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REGULAR ARTICLE

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Binding energies of hydrogen-bonded clusters from extrapolation-oriented basis sets

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Abstract The MP2 and CCSD(T) basis set limit binding energies of various hydrogen-bonded clusters were estimated via basis set extrapolation employing the correlation consistent aug-cc-pVDZ and modified aug-cc-pVDZ set containing extra polarization functions from cc-pVTZ set. By adopting the optimal interval for the difference between the cardinal numbers (X) corresponding to two basis sets in the X^{-3} type extrapolation scheme the estimated binding energies for $(H_2O)_n$ and $(HF)_n$ ($n = 3 - 5$) are shown to be close to the reference basis set limit values within the error bounds in many cases, manifesting the significance of these basis sets in studying the structures and binding of large hydrogen-bonded clusters.

1 Introduction

In an effort to reduce the size of a basis set without sacrificing the accuracy in an ab initio correlated calculation using correlation consistent (aug-)cc-pVXZ(X =D(2),T(3),Q(4),5) basis set [1–6], Huh and Lee [7] recently devised a basis set extrapolation formula of $(X+\gamma)^{-3}$ where γ is varied to accurately estimate the basis set limit of the correlation energy according to correlation treatment and quality of the basis sets employed. Among their various extrapolation formulas suggested for specific basis set sequence, the most useful formula practically applicable to large clusters would be the formula corresponding to the smallest basis set sequence of cc-pVDZ and cc-pVTZ. However, even in this case, since one must perform ab initio correlated calculations using the basis sets up to cc-pVTZ set (which is composed of [4s3p2d1f] for the second row elements), the computational task would still be very demanding as the system becomes larger and eventually limits the size of the molecular systems which can be studied by the ab inito method. It would be highly desirable if one could develop a basis set smaller than cc-pVTZ, yet effective enough to be used for extrapolation with cc-pVDZ set to yield the reliable CBS (complete basis set) limit correlation energy. In this article, we explore the possibility of reducing the size of the basis sets required for extrapolation to the basis set limit in ab initio correlated calculations further, which would provide an effective path for studying the accurate structures and energetics of large molecular clusters. In the next section we explain how one can construct a new basis set suitable for extrapolation to the basis set limit with cc-pVDZ set as well as extrapolation procedure. The results and discussion for the application of this extrapolation method to various hydrogen-bonded clusters are given in Sect. 3. The concluding remarks are in sect. 4.

2 Extrapolation scheme and basis sets

We start from the MP2 [8] and CCSD(T) [9] level extrapolation formula for cc-pVDZ and cc-pVTZ basis sets by Huh and Lee [7],

$$E_{corr}(\infty) = E_{corr}(X) + A/(X + \gamma)^3 \tag{1}$$

Here, $E_{corr}(X)$ and $E_{corr}(\infty)$ represent the correlation energy with the cc-pVXZ(X = D,T) and complete basis set, respectively, with correlation dependent parameter γ equal to 1 at the MP2 and 1/2 at the CCSD(T) level. The cardinal number X varies from 2 for cc-pVDZ to 3 for cc-pVTZ set, so the interval between the cardinal numbers for DZ and TZ set corresponds to 1.0 in this case. For two-point extrapolation employing the correlation energies with cc-pVDZ and cc-pVTZ sets, we can use, it is true, alternative formulas such as $X^{-\beta}$ (with optimized β) [10] or extrapolation scheme exploiting the similar basis set convergence behavior of monomer and cluster correlation energies [11]. We nevertheless adopted the extrapolation formula of Eq. 1 in

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Table 1 CBS limit binding energy estimates[a] from extrapolations with aug-cc-pVDZ and aug-cc-pVTZ basis sets

	MP2					CCSD(T)				
Cluster[b]	$\Delta E_1(\infty)$[c]	$\Delta E_2(\infty)$[d]	$\Delta E_3(\infty)$[e]	$\Delta E_4(\infty)$[f]	$\Delta E_{ref}(\infty)$[g]	$\Delta E_1(\infty)$[c]	$\Delta E_2(\infty)$[d]	$\Delta E_3(\infty)$[e]	$\Delta E_4(\infty)$[f]	$\Delta E_{ref}(\infty)$[g]
He_2	18.5(47.7)	21.5(50.7)	22.6(51.8)	19.5(48.7)	21.4(50.6)[h]	30.8(60.0)	32.7(61.9)	35.2(64.4)	30.8(60.0)	33.8(63.0)[i]
$(H_2O)_2$	7.67(2.05)	7.83(2.21)	7.90(2.28)	7.79(2.17)	7.82(2.20)[j]	7.79(2.17)	7.89(2.27)	8.03(2.41)	7.86(2.24)	7.87(2.25)[k]
$(HF)_2$	6.87(0.94)	7.01(1.08)	7.06(1.13)	6.99(1.06)	7.04(1.11)[j]	7.10(1.17)	7.18(1.25)	7.30(1.37)	7.19(1.26)	7.22(1.29)[l]

[a] All CBS limit binding energy estimates including reference values are the sum of correlation part (values in parentheses) and Hartree-Fock part which were taken as the CP corrected Hartree-Fock binding energies with aug-cc-pV5Z basis set. Binding energies are in units of mE_h except He_2 which is in units of μE_h

[b] He-He distance is 5.6 a.u.. The geometries of $(H_2O)_2$ and $(HF)_2$ are from Ref. [14]

[c] The correlation part of $\Delta E_1(\infty)$ is obtained by X^{-3} extrapolation of the CP corrected correlation contributions to the binding energies with aug-cc-pVDZ and aug-cc-pVTZ sets

[d] The correlation part of $\Delta E_2(\infty)$ is obtained by extrapolating the CP corrected correlation contributions to the binding energies with aug-cc-pVDZ and aug-cc-pVTZ sets according to Eq. (1) in the text

[e] The correlation part of $\Delta E_3(\infty)$ is obtained by $X^{-\beta}$ extrapolation of the CP corrected correlation contributions to the binding energies with aug-cc-pVDZ and aug-cc-pVTZ sets where optimized β values from Ref. [10] were adopted

[f] The correlation part of $\Delta E_4(\infty)$ is obtained by the extrapolation scheme assuming the same basis set convergence behavior of the correlation energies for the monomer and dimer in Ref. [11]

[g] Reference CBS limit binding energies

[h] Ref. [15]

[i] Ref. [16]

[j] CP corrected MP2-R12 results in Ref. [17]

[k] Ref. [18]

[l] X^{-3} extrapolated result of CP corrected correlation contributions to binding energies with aug-cc-pVQZ and aug-cc-pV5Z sets in Ref. [14]

this study for simplicity and accuracy as well as its asymptotic behavior of $\sim X^{-3}$ for large X [12–14]. This is well manifested in Table 1 where the performances of various extrapolation methods such as X^{-3}, $X^{-\beta}$ and $(X+\gamma)^{-3}$ formulas as well as the extrapolation scheme assuming the same convergence behavior of monomer and cluster correlation energies with basis set (aug-cc-pVDZ and aug-cc-pVTZ sets in this case) are compared. Generally, the use of $(X+\gamma)^{-3}$ extrapolation formula appears to yield the more stable and reliable results compared to the other extrapolation formulas (or method).

Since it was shown that despite simplicity the $(X+\gamma)^{-3}$ type extrapolation formula with cc-pVDZ and cc-pVTZ basis sets could reproduce the basis set limit correlation energies and binding energies of various weakly bound systems accurately [7], one could conjecture that the substitution of the cc-pVTZ basis set by a basis set smaller than cc-pVTZ (but larger than cc-pVDZ) coupled with appropriate change in the extrapolation scheme might yield the similar accuracy exhibited for cc-pVTZ basis set. The appropriate change here would be to adopt the optimum value for the cardinal number for the new basis set.

Although several attempts have been made to construct a basis set which can recover the correlation energy effectively with a minimum number of functions and replace the cc-pVTZ set in Eq. 1, we have found that a basis set including the extra polarization functions to the cc-pVDZ set can accurately reproduce the basis set limit correlation energy through extrapolation with cc-pVDZ set if the change in the displacement of X can be made such as $X=2$ to $X=2+\alpha$ where α conceptually represents the contribution of extra polarization functions to the correlation energy. Among the various polarization functions which can be added to cc-pVDZ set (which is composed of [3s2p1d] for the second row elements), the f-type (d-type in case of H and He) functions were found to make the most significant contribution to the correlation energy. This could be expected considering the f-type functions are the next highest polarization functions available other than d-type functions which are already included in the cc-pVDZ set. Therefore, the desired basis set which can replace cc-pVTZ set in the above extrapolation formula (Eq. 1) has been constructed by adding f-type (d-type in case of H and He) functions from cc-pVTZ set to the original cc-pVDZ set as the variation and reoptimization of the exponents of the f-type functions little affected the correlation energy. Although addition of only f-type functions (without other s.p.d-type functions) to the (aug-)cc-pVDZ set is not in accord with the general principle of constructing the correlation consistent basis sets, it will be shown that the basis set thus obtained could be effectively used along with (aug-)cc-pVDZ set for extrapolation to predict the accurate binding energies close to the basis set limits in case of hydrogen-bonded clusters. Table 2 shows the contributions of the extra f type functions in the modified aug-cc-pVDZ basis set (which will be denoted aug-cc-pVDZ* hereafter) to the total correlation energies for some sample systems. Except for He (in which d type functions from cc-pVTZ set are added to the aug-cc-pVDZ set), the correlation energies recovered by the additional f-type functions from the cc-pVTZ set appears to be roughly close to the average between the correlation energies of aug-cc-pVDZ and aug-cc-pVTZ sets at both the MP2 and CCSD(T) levels. This is a relatively large recovery ratio by these functions considering that the number of basis functions of aug-cc-pVDZ, aug-cc-pVDZ*, and aug-cc-pVTZ set are 23, 30, and 46, respectively, for the second row elements. The remaining task would be to find the optimal value for α

Table 2 Variation of correlation energies (in E_h) with basis set

	Basis set	He	Ne	CH_2	HF	H_2O	CO	N_2	F_2
MP2	aug-cc-pVDZ	−0.026963	−0.206874	−0.115400	−0.222200	−0.219348	−0.299378	−0.317325	−0.427926
	aug-cc-pVDZ*[a]	−0.029136	−0.230200	−0.128365	−0.245994	−0.243279	−0.325933	−0.343943	−0.468957
	aug-cc-pVTZ	−0.033621	−0.272519	−0.141033	−0.279729	−0.268361	−0.360831	−0.379586	−0.535987
CCSD(T)	aug-cc-pVDZ	−0.033844	−0.212945	−0.146745	−0.230050	−0.232323	−0.318686	−0.333336	−0.448145
	aug-cc-pVDZ*[a]	−0.035467	−0.238538	−0.159653	−0.256035	−0.257927	−0.347052	−0.361522	−0.493220
	aug-cc-pVTZ	−0.039415	−0.279375	−0.171202	−0.288426	−0.281691	−0.380720	−0.396144	−0.558760

[a] Aug-cc-pVDZ set added by f (d in case of H and He) type functions from cc-pVTZ basis set

which can be generally applied to yield the accurate binding energies of clusters via Eq. 1.

To derive the optimal value for α which can yield the accurate basis set limit correlation energy through extrapolation of correlation energies with (aug-)cc-pVDZ and (aug-)cc-pVDZ* set, we have chosen the same sample systems used to derive Eq. 1 for which highly accurate R12 correlation energies are available [19,20]. Table 3 shows the optimized values for α at the MP2 and CCSD(T) levels which can reproduce the R12 reference correlation energies through extrapolation via Eq. 1 with the aug-cc-pVDZ and aug-cc-pVDZ* set which contains f type (d type in case of H and He) functions from cc-pVTZ set in addition to aug-cc-pVDZ set. All calculations in this study were performed using Gaussian program package [21] and only Gaussian functions with spherical harmonics for the angular functions were employed throughout. As clearly seen in Table 3, most of the optimized α values for extrapolation with aug-cc-pVDZ and aug-cc-pVDZ* basis sets lie between 0.2 and 0.4, giving average values of 0.3 for both the MP2 and CCSD(T) levels. This suggests that one may effectively use the extrapolation formula of Eq. 1 with (aug-)cc-pVDZ and (aug-)cc-pVDZ* basis set to estimate the accurate correlation and binding energies of the clusters if the cardinal numbers (X) corresponding to these basis sets are assigned to 2.0 and 2.3, respectively. For homogeneous clusters such as H_2O and HF clusters, although one could consider employing the interval (α value) specifically optimized for the individual monomer instead of the averaged value, employment of individually optimized interval was found to have a negligible effect on the actual binding energies in case of H_2O and HF clusters.

3 Results and discussion

Table 4 shows the CBS limit binding energies of various hydrogen-bonded clusters estimated by the extrapolation scheme described above($\Delta E_1(\infty)$), which employs the correlation energies of fragments and the complex with aug-cc-pVDZ and aug-cc-pVDZ* basis set for extrapolation according to Eq. 1 but with X value changing from $X = 2.0$ for aug-cc-pVDZ to $X = 2.3$ for aug-cc-pVDZ* set. All energies are computed with the basis set of the complex, so the extrapolation is performed on the counterpoise (CP) [22] corrected correlation contribution to the binding energies in actuality. For comparison, we also present the CBS limit binding energies estimated by X^{-3} and $(X + \gamma)^{-3}$ extrapolation of correlation energies with aug-cc-pVDZ and aug-cc-pVTZ basis sets ($\Delta E_2(\infty)$ and $\Delta E_3(\infty)$) as well as the CP corrected binding energies with aug-cc-pVTZ basis set (ΔE_{CP}). To be consistent with the reference CBS limit results, the extrapolated CBS limit binding energies contained the CP corrected Hartree-Fock (H-F) contributions with aug-cc-pV5Z basis sets except $(H_2O)_n$ (n=3,4,5) for which extrapolated values with aug-cc-pVTZ, aug-cc-pVQZ, aug-cc-pV5Z H-F results by exponential formula [27] were employed as H-F contributions. The monomer deformation energies computed with aug-cc-pV5Zbasis set were added to the CBS limit estimate in case monomer geometries are relaxed as the complex dissociates.

Remarkably, except for some cases (mostly in cases of weakly bound dimers), the CBS limit binding energies estimated with aug-cc-pVDZ and aug-cc-pVDZ* basis sets by this scheme are similar to the original $(X + \gamma)^{-3}$ extrapolated results with aug-cc-pVDZ and aug-cc-pVTZ set by Huh and Lee [7] in accuracy and better than the corresponding X^{-3} extrapolated results with aug-cc-pVDZ and aug-cc-pVTZ set in most cases. For the clusters of $(H_2O)_5$ and $(HF)_5$ for which the total binding energies amount to about 60 mE_h (∼38 kcal/mol), our estimated MP2 (or CCSD(T)) CBS limit results with aug-cc-pVDZ and aug-cc-pVDZ* sets appear to be close to the exact basis set limits to within 1 kcal/mol. For the largest cluster of $(H_2O)_6$ (prism configuration) with the binding energy of about 46 kcal/mol, the estimated MP2 basis set limit appears to be close to the reference basis set limit result to within 1.7 kcal/mol. This is an impressive accuracy improvement compared to the results from density functional theory (DFT) based methods which are known to differ from the more accurate MP2 or CCSD(T) results by a few kcal/mol in favorable cases for this kind of clusters [28,29].

Table 4 also confirms the previous study by Huh and Lee [7] that use of $(X + \gamma)^{-3}$ extrapolation formula with aug-cc-pVDZ and aug-cc-pVTZ basis set yields a very accurate estimate to the basis set limit binding energy in the case of hydrogen-bonded clusters. For the water clusters of $(H_2O)_n$ ($n = 2 - 6$) where accurate reference basis set limits are available, the MP2 reference basis set limits and corresponding $\Delta E_3(\infty)$ values are close to each other within 0.3 mE_h in most cases. Therefore, in cases the accurate reference basis set limit results are not available, the extrapolated estimate by $(X + \gamma)^{-3}$ formula with aug-cc-pVDZ and aug-cc-pVTZ basis sets (Δ $E_3(\infty)$) might be used as the approximate basis set limit results for these clusters to which other estimates could be compared. In this respect it is encouraging to

Table 3 Optimized interval values (α_{opt}) corresponding to aug-cc-pVDZ and aug-cc-pVDZ* basis set to reproduce the CBS limit correlation energy by extrapolation[a]

	He	Ne	CH_2	HF	H_2O	CO	N_2	F_2	aver[b]
MP2									
α_{opt}	0.243	0.239	0.411	0.293	0.370	0.307	0.311	0.263	0.305
CCSD(T)									
α_{opt}	0.191	0.234	0.425	0.291	0.372	0.308	0.311	0.260	0.299

[a] Two-point extrapolation by Eq. (1) with $X = 2$(for aug-cc-pVDZ) and $X = 2 + \alpha_{\mathrm{opt}}$ (for aug-cc-pVDZ*)

[b] Average values for α_{opt}

Table 4 CBS limit binding energy estimates ($\Delta E_i(\infty)$ i=1,2,3, in mE_h) by various extrapolation schemes[a]

	MP2					CCSD(T)				
Cluster[b]	$\Delta E_1(\infty)$[c]	$\Delta E_2(\infty)$[d]	$\Delta E_3(\infty)$[e]	ΔE_{CP}[f]	$\Delta E_{\mathrm{ref}}(\infty)$[g]	$\Delta E_1(\infty)$[c]	$\Delta E_2(\infty)$[d]	$\Delta E_3(\infty)$[e]	ΔE_{CP}[f]	$\Delta E_{\mathrm{ref}}(\infty)$[g]
$(H_2O)_2$	7.83(2.21)	7.67(2.05)	7.83(2.21)	7.38(1.76)	7.82(2.20)[h]	7.77(2.15)	7.79(2.17)	7.89(2.27)	7.45(1.83)	7.87(2.25)[i]
$(HF)_2$	6.90(0.97)	6.87(0.94)	7.01(1.08)	6.56(0.63)	7.04(1.11)[h]	6.96(1.03)	7.10(1.17)	7.18(1.25)	6.74(0.81)	7.22(1.29)[j]
$(HCl)_2$	3.46(3.08)	3.46(3.08)	3.60(3.22)	3.21(2.83)	3.57(3.19)[h]	2.87(2.49)	3.05(2.67)	3.15(2.77)	2.79(2.41)	3.09(2.71)[j]
H_2OHF	13.54(2.04)	13.17(1.67)	13.40(1.90)	12.82(1.32)	13.47(1.97)[h]	13.43(1.93)	13.34(1.84)	13.48(1.98)	12.91(1.41)	13.55(2.05)[j]
HCNHF	11.67(2.53)	11.76(2.62)	11.92(2.78)	11.57(2.43)	12.00(2.86)[h]	11.29(2.15)	11.52(2.38)	11.62(2.48)	11.26(2.12)	11.65(2.51)[j]
$(H_2O)_3$	22.91(6.89)	22.70(6.68)	23.18(7.16)	21.98(5.96)	23.1±0.3(7.08)[k]	22.45(6.43)	22.69(6.67)	22.97(6.95)	21.85(5.83)	22.9±0.4(6.88)[k]
$(HF)_3$	23.80(7.87)	22.99(7.06)	23.61(7.68)	22.10(6.17)	23.6±0.4(7.67)[k]	23.80(7.87)	23.68(7.75)	24.05(8.12)	22.64(6.71)	24.1±0.5(8.17)[k]
$(H_2O)_4$	44.71	47.74	42.73	41.44	44.0[l]	43.67	42.76	43.35	41.18	–
$(HF)_4$	44.15	42.39	43.34	41.22	–	43.71	43.10	43.68	41.70	44.0±1.2[m]
$(H_2O)_5$	58.76	56.18	57.45	54.49	57.8[l]	57.31	–	–	–	–
$(HF)_5$	60.60	58.06	59.29	56.63	–	59.77	58.77	59.53	57.03	60.0±1.6[m]
$(H_2O)_6$	75.80	71.30	73.11	69.64[l]	73.1[l]					

[a] All CBS limit binding energy estimates including reference values are the sum of correlation contributions (values in parentheses) and converged Hartree-Fock binding energies with aug-cc-pV5Z basis set

[b] The geometries of dimers are from Ref. [17] The geometries of $(HF)_n$ ($n = 3, 4, 5$) are from Ref. [24] The geometries of $(H_2O)_3$ and $(H_2O)_n$ ($n = 4, 5, 6$) are from Ref. [23] and Ref. [26], respectively

[c] The correlation part of $\Delta E_1(\infty)$ is obtained by extrapolation of CP corrected correlation contributions to the binding energies with aug-cc-pVDZ and aug-cc-pVDZ* sets using Eq. (1) with X corresponding to 2.0 and 2.3 for aug-cc-pVDZ and aug-cc-pVDZ* set, respectively

[d] The correlation part of $\Delta E_2(\infty)$ is obtained by X^{-3} extrapolation of CP corrected correlation contribution to the binding energies with aug-cc-pVDZ and aug-cc-pVTZ basis sets

[e] The correlation part of $\Delta E_3(\infty)$ is obtained by $(X + \gamma)^{-3}$ extrapolation of CP corrected correlation contribution to the binding energies with aug-cc-pVDZ and aug-cc-pVTZ basis sets, respectively, with γ defined in Eq. (1) in the text

[f] CP corrected binding energies with the aug-cc-pVTZ basis set

[g] Reference basis set limit binding energies

[h] CP corrected MP2-R12 results in Ref. [17]

[i] Ref. [18]

[j] X^{-3} extrapolated results of CP corrected correlation contributions to binding energies with aug-cc-pVQZ and aug-cc-pV5Z sets in Ref. [14]

[k] Ref. [24]

[l] Ref. [26]

[m] Ref. [25]

observe that $\Delta E_1(\infty)$ and $\Delta E_3(\infty)$ values for $(H_2O)_4$ at the CCSD(T) level are only different by 0.3 mE_h, which suggests that the extrapolated CCSD(T) CBS limit binding energies with aug-cc-pVDZ and aug-cc-pVDZ* sets for $(H_2O)_4$ and $(H_2O)_5$ could be considered as the reliable estimates to the exact CCSD(T) CBS limit binding energies for these systems. (For H_2O or HF monomer, the replacement of aug-cc-pVTZ with aug-cc-pVDZ* basis set reduces the number of basis functions from 92 to 58.) Since the computational demand increases steeply with the number of basis functions at the highly correlated level such as CCSD(T), our extrapolation scheme appears to provide an effective path for obtaining the reliable basis set limit binding energies of large hydrogen-bonded clusters by substantially reducing the computational task involved.

4 Concluding remarks

In this paper we have explored the idea of utilizing the basis sets specifically oriented for extrapolation to the basis set limit to obtain the accurate binding energies of large weakly bound clusters which could reduce the computational demand significantly in ab initio electronic structure calculations without sacrificing the accuracy. As an example, we have demonstrated the utility of (aug-)cc-pVDZ basis set and (aug-)cc-pVDZ* basis set composed of (aug-)cc-pVDZ set and highest polarization functions from cc-pVTZ basis sets in the X^{-3} type extrapolation of correlation binding energies of hydrogen-bonded clusters. It is very encouraging to observe that the CBS limit binding energies estimated by this scheme for the larger clusters than the dimers are within the error bound of the reference CBS limits in many cases, which is only achievable with the basis sets larger than aug-cc-pVQZ set in conventional calculations. Since one of the main obstacles in performing the high level ab initio electronic computations of large molecular clusters is the steep dependence of the computational demand on the number of basis functions employed, our extrapolation procedure could save a huge computational time in the study of large hydrogen-bonded clusters. For example, for the largest clusters examined here, $(H_2O)_6$, the number of basis functions for aug-cc-pVDZ*, aug-cc-pVTZ, and aug-cc-pVQZ set increases from 348 to 552 up to 1032, which exemplifies the difficulty in performing accurate ab initio electronic computations using conventional methods and the advantage to adopt the extrapolation technique in conjunction with the "extrapolation-oriented" basis sets such as the ones used here, especially at the highly correlated levels of theory. Therefore, by using the extrapolation scheme developed here, it is expected that one would be able to effectively investigate the accurate structures and binding energies of various kinds of large hydrogen-bonded clusters. It appears quite straightforward to extend the extrapolation scheme suggested here by stepping up the cardinal numbers (such as cc-pVTZ and cc-pVTZ* which should include the highest polarization functions from cc-pVQZ set) to the systems where higher level accuracy than obtained here is needed (such as van der Waals complexes). Further reduction of basis set size may also be possible by removing some of the diffuse functions in the basis set (such as containing the diffuse functions only for the heavy atoms) in conjunction with reparametrization of the cardinal numbers corresponding to basis sets. Extension and application of the suggested extrapolation scheme to other molecular clusters are in progress.

References

1. Dunning TH, Jr (1989) J Chem Phys 90:1007
2. Woon DE, Dunning TH, Jr (1993) J Chem Phys 98:1358
3. Woon DE, Dunning TH, Jr (1994) J Chem Phys 100:2975
4. Peterson KA, Woon DE, Dunning TH, Jr (1994) J Chem Phys 100:7410
5. Wilson A, van Mourik T, Dunning TH, Jr (1997) J Mol Struct (THEOCHEM) 388:339
6. Wilson A, Woon DE, Peterson KA, Dunning TH, Jr (1999) J Chem Phys 110:7667
7. Huh SB, Lee JS (2003) J Chem Phys 118:3035
8. Moller C, Plesset MS (1934) Phys Rev 46:618
9. Pople JA, Head-Gordon M, Raghavachari K (1987) J Chem Phys 87:5968
10. Fast PL, Sanchez ML, Truhlar DG (1999) J Chem Phys 111:2921
11. Park SY, Lee JS (2002) J Chem Phys 116:5389
12. Wilson A, Dunning TH, Jr (1997) J Chem Phys 106:8718
13. Helgaker T, Klopper W, Koch H, Noga J (1997) J Chem Phys 106:9639
14. Halkier A, Helgaker T, Jorgensen P, Klopper W, Koch H, Olsen J, Wilson AK (1998) Chem Phys Lett 286:243
15. Klopper W (1995) J Chem Phys 102:6168
16. Lee JS, Park SY (2000) J Chem Phys 112:10746
17. Halkier A, Klopper W, Helgaker T, Jorgensen P, Taylor PR (1999) J Chem Phys 111:9157
18. Klopper W, van Duijneveldt-vande Rigdt JGCM, van Duijneveldt FB (2000) Phys Chem Chem Phys 2:2227
19. Klopper W (2001) Mol Phys 99:481
20. Noga J, Valiron P, Klopper W (2001) J Chem Phys 115:2022
21. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (1998) Gaussian, Inc, Pittsburgh
22. Boys SF, Bernardi F (1970) Mol Phys 19:553
23. Klopper W, Schutz M, Luthi H, Leutwyler S (1995) J Chem Phys 103:1085
24. Hwang R, Huh SB, Lee JS (2003) Mol Phys 101:1429
25. Klopper W, Quack M, Suhm MA (1998) Mol Phys 94:105
26. Xantheas SS, Burnham CJ, Harrison RJ (2002) J Chem Phys 116:1493
27. Feller D (1992) J Chem Phys 96:6104
28. Xantheas SS (1995) J Chem Phys 102:4504
29. Kim J, Kim K (1998) J Chem Phys 109:5886