	B3PW91	B3P86	BLYP	BPW91	BP86
H_2O	cc-pVDZ	3.51	2.84	2.73	4.47	3.44	3.48
	T	0.46	0.84	0.77	1.34	1.05	1.02
	Q	0.46	0.39	0.34	0.67	0.54	0.50
	5	0.08	0.07	0.06	0.14	0.12	0.11
	aug-cc-pVDZ	0.49	0.50	0.48	0.59	0.53	0.50
	T	0.18	0.25	0.25	0.18	0.26	0.24
	Q	0.12	0.12	0.13	0.15	0.15	0.16
	5	0.03	0.03	0.03	0.05	0.04	0.04
HF	cc-pVDZ	1.75	1.43	1.38	2.26	0.96	0.97
	T	0.40	0.32	0.29	0.24	0.19	0.18
	Q	0.20	0.16	0.14	0.16	0.13	0.12
	5	0.04	0.03	0.03	0.04	0.03	0.03
	aug-cc-pVDZ	0.25	0.25	0.24	0.46	0.45	0.43
	T	0.14	0.18	0.17	0.09	0.12	0.12
	Q	0.08	0.09	0.10	0.10	0.10	0.10
	5	0.02	0.02	0.02	0.03	0.03	0.03
HCN	cc-pVDZ	1.58	1.19	1.17	2.43	1.65	1.75
	T	0.44	0.39	0.36	0.65	0.54	0.52
	Q	0.34	0.30	0.26	0.55	0.45	0.41
	5	0.08	0.06	0.05	0.12	0.10	0.09
	aug-cc-pVDZ	0.91	0.99	0.92	1.26	1.14	1.05
	T	0.34	0.43	0.44	0.45	0.57	0.55
	Q	0.26	0.23	0.24	0.38	0.32	0.67
	5	0.05	0.04	0.04	0.08	0.05	0.06
CO	cc-pVDZ	2.68	2.15	2.10	2.67	2.13	2.20
	T	0.74	0.62	0.57	0.82	0.66	0.64
	Q	0.42	0.35	0.30	0.54	0.44	0.41
	5	0.08	0.07	0.06	0.13	0.11	0.09
	aug-cc-pVDZ	0.71	0.78	0.73	0.70	0.83	0.79
	T	0.27	0.36	0.35	0.30	0.43	0.40
	Q	0.18	0.17	0.18	0.24	0.21	0.22
	5	0.04	0.03	0.04	0.06	0.05	0.05
N_2	cc-pVDZ	1.17	0.89	0.90	1.54	1.12	1.18
	T	0.26	0.22	0.21	0.38	0.31	0.31
	Q	0.21	0.18	0.16	0.33	0.27	0.25
	5	0.06	0.04	0.04	0.09	0.07	0.06
	aug-cc-pVDZ	0.87	0.91	0.87	1.02	1.03	0.97
	T	0.24	0.30	0.30	0.30	0.38	0.38
	Q	0.18	0.16	0.17	0.24	0.21	0.22
	5	0.04	0.03	0.03	0.07	0.05	0.05
HNO	cc-pVDZ	2.34	1.85	1.81	3.02	2.26	2.33
	T	0.59	0.48	0.45	0.79	0.61	0.60
	Q	0.36	0.40	0.35	0.53	0.43	0.52
	5	0.11	0.10	0.08	0.16	0.11	0.11
	aug-cc-pVDZ	0.97	1.06	1.00	1.00	1.06	0.98
	T	0.27	0.37	0.37	0.28	0.40	0.38
	Q	0.20	0.19	0.21	0.26	0.24	0.25
	5	0.05	0.04	0.04	0.08	0.06	0.06
HOF	cc-pVDZ	4.42	3.70	3.57	5.52	4.42	4.45
	T	1.21	1.01	0.94	1.57	1.24	1.22
	Q	0.52	0.46	0.40	0.69	0.64	0.59
	5	0.09	0.09	0.09	0.18	0.16	0.12
	aug-cc-pVDZ	0.87	0.95	0.90	0.86	0.92	0.86
	T	0.31	0.42	0.41	0.24	0.40	0.37
	Q	0.18	0.19	0.21	0.21	0.22	0.24
	5	0.05	0.05	0.06	0.08	0.07	0.08
CO_2	cc-pVDZ	5.60	4.52	4.41	7.11	5.44	5.58
	T	1.69	1.41	1.31	2.25	1.77	1.73
	Q	0.92	0.77	0.67	1.36	1.09	1.01
	5	0.17	0.16	0.13	0.28	0.25	0.21
	aug-cc-pVDZ	1.65	1.80	1.71	1.86	1.93	1.81
	T	0.60	0.77	0.76	0.67	0.88	0.84
	Q	0.38	0.36	0.38	0.50	0.46	0.48
	5	0.09	0.07	0.07	0.13	0.10	0.10

[a] The energies are in kcal/mol

As noted for ab initio methods, DFT in combination with aug-cc-pV*n*Z shows less BSSE as compared with cc-pV*n*Z, especially for the lower-level basis sets. For example, the BSSE is reduced to 1.86 kcal/mol for CO_2 with aug-cc-pVDZ, as compared to 7.11 kcal/mol for cc-pVDZ. In general, the BSSE does decrease as the basis set size increases. For several cases, similar amounts of BSSE were noted at the triple- and quadruple-ζ basis set levels. Examples include the BSSE for H_2O (B3LYP/cc-pV*n*Z) and N_2 (all functionals/cc-pV*n*Z), while the BSSE at the quintuple-ζ level drops ($<$0.2 kcal/mol). For

TABLE 2: Uncorrected (no corr.) and BSSE-Corrected (corr.) Atomization Energies (in kcal/mol)[a]

		B3LYP		B3PW91		B3P86		BLYP		BPW91		BP86	
exptl[b]	basis sets	no corr.	corr.	no corr.	corr.	no corr.	corr.	no corr.	corr.	no corr.	corr.	no corr.	corr.
H_2O													
219.3	cc-pVDZ	206.14	202.64	205.40	202.56	214.10	211.46	207.84	203.40	207.40	203.96	215.95	212.61
	T	214.85	214.38	213.37	212.53	222.22	221.49	216.81	215.48	215.59	214.54	224.29	223.35
	Q	216.78	216.32	215.02	214.63	223.87	223.59	218.91	218.24	217.33	216.79	226.08	225.71
	5	217.57	217.49	215.66	215.58	224.51	224.48	219.81	219.67	218.03	217.90	226.81	226.78
	aug-cc-pVDZ	215.20	214.70	213.56	213.06	222.36	222.11	217.53	216.93	215.99	215.45	224.74	224.52
	T	217.29	217.10	215.47	215.22	224.31	223.96	219.59	219.39	217.91	217.64	226.69	226.29
	Q	217.83	217.71	215.89	215.77	224.73	224.49	220.17	220.02	218.34	218.19	227.12	226.80
	5	217.86	217.82	215.91	215.88	224.74	224.50	220.20	220.15	218.35	218.31	227.12	226.64
HF													
135.2	cc-pVDZ	124.58	122.82	124.61	123.17	129.11	127.73	126.08	123.81	126.34	125.38	130.60	129.66
	T	131.30	130.89	130.80	130.48	135.35	135.06	133.07	132.83	132.76	132.58	137.11	136.93
	Q	132.78	132.58	132.06	131.89	136.59	136.45	134.74	134.59	134.13	134.01	138.49	138.38
	5	133.37	133.33	132.53	132.49	137.04	137.02	135.43	135.39	134.68	134.65	139.04	139.03
	aug-cc-pVDZ	132.00	131.77	131.35	131.11	135.82	135.65	134.17	133.74	133.57	133.14	137.89	137.55
	T	133.28	133.15	132.52	132.34	137.04	136.89	135.41	135.32	134.73	134.60	139.10	138.99
	Q	133.57	133.48	132.72	132.62	137.22	137.14	135.72	135.62	134.93	134.83	139.30	139.20
	5	133.56	133.54	132.70	132.68	137.20	137.16	135.71	135.71	134.91	134.88	139.27	139.18
HCN													
301.8	cc-pVDZ	295.79	294.25	294.45	293.29	303.84	303.02	303.84	302.50	303.43	301.80	311.77	310.64
	T	302.78	302.35	300.73	300.35	310.36	310.35	310.36	310.75	309.19	308.66	317.62	317.65
	Q	303.74	303.43	301.65	301.37	311.29	311.22	311.21	311.70	309.99	309.55	318.42	318.19
	5	303.63	303.58	301.59	301.55	311.26	310.66	310.92	310.80	309.80	309.70	318.25	317.11
	aug-cc-pVDZ	295.68	294.79	294.42	293.44	303.92	303.10	303.12	302.87	302.88	301.76	311.19	310.53
	T	302.60	302.26	300.68	300.25	310.39	309.44	310.46	311.04	308.93	308.36	317.40	316.21
	Q	303.58	303.27	301.51	301.30	311.22	311.10	310.89	311.54	309.73	309.38	318.21	317.70
	5	303.60	303.57	301.58	301.55	311.25	310.79	310.85	310.78	309.73	309.68	318.20	317.69
CO													
256.2	cc-pVDZ	295.79	294.25	248.77	246.62	254.18	252.08	256.35	253.69	257.70	255.58	261.90	259.71
	T	302.78	302.35	252.23	251.61	257.84	257.26	259.25	258.44	260.43	259.77	264.71	264.06
	Q	303.74	303.43	252.97	252.63	258.61	258.30	259.76	259.22	260.99	260.55	265.25	264.84
	5	303.63	303.58	252.76	252.69	258.43	258.37	259.26	259.14	260.63	260.52	264.90	264.81
	aug-cc-pVDZ	295.68	294.79	247.79	247.01	253.33	252.59	254.29	253.59	256.05	255.22	260.22	259.43
	T	302.60	302.26	251.68	251.32	257.36	257.01	258.66	258.36	259.60	259.17	263.88	263.48
	Q	303.58	303.27	252.66	252.49	258.36	258.18	259.16	258.92	260.51	260.30	264.81	264.59
	5	303.60	303.57	252.73	252.70	258.42	258.38	259.19	259.13	260.55	260.51	264.85	264.85
N_2													
225.1	cc-pVDZ	248.42	245.74	215.60	214.71	223.51	222.62	231.22	229.69	228.07	226.95	235.22	234.04
	T	252.12	251.38	221.50	221.28	229.52	229.31	236.49	236.11	233.12	232.81	240.24	239.94
	Q	252.84	252.42	222.40	222.22	230.46	230.30	237.27	236.94	233.87	233.60	241.03	240.78
	5	252.56	252.47	222.46	222.41	230.55	230.51	237.19	237.10	233.83	233.76	241.00	240.93
	aug-cc-pVDZ	247.20	246.49	215.88	214.97	223.84	222.97	230.53	229.51	227.71	226.67	234.80	233.83
	T	251.36	251.09	221.48	221.19	229.58	229.27	236.25	235.94	232.93	232.54	240.10	239.72
	Q	252.47	252.28	222.50	222.34	230.60	230.43	237.33	237.09	233.90	233.68	241.08	240.14
	5	252.53	252.48	222.60	222.56	230.68	230.65	237.38	237.31	233.98	233.92	241.14	241.09
HNO													
198.7	cc-pVDZ	192.98	190.63	190.78	188.93	200.74	198.99	206.22	203.21	204.55	202.29	213.96	211.74
	T	196.94	196.35	194.78	194.30	204.91	204.50	209.05	208.25	207.57	206.97	217.00	216.45
	Q	198.00	197.64	195.78	195.39	205.94	205.69	209.98	209.44	208.47	208.03	217.91	217.53
	5	198.13	198.03	195.92	195.83	206.11	206.03	209.96	209.81	208.49	208.37	217.95	217.82
	aug-cc-pVDZ	194.64	193.67	192.76	191.69	202.86	201.95	206.87	205.87	205.69	204.64	215.10	214.29
	T	197.27	197.01	195.17	194.81	205.37	204.84	209.08	208.80	207.73	207.34	217.22	216.61
	Q	198.26	198.07	196.04	195.85	206.24	205.98	210.12	209.86	208.62	208.38	218.11	217.79
	5	198.29	198.25	196.07	196.03	206.26	206.06	210.14	210.05	208.63	208.57	218.11	217.80
HOF													
151.9	cc-pVDZ	144.19	139.75	142.49	138.77	150.51	146.97	156.42	150.92	154.70	150.26	162.29	157.92
	T	148.35	147.15	147.16	146.16	155.33	154.42	159.55	157.97	158.52	157.29	166.15	164.99
	Q	148.77	148.25	147.59	147.14	155.80	155.45	159.85	159.17	158.85	158.21	166.49	166.01
	5	148.75	148.66	147.57	147.48	155.81	155.75	159.73	159.54	158.72	158.55	166.39	166.35
	aug-cc-pVDZ	146.71	145.85	145.52	144.58	153.73	152.99	158.10	157.28	157.05	156.14	164.70	164.08
	T	148.50	148.19	147.42	147.01	155.68	155.17	159.44	159.20	158.58	158.18	166.27	165.75
	Q	148.83	148.64	147.66	147.47	155.92	155.64	159.80	159.58	158.81	158.58	166.50	166.16
	5	148.82	148.77	147.63	147.59	155.88	155.63	159.79	159.71	158.77	158.70	166.45	166.01
CO_2													
381.9	cc-pVDZ	375.18	369.60	378.49	373.98	387.69	383.30	390.46	383.35	395.87	390.43	402.33	396.76
	T	380.63	378.97	383.85	382.44	393.37	392.07	394.00	391.77	399.60	397.84	406.14	404.41
	Q	381.49	380.57	384.74	383.99	394.30	393.61	394.46	393.11	400.18	399.09	406.67	405.65
	5	380.95	380.78	384.34	384.18	393.98	393.85	393.52	393.24	399.48	399.23	406.02	406.73
	aug-cc-pVDZ	372.82	371.18	376.99	375.20	386.43	384.72	386.01	384.17	392.80	390.89	399.17	397.37
	T	379.21	378.62	382.80	382.03	392.49	391.73	392.31	391.65	397.98	397.10	404.55	403.72
	Q	380.85	380.47	384.22	383.87	393.92	393.53	393.38	392.88	399.33	398.88	405.92	405.45
	5	380.86	380.77	384.25	384.18	393.92	393.85	393.32	393.20	399.30	399.20	405.88	405.78

[a] The BSSE-corrected atomization energies include BSSE-corrected zero-point energies. Thus, the differences between uncorrected and corrected energies in this table are not necessarily equal to the values given for BSSE in Table 1, where the effects of zero-point energies have not been included. [b] Reference 51.

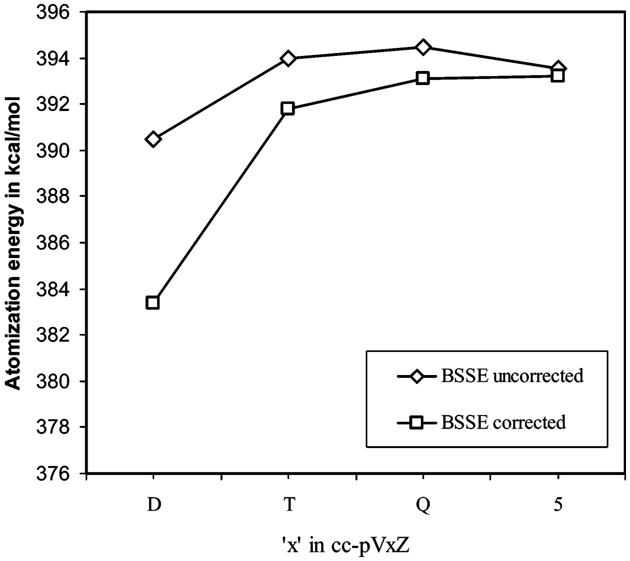

Figure 1. A comparison of BSSE-corrected and uncorrected atomization energies for CO_2, reported in kcal/mol.

all molecules but HF, the pure functionals BLYP, BPW91, and BP86 result in a larger BSSE at the double-ζ level than the hybrid functionals B3LYP, B3PW91, and B3P86, respectively. For the HF molecule, BLYP predicts a larger BSSE than B3LYP, while BPW91 and BP86 give smaller BSSE than B3PW91 and B3P86.

C. The Effect of BSSE on the Convergence Behavior of Atomization Energies. The BSSE-corrected and uncorrected atomization energies for eight molecules are presented in Table 2. The previous section discussed that, for DFT, the BSSE is nonnegligible at the double-ζ level, even for strongly bound systems. However, relative to the energy change due to the basis set effect (difference between energies calculated at the double- and quintuple-ζ levels), the energy change arising from BSSE is small. For the B3LYP/cc-pVDZ atomization energy of H_2O, the energy change due to the basis set effect is about 11 kcal/mol, while the BSSE results in an energy change of 3.51 kcal/mol. It must be noted that these two effects are in opposite directions. The basis set effect increases the atomization energy, whereas the BSSE effect decreases the atomization energy.

Another effect of BSSE on the atomization energy is that the convergence behavior of atomization energy is improved for most of the molecules. As compared with the irregular convergence behavior of the uncorrected energies, which have a slight dip at the quintuple-ζ level, the corrected atomization energies generally converge smoothly toward the saturated, or Kohn−Sham limit. However, this improvement does not occur for all molecules and functionals. In general, the irregular convergence observed for the hybrid functionals has been improved for almost all molecules. For pure functionals, the convergence behavior for some of the molecules is not improved, and even worsens. Examples include HCN when BLYP and BP86 are used in combination with cc-pV*n*Z and CO when BLYP, BPW91, and BP86 are used with cc-pV*n*Z.

The uncorrected and corrected B3LYP/cc-pV*n*Z atomization energies for CO_2 with increasing basis set size are provided in Figure 1. Among all of the molecules studied, CO_2 shows the largest dip (∼0.5 kcal/mol) for the uncorrected atomization energies. As expected, both uncorrected and corrected atomization energies converge to the same basis set limit. The main differences resulting from the BSSE corrections occur for energies at the double-, triple-, and quadruple-ζ levels. These corrections lead to improved convergence behavior of the energies.

IV. Conclusions

Though the effect of BSSE on geometry is small for molecules in this study, the impact of BSSE upon atomization energies is not insignificant. The largest BSSE occurs at the double-ζ level and decreases with increasing basis set size. Overall, accounting for the BSSE through the counterpoise procedure restores the convergent behavior of the energies toward the saturated basis set limit. For molecule/functional combinations where uncorrected energies converge smoothly to the saturated basis set limit, both the BSSE-corrected and uncorrected energies converge toward the same limit, as expected. For HCN and CO energies, the BSSE correction did not correct the irregular convergence behavior, most notably for the pure density functionals. The improvements in convergence behavior observed in this work can be largely attributed to changes at the triple- and quadruple-ζ basis set levels.

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Supporting Information Available: The BSSE-corrected and uncorrected geometries are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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