MP2 Basis Set Limit Binding Energy Estimates of Hydrogen-bonded Complexes from Extrapolation-oriented Basis Sets

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By use of a simple two-point extrapolation scheme estimating the correlation energies of the molecules along with the basis sets specifically targeted for extrapolation, we have shown that the MP2 basis set limit binding energies of large hydrogen-bonded complexes can be accurately predicted with relatively small amount of computational cost. The basis sets employed for computation and extrapolation consist of the smallest correlation consistent basis set cc-pVDZ and another basis set made of the cc-pVDZ set plus highest angular momentum polarization functions from the cc-pVTZ set, both of which were then augmented by diffuse functions centered on the heavy atoms except hydrogen in the complex. The correlation energy extrapolation formula takes the $(X+1)^{-3}$ form with X corresponding to 2.0 for the cc-pVDZ set and 2.3 for the other basis set. The estimated MP2 basis set limit binding energies for water hexamer, hydrogen fluoride pentamer, alanine-water, phenol-water, and guanine-cytosine base pair complexes of nucleic acid by this method are 45.2(45.9), 36.1(37.5), 10.9(10.7), 7.1(6.9), and 27.6(27.7) kcal/mol, respectively, with the values in parentheses representing the reference basis set limit values. A comparison with the DFT results by B3LYP method clearly manifests the effectiveness and accuracy of this method in the study of large hydrogen-bonded complexes.

Key Words : Hydrogen bonding, MP2 basis set limit, Extrapolation

Introduction

Hydrogen bonding plays an important role in the chemistry of living organisms. It is responsible for the unique properties of water essential for life, serving as the vital link between water and various organic and inorganic molecules in the solvation process. Among various non-covalent interactions present in large biomolecules such as proteins and DNA, hydrogen bonding is one of the dominant forces determining the basic structure of these molecules such as α-helix or β-sheet structure in proteins and double helix structure in DNA. Despite this fundamental importance of hydrogen bonding in nature, an accurate theoretical description of structures and energetics of such large hydrogen-bonded systems is a formidable task. Although the structures and vibrational frequencies of the hydrogen-bonded systems are usually known to be reliably determined using appropriate density functional theory (DFT) methods, the determination of the binding energies using DFT methods has been proven to be insufficient in many cases to yield the accurate results which could interpret and guide the experimental investigations.[1-10] This necessitates the use of more conventional *ab initio* electron correlation methods and so far, among various *ab initio* methods, second order Mϕller-Plesset method (MP2)[11-13] has been shown to be one of the most effective and accurate *ab initio* methods for studying the hydrogen-bonded systems.[14] However, correlation energy at the MP2 level, unlike the Hartree-Fock or DFT energy, is known to converge very slowly to the complete basis set (CBS) limit with basis set increase,[15,16] making it difficult to evaluate the accurate binding energies of large hydrogen-bonded molecular complexes. The critical issue thus would be to reduce the size of the basis set employed as much as possible in an *ab initio* (MP2 method here) computation without sacrificing the accuracy of the computed results. This is why development of proper basis set extrapolation scheme is of prior importance in contemporary quantum chemistry relevant to large molecular systems.

Recently Hwang *et al.*[17] have developed an extrapolation scheme which employs the smallest correlation consistent basis set, cc-pVDZ, and another basis set which contains extra polarization functions in addition to the functions of the cc-pVDZ set. Though small in size, these basis sets were specifically designed to yield the accurate MP2 basis set limit correlation energies of sample systems through extrapolation. The initial application of the extrapolation scheme with these basis sets to a wide variety of hydrogen-bonded systems has been shown quite fruitful in evaluating the accurate binding energies of these complexes when the basis set of each atom was augmented by diffuse functions, which are known to be important to represent the weak interactions of the hydrogen-bonded systems. From a viewpoint of computational efficiency, however, addition of diffuse functions to the basis set severely reduces the number of molecular systems which could be handled by *ab initio* method such as MP2. The focus of this paper is to explore the possibility of reducing the basis set size further to extend the extrapolation scheme by Hwang *et al.*[17] to large hydrogen-bonded systems for which use of large basis set at the MP2 or even at the DFT level is very demanding computationally. For this purpose, we examine the effect of diffuse functions on bind-

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ing energies for various hydrogen-bonded systems including water hexamer, hydrogen fluoride pentamer, alanine-water complex, phenol-water complex, and, guanine-cytosine pair of nucleic acid bases and show that the presence of diffuse functions on heavy atoms only in conjunction with the aforementioned extrapolation scheme appears to be enough to yield the accurate estimates to the CBS limit binding energies of large hydrogen-bonded systems at the MP2 level. The superiority of the estimated basis set limit binding energies via this extrapolation scheme would become more evident through the comparison of the extrapolated results with the DFT based results by B3LYP method[18,19] which are often used for this kind of hydrogen-bonded system.

This paper is organized as follows: in the next section we briefly review the extrapolation method by Hwang *et al*.[17] and detailed computational and extrapolation procedure employed in this study is presented. The results and discussion are presented in section III. The conclusion of our study is given in section IV.

Computation and Extrapolation Scheme

The counterpoise (CP) corrected[20] binding energies (ΔE_{AB}) of complex A ⋯B which undergoes geometrical changes of monomers from G2 (monomer geometries in the complex) to G1 (monomer geometries in the fragments) as it dissociates into fragments can be computed as follows.

$$\begin{aligned}\Delta E_{AB} = &[E_A(G2; DBS) + E_B(G2; DBS) - E_{AB}(G2; D_{BS})] \\ &+ [E_A(G1; MBS) - E_A(G2; MBS)] \\ &+ [E_B(G1; MBS) - E_B(G2; MBS)] \end{aligned} \quad (1)$$

Here, $E_X(G; MBS)$ and $E_X(G; DBS)$ are the energies of monomer X at the geometry G with the monomer and dimer basis set, respectively, and $E_{AB}(G2; DBS)$ is the energy of the complex with the geometries of the monomers placed at G2.

The computed binding energies ΔE_{AB} is composed of the Hartree-Fock (ΔE_{AB}^{HF}) and correlation contribution (ΔE_{AB}^{CORR}).

$$\Delta E_{AB} = \Delta E_{AB}^{HF} + \Delta E_{AB}^{CORR} \quad (2)$$

While ΔE_{AB}^{HF} can be reliably computed with a basis set of manageable size for most of the complexes (which are not unusually large), the slow convergence of ΔE_{AB}^{CORR} with basis set often makes it difficult to obtain the accurate binding energies of the complexes, especially for weakly bound complexes. Among various basis set extrapolation techniques developed to circumvent the problem of slow convergence of ΔE_{AB}^{CORR} with basis set,[15-17,21-26] the extrapolation technique utilizing the smallest basis sets of the correlation consistent basis set family (aug-)cc-pVXZ (X = D, T, Q, 5, 6)[27-31] (thereby reducing the computational demand significantly) was recently suggested, which appears to need a brief review at this point. Hwang *et al*.[17] devised a basis set composed of the (aug-)cc-pVDZ set and highest polarization function set (f type functions for B-Ne, d type functions for H and He) from the cc-pVTZ set. This basis set, denoted (aug-)cc-pVDZ* hereafter, along with the (aug-)cc-pVDZ set was then employed in the correlation and basis set dependent extrapolation formula for the (aug-)cc-pVDZ and (aug-)cc-pVTZ sets by Huh and Lee.[25]

$$\Delta E_{AB}^{CORR}(\infty) = \Delta E_{AB}^{CORR}(X) + A/(X + \gamma)^3 \quad (3)$$

The critical element in using the (aug-)cc-pVDZ* instead of the (aug-)cc-pVTZ set in this formula was to assign the proper value for the cardinal number X for the (aug-)cc-pVDZ* set which was optimized to be 2.3 from the computation and extrapolation of the chosen sample systems. (the values for cardinal number X for the cc-pVDZ and cc-pVTZ sets are 2.0 and 3.0 in the common extrapolation using these basis sets). Although the basis set (aug-)cc-pVDZ* thus obtained is not constructed in the usual correlation consistent manner, it was shown very effective to estimate the accurate binding energies of hydrogen-bonded complexes through extrapolation with the basis sets containing the appropriate diffuse functions such as the aug-cc-pVDZ and aug-cc-pVDZ* sets. This is because these basis sets are, in some sense, optimized for extrapolation to yield the results close to the basis set limit correlation energies of the molecules. However, as the molecular size increases, the need for reducing the size of the basis set further without seriously affecting the accuracy of the computation would become increasingly important for effective *ab initio* computation. Thus, if the basis sets are adapted to the extrapolation like the aug-cc-pVDZ and aug-cc-pVDZ* sets, one might consider removing some of the functions from the conventional basis set which are not critical to representing the electronic motion in the complex. As the first attempt of testing this conjecture, we examine the applicability of the extrapolation method by Hwang *et al.* with the basis sets containing the diffuse functions on the heavy atoms only except hydrogen (denoted as the aug'-cc-pVXZ and aug'-cc-pVXZ*) in large hydrogen-bonded complexes. The sample systems examined in this study represent the various type of hydrogen-bonded complexes including water hexamer, hydrogen fluoride pentamer, alanine-water and phenol-water complexes. and guanine-cytosine pair of nucleic acid bases, for which accurate basis set limits at the MP2 level binding energies are available. All computations of the binding energies were performed under frozen core approximation with the CP correction for basis set superposition error. The computed binding energies of the complexes with the aug'-cc-pVDZ and aug'-cc-pVDZ* were then extrapolated using eq. (3) to estimate the MP2 basis set limit binding energies.

For the alanine-water and phenol-water complexes in which monomer geometries appeared to be little affected after dissociation, monomer geometries in the fragments were held same as in the complexes, which were optimized at the MP2/6-311G** level under frozen core approximation. Meanwhile, in case of the water hexamer (prism configuration), $(HF)_5$, and guanine-cytosine base pair, for comparison with the more accurate results available from literature, the binding energies were computed at the respective optimal geometries of the fragments and complexes. While geometries

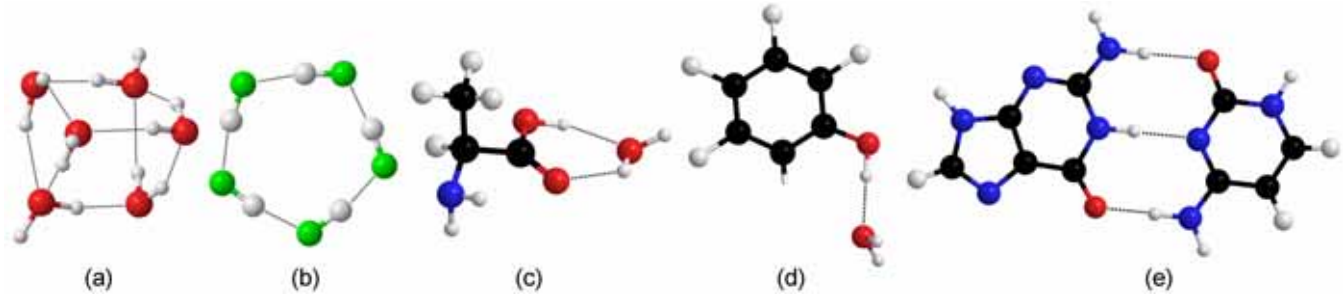

Figure 1. Schematic view of hydrogen-bonded complexes examined in this study. Different colors are used to represent the atoms in the complex (red: oxygen, green: fluorine, blue: nitrogen, black: carbon, white: hydrogen) Dotted lines represent the hydrogen bonding in the complex. (a) water hexamer (prism configuration) (b) hydrogen fluoride pentamer (c) alanine-water complex (d) phenol-water complex (e) guanine-cytosine base pair.

of the complex and fragments of the water hexamer correspond to the MP2/aug-cc-pVTZ geometries adopted by Xantheas *et al.*,[33] the geometries of hydrogen fluoride monomer and pentamer examined here correspond to the equilibrium geometries adopted by Klopper *et al.*[34] For guanine-cytosine base pair, optimization at the B3LYP/aug'-cc-pVDZ level was performed for the fragments and complex, respectively, which yielded the geometries similar to the ones adopted by Schaefer and coworkers who employed the B3LYP/DZP++ method for optimization.[35] In Figure 1 the schematic view of the complex geometries is shown. The comparison of the extrapolated *ab initio* results with the DFT methods was performed using B3LYP method.[18,19] All *ab initio* and DFT computations were performed with Gaussian program packages.[36]

Results and Discussion

Although it is generally known that diffuse functions play an important role in describing the interaction in hydrogen-bonded clusters, the effect of employing a basis set containing diffuse functions on the heavy atoms only (except hydrogen) on binding energies of the complexes has not been systematically examined. Therefore, before performing extrapolation, we first examined the effect of diffuse functions on the Hartree-Fock (ΔE^{HF}) and correlation (ΔE^{CORR}) binding energies of hydrogen-bonded complexes employing the aug-cc-pVXZ and aug'-cc-pVXZ (X=D,T) basis sets as well as the effect of additional f-type (d-type in case of hydrogen) polarization functions present in the aug'-cc-pVDZ* basis set employed in this study, which is presented in Table 1. The first noticeable feature in Table 1 is that the binding energies with the aug'-cc-pVXZ and aug-cc-pVXZ basis sets are very similar, thus strongly suggesting the utility of the aug'-cc-pVXZ basis sets for these hydrogen-bonded complexes. Another important finding is that in contrast to the diffuse functions on the light (hydrogen) atom, addition of extra polarization functions (f or d) to the aug'-cc-pVDZ basis set induces the substantial change in the correlation binding energies from the results without them. The capability of these extra polarization functions to recover substantial amount of atomic and molecular correlation energies was already observed in the previous study.[17] As expected, the Hartree-Fock binding energies converge much more rapidly with basis set[37] compared to the correlation contributions to the binding energies.

Table 2 presents the CBS limit estimates of binding energies by various extrapolation methods. Here, $\Delta E_1(\infty)$ and $\Delta E_2(\infty)$ are the CBS limit estimates obtained by X^{-3} and $(X + 1)^{-3}$ extrapolation of correlation energies with the aug-cc-pVDZ (X = 2.0) and aug-cc-pVTZ (X = 3.0) basis sets,[15,25] and $\Delta E_3(\infty)$ are the CBS limit estimates according to eq. (3) with the aug'-cc-pVDZ (X=2.0) and aug'-cc-pVDZ* (X=2.3) basis sets.[17] In all estimated CBS results, the Hartree-Fock (H-F) binding contributions were estimated by $X^{-3.4}$ extrapolation[21] of the counterpoise corrected H-F binding energies with the aug-cc-pVDZ and aug-cc-pVTZ basis sets except for $(H_2O)_6$, where the Hartree-Fock results with the aug-cc-pV5Z basis set was employed as the estimated CBS limit binding energy to be consistent with the

Table 1. Basis set convergence of the Hartree-Fock (ΔE^{HF}) and correlation (ΔE^{CORR}) binding energies[a] (in kcal/mol) of hydrogen-bonded complexes

Basis set	$(H_2O)_6$			$(HF)_5$			Alanine-H_2O			Phenol-H_2O			Guanine-Cytosine		
	ΔE^{HF}	ΔE^{CORR}	ΔE^{TOT}	ΔE^{HF}	ΔE^{CORR}	ΔE^{TOT}	ΔE^{HF}	ΔE^{CORR}	ΔE^{TOT}	ΔE^{HF}	ΔE^{CORR}	ΔE^{TOT}	ΔE^{HF}	ΔE^{CORR}	ΔE^{TOT}
aug'-DZ[b]	26.88	13.09	39.97	25.22	6.93	32.15	7.66	1.56	9.22	4.46	1.60	6.06	20.06	5.50	25.56
aug-DZ[c]	26.74	13.72	40.47	25.15	7.01	32.15	7.62	1.61	9.23	4.43	1.64	6.07	20.22	5.70	25.91
aug'-DZ*[d]	26.45	14.44	40.89	25.87	7.50	33.37	7.59	1.97	9.55	4.38	1.85	6.23	20.21	5.99	26.20
aug'-TZ[e]	26.57	16.67	43.24	26.34	9.00	35.33	7.68	2.36	10.04	4.42	2.11	6.52		–	
aug-TZ[f]	26.62	17.08	43.71	26.41	9.13	35.53	7.69	2.41	10.10	4.43	2.15	6.58		–	

[a]Counterpoise corrected binding energies (in kcal/mol). $\Delta E^{TOT} = \Delta E^{HF} + \Delta E^{CORR}$. [b]Aug'-cc-pVDZ set. [c]Aug-cc-pVDZ set. [d]Aug'-cc-pVDZ* set. [e]Aug'-cc-pVTZ set. [f]Aug-cc-pVTZ set.

Table 2. MP2 basis set limit estimates ($\Delta E_i(\infty)$, i = 1, 2, 3, in kcal/mol) by different extrapolation methods

	$(H_2O)_6$	$(HF)_5$	Alanine-H_2O	Phenol-H_2O	Guanine-Cytosine
$\Delta E_1(\infty)^a$	45.16	36.85	10.46	6.79	–
$\Delta E_2(\infty)^b$	46.20	37.51	10.71	6.94	–
$\Delta E_3(\infty)^c$	45.21	36.06	10.91	7.05	27.57
$\Delta E_{B3LYP}{}^d$	41.06	39.48	9.51	5.64	24.97
CBS^e	45.9^f	37.5^g	10.67^g	6.91^g	27.7^h

[a]The correlation contributions to the binding energy with the aug-cc-pVXZ (X=D(2),T(3)) basis sets were extrapolated by X^{-3} formula. [b]The correlation contributions to the binding energy with the aug-cc-pVXZ (X=D(2),T(3)) basis sets were extrapolated by $(X+1)^{-3}$ formula. [c]The correlation contributions to the binding energy with the aug'-cc-pVDZ and aug'-cc-pVDZ* basis sets were extrapolated by $(X+1)^{-3}$ formula with X varying from X=2.0 to 2.3. [d]Binding energy by B3LYP method. [e]Reference CBS limit values. [f]From ref. 33. [g]The correlation contributions to the binding energy with the aug-cc-pVXZ (X=T(3), Q(4)) basis sets were extrapolated by X^{-3} formula. [h]From ref. 35.

reference CBS limit result. Except for $(H_2O)_6$ and guanine-cytosine base pair where accurate MP2 CBS limits were available from previous studies,[33,38] reference MP2 CBS limits for the other complexes were obtained by extrapolating the correlation energies with the aug-cc-pVTZ and aug-cc-pVQZ basis sets by X^{-3} (X = 3, 4) formula. For comparison we also present the DFT based B3LYP results (ΔE_{B3LYP}) which were computed with the aug-cc-pVTZ basis sets.

The first point to be noted from the results in Table 2 is of course the close agreement between the reference CBS limit values and $\Delta E_3(\infty)$ results obtained with the aug'-cc-pVDZ and aug'-cc-pVDZ* sets of [4s3p2d/2s1p] and [4s3p2d1f/2s1p1d] functions, respectively, exploiting the extrapolation scheme adopted in this study. With respect to the reference CBS limit values, $\Delta E_3(\infty)$ results are comparable to the X^{-3} extrapolated $\Delta E_1(\infty)$ results (which are obtained with the aug-cc-pVDZ and aug-cc-pVTZ sets of [4s3p2d/3s2p] and [5s4p3d2f/4s3p2d] quality, respectively) in accuracy and only slightly less accurate than $\Delta E_2(\infty)$ results (which also are obtained with the aug-cc-pVDZ and aug-cc-pVTZ sets but with different extrapolation formula from $\Delta E_1(\infty)$). The close agreement of $\Delta E_2(\infty)$ results with the reference values confirms the previous study results by Huh and Lee which found the utility of the $(X+1)^{-3}$ formula (with the aug-cc-pVDZ and aug-cc-pVTZ basis sets) in estimating accurate CBS limit binding energies for a wide variety of weakly bound molecular complexes.[25] In contrast, the DFT results by B3LYP method, which is known to be one of the most appropriate DFT methods for the hydrogen-bonded systems, with the aug-cc-pVTZ basis set are well off the reference CBS limit values, the differences between them amounting to more than 10% of total binding energies compared to the corresponding ratio of less than 3% for the extrapolated estimate $\Delta E_3(\infty)$ with much smaller aug'-cc-pVDZ and aug'-cc-pVDZ* sets in most cases. Compared to the small hydrogen-bonded systems such as water dimer and hydrogen fluoride dimer where the differences between the DFT based B3LYP and *ab initio* MP2 results amount to less than one kcal/mol,[8] the large differences between the B3LYP and MP2 results in these complexes indicate that the difference between the MP2 and DFT based results would increase with the size of the molecular system, which signifies the importance of the extrapolation method employed here for calculation of interaction energies for large hydrogen-bonded systems. Furthermore, in terms of the computational efficiency, it was found that the computation of the complex energies at the B3LYP/aug-cc-pVTZ level takes much longer than the corresponding computation at the MP2/aug'-cc-pVDZ* level, typically more than three times longer in CPU time, suggesting that the basis set increase with the size of the complex would pose a formidable problem even in the DFT based methods. This again implies the extrapolation method employed here would be more valuable as the size of the hydrogen-bonded complex increases, shedding the light on the future study of hydrogen bonding in a very large molecular system such as protein.

Conclusion

The accurate determination of hydrogen bonding energies of large molecular complexes is an important issue toward the understanding the relative importance of various interactions present in biomolecular systems. By employing an effective extrapolation scheme which incorporates the extrapolation-targeted basis sets and simple extrapolation formula with adjustable parameters corresponding to the quality of the basis set, we were able to obtain the accurate estimates to the MP2 basis set limit binding energies for water hexamer, alanine-water, phenol-water, and guanine-cytosine nucleic acid base pair systems. The estimated MP2 basis set limit binding energies for $(H_2O)_6$, $(HF)_5$, alanine-water, phenol-water, and guanine-cytosine nucleic acid base pair complexes by this method are 45.2(45.9), 36.1(37.5), 10.9(10.7), 7.1(6.9), and 27.6(27.7) kcal/mol, respectively, with the values in parentheses representing the reference basis set limit values. In contrast, the corresponding DFT based B3LYP binding energies, with the relatively large aug-cc-pVTZ basis set, only amount to 41.1, 39.5, 9.5, 5.6, and 27.1 kcal/mol. The idea of utilizing the extrapolation-targeted basis sets for accurate estimate of the binding energies of the molecular complexes could be extended and applied to the other weakly bound systems of different type of interactions such as complexes dominated by dispersion or dipole induced interactions if one could find the optimal values of cardinal numbers corresponding to the chosen basis sets along with proper extrapolation formula for specific class of complexes or interactions. It would be interesting to examine whether one could further reduce the basis set without sacrificing the accuracy of computation by adopting a basis set which contains only the diffuse functions on the specific atoms involved in bonding or interaction of the complex.

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