Binding Energies and Three Body Potentials of He_3 and Ne_3: A Hierarchical Approach toward the Basis Set and Correlation Limit

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The basis set limit electronic binding energies of small rare gas clusters X_n (X = He and Ne; $n = 2$ and 3) and nonadditive three body potential at the MP2, CCSD, and CCSD(T) levels (coupled cluster single and double excitations with perturbative triples correction) were obtained assuming the correlation energies of the monomer and cluster have the same convergence behavior toward the corresponding basis set limits with correlation consistent aug-cc-pVXZ (X = D(2), T(3), Q(4), 5, 6) basis set. The comparison of the estimated basis set limits with the estimates obtained from $1/X^3$ extrapolation schemes and the exact (reference) basis set limits shows that the new extrapolation scheme is capable of yielding a much more accurate estimate to the basis set limit than two-point $1/X^3$ extrapoation scheme with small basis sets, though estimated basis set limits by both extrapolation schemes appear to converge as the basis set increases. The three body potentials of He_3 and Ne_3 are found negligible at their equilateral configurations near equilibrium. An effective procedure is explored to derive the basis set limit binding energies at the CCSD(T) level from the results at the MP2 level in a hierarchical manner based on the appropriate extrapolation of correlation consistent energies.

I. Introduction

The ab initio determination of binding energies of weakly bound complexes such as van der Waals and hydrogen-bonded molecular clusters has been the subject of intensive study for molecular theorists for the last two decades. The difficulty in obtaining the binding energies of weakly bound clusters by ab initio electronic computation is now well-known: to account for the weak, long range interactions between the fragments in the complex, one has to employ a highly correlated method along with a fairly large basis set which could describe the very diffuse motion of electrons in such clusters. This means one has to deal with the errors arising from the limited electron correlation treatment and basis set truncation in actual computation due to the limited computational resources, which could be critical to understand the binding of the complex in some cases. Among these two sources of error, recent studies[1−3] indicate that the error caused by basis set truncation generally plays a more significant role in determining the accurate binding energies of the rare gas complexes than the deficiency in correlation treatment, though the degree of contributions by two error factors could certainly vary depending on the type of complexes involved. In this paper, we primarily deal with the error caused by basis set truncation in the computation of binding energies of small rare gas clusters of He_n and Ne_n ($n =$ 2 and 3) at the MP2, CCSD, and CCSD(T) level and apply the extrapolation method recently proposed by Park and Lee,[4] which exploits the similar convergence behavior of monomer and cluster correlation energies with the correlation consistent basis set by Dunning and co-workers[5−10] to estimate the basis set limit binding energies of weakly bound clusters.

Unlike the conventional basis sets, the family of correlation-consistent basis set cc-pVXZ or aug-cc-pVXZ (X = D(2), T(3), Q(4), 5, 6) has an unique property to make the energies (correlation or total) converge systematically to the basis set limit as the basis set (or X) increases. Among the various extrapolation schemes employing a finite number of energies with the correlation consistent basis set, extrapolation of successive correlation energies with basis set of cardinal number X − 1 and X by $1/X^3$, which is based on the previous partial wave expansion studies on small atomics systems,[11−13] appears attractive as it provides a simple and effective way to estimate the basis set limit energies at the correlated levels. For a given set of energies, it is not difficult to see why the two-point (energy) extrapolation would be more advantageous than three- or four-point extrapolation as it involves only the energies with best basis qualities (X − 1 ∼ X) compared to the three-point (X − 2 ∼ X) or four-point (X − 3 ∼ X) extrapolation scheme which necessarily involves the energies farther away from the basis set limit. For smaller basis sets such as cc-pVDZ or cc-pVTZ, however, the estimated basis set limits by two-point $1/X^3$ extrapolation were often found to be quite different from the exact limits,[14,15] which could be attributed to the unsaturation of radial space in the case of smaller basis sets. One way to resolve this problem is to optimize the exponents according to basis set quality and correlation level with respect to the known basis set limits, which have been shown quite effective computationally and successfully applied to the geometry optimization and computation of atomization energies of various molecules.[16−18] However, as the method depends on the known (or estimated) basis set limits for optimization of the exponents, it is difficult to extend this method to large molecular clusters for which accurate basis set limits are not known or difficult to compute at the present time. Therefore, for large molecular clusters where only small basis set calculations are only possible in practice, a more elaborate extrapolation scheme appears necessary to estimate the basis set limit accurately. For this purpose Park and Lee[4] have recently proposed that one could use a two-point $1/X^p$ extrapolation scheme to estimate the basis set limit correlation energies of the dimer in which the exponent

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p is determined from the basis set convergence behavior of the monomer correlation energies if the exact basis set limits of the monomer are known. Motivated by the success of this extrapolation scheme exhibited for the binding energies of the dimers He_2, $(H_2O)_2$, and $(HF)_2$,[4] our focus in this study is to extend this method to the computation of binding energies and nonadditive three body potentials of rare gas trimers He_3 and Ne_3 in their equilibrium equilateral triangluar configurations.

The nonadditive interaction part of the many body potential can play an important role in determining the various properties of the matter including third virial coefficients of fluids, absorption spectra of fluids, and binding energies of solids.[19−26] In this paper, by incorporating the well-known basis set convergence behavior of the monomer correlation energies of He and Ne at the MP2, CCSD, and CCSD(T) level into the aforementioned extrapolation scheme, we compute the binding energies and nonadditive three body potentials of rare gas trimers He_3 and Ne_3 as well as the closer investigation of the binding energies of the dimers He_2 and Ne_2. We also examine the performance of the two-point $1/X^3$ extrapolation schemes in estimating the binding energies and nonadditive three body potentials of these clusters and investigate the most appropriate extrapolation method for these kinds of complexes. Finally, we discuss the systematic procedure to estimate the basis set limit binding energies of the cluster at the higher correlation level from the results at the lower correlation level which could reduce the computational demands significantly and provide an efficient path to evaluate the basis set and correlation effect on the binding of weakly bound clusters. This paper is organized as follows: In section II, we explain the methodology and computational procedures employed in this study. The results and discussion are presented in section III. The summary and conclusion is in section IV.

II. Methodology

Although the primary extrapolation scheme employed in this study was presented in detail elsewhere,[4] a brief review of the important features of the extrapolation scheme appears in order. The key point of the extrapolation scheme proposed by Park and Lee[4] to estimate the basis set limit correlation energies of the weakly bound cluster composed of a single species is to assume that the convergence behavior of the correlation energies of the cluster toward the basis set limit with correlation consistent basis set would be close to the convergence behavior of the monomer composing the cluster as the electron correlation in the cluster would be mainly dominated by the intramonomer correlation effect. Since the basis set limit correlation energies of the monomer is much easier to compute than the basis set limit correlation energies of the cluster, one could deduce the approximate convergence behavior of the correlation energies of the cluster from the known convergence behavior of the monomer correlation energies with a correlation consistent basis set. In our study of He_n and Ne_n ($n = 2$ and 3), this was done by examining the difference of monomer correlation ($\epsilon^{mon}(X)$) energies with basis set from its known corresponding basis set limits $\epsilon^{mon}_{ref}(\infty)$, and then the ratio ($\gamma$) of two differences with aug-cc-pVXZ and aug-cc-pV(X+1)Z basis set for the monomer is set to be equal to the corresponding ratio for the cluster to derive the basis set limit correlation energies of the cluster, $\epsilon^{clus}(\infty)$:

$$\gamma^{mon} = \frac{\epsilon^{mon}(X) - \epsilon^{mon}_{ref}(\infty)}{\epsilon^{mon}(X+1) - \epsilon^{mon}_{ref}(\infty)} \qquad (1)$$

If we assume $\gamma^{mon} = \gamma^{clus}$, where γ^{mon} and γ^{clus} are the ratios for the monomer and cluster, respectively, the basis set limit correlation energy of the cluster can be obtained from the following formula:

$$\epsilon^{clus}(\infty) = \frac{\epsilon^{clus}(X) - \gamma^{mon}\epsilon^{clus}(X+1)}{1 - \gamma^{mon}} \qquad (2)$$

For example, the basis set limit correlation contribution to the binding energy of the dimer, $\Delta\epsilon^{dim}(\infty)$, is computed as

$$\Delta\epsilon^{dim}(\infty) = 2\epsilon^{mon}_{ref}(\infty) - \epsilon^{dim}(\infty) \qquad (3)$$

For the trimer which dissociates into a dimer and monomer, the basis set limit correlation contribution to the binding energies of the trimer, $\Delta\epsilon^{tri}(\infty)$, is

$$\Delta\epsilon^{tri}(\infty) = \epsilon^{mon}_{ref}(\infty) + \epsilon^{dim}(\infty) - \epsilon^{tri}(\infty) \qquad (4)$$

where $\epsilon^{dim}(\infty)$ and $\epsilon^{tri}(\infty)$ represent the basis set limit correlation energies obtained from eq 2 for the dimer and trimer, respectively. Once the basis set limit correlation contribution to the binding energy of the cluster is determined in this way, the basis set limit total binding energy ($\Delta E(\infty)$) of the cluster (dimer or trimer) was obtained by adding the correlation contribution $\Delta\epsilon(\infty)$ to the basis set limit Hartree−Fock (H−F) binding energies of the cluster which was taken as the result with the aug-cc-pV6Z basis set in our study. Meanwhile, for the equilateral configuration of X_3 (X = He and Ne), the nonadditive three body potential (V_3) can be expressed as

$$V_3 = E^{tri} - 3E^{mon} + 3\Delta E^{dim} = 2\Delta E^{dim} - \Delta E^{tri} \qquad (5)$$

where $E^{dim}(E^{tri})$ and $\Delta E^{dim}(\Delta E^{tri})$ are the total and binding energies of the dimer(trimer), respectively. Therefore, in our study, the basis set limit three body correction term $V_3(\infty)$ is computed from the basis set limit binding energies of the dimer and trimer as

$$V_3(\infty) = 2\Delta E^{dim}(\infty) - \Delta E^{tri}(\infty) \qquad (6)$$

where the correlation contributions of $\Delta E^{dim}(\infty)$ and $\Delta E^{tri}(\infty)$ are obtained from eqs 3 and 4, respectively.

In addition to the estimated basis set limits obtained from the extrapolation of correlation energies of the cluster exploiting the basis set convergence behavior of the monomer correlation energies, they were also estimated by the more simple and common $1/X^3$ extrapolation of two successive correlation(or total) energies with aug-cc-pVXZ and aug-cc-pV(X+1)Z basis sets. In this case, the basis set limit binding energies ($\Delta E(\infty)$) or correlation contributions to the binding energies (($\Delta\epsilon(\infty)$) can be estimated directly by the extrapolation of the binding energies (($\Delta E(X)$) or correlation contributions to the binding energies ($\Delta\epsilon(X)$) with aug-cc-pVXZ and aug-cc-pV(X+1)Z basis sets by $1/X^3$:

$$\Delta\epsilon(\infty) = \Delta\epsilon(X) - \alpha/X^3 \qquad (7)$$

$$\Delta E(\infty) = \Delta E(X) - \beta/X^3 \qquad (8)$$

For the geometries of dimers and equilateral trimers, the He−He distance and the Ne−Ne distance were fixed at 5.6 au and 3.1 Å (=5.85815 au) which correspond to the (approximate) equilibrium internuclear distances for the He and Ne clusters, respectively. These geometries were chosen primarily because

TABLE 1: Basis Set Limit Binding Energy Estimates ($\Delta E(\infty)$ in μE_h) of He_2 and Ne_2

	X∼X+1	$\Delta E_1(\infty)^a$	$\Delta E_2(\infty)^b$	$\Delta E_3(\infty)^c$	$\Delta E_{CP}(\infty)^d$	$\Delta E_{ref}(\infty)^e$
			MP2			
He_2	D∼T	20.3	19.0	19.6	15.1	
	T∼Q	19.7	19.4	19.3	17.6	
	Q∼5	21.3	21.3	20.9	19.2	21.4^f
	5∼6	21.4	21.3	21.6	20.2	
	$\bar{\Delta}_{abs}{}^g$	0.7	1.2	1.2	3.4	
Ne_2	D∼T	74.3	61.5	63.1	43.8	
	T∼Q	79.2	75.5	78.1	63.6	
	Q∼5	84.2	83.1	81.4	72.3	81.7^h
	5∼6	82.5	81.8	82.1	76.4	
	$\bar{\Delta}_{abs}{}^g$	3.3	7.0	5.7	17.7	
			CCSD			
He_2	D∼T	27.2	26.7	27.3	22.4	
	T∼Q	27.1	27.4	27.3	25.2	
	Q∼5	28.1	28.5	28.1	26.6	29.0^f
	5∼6	29.1	29.1	29.4	27.8	
	$\bar{\Delta}_{abs}{}^g$	1.2	1.1	1.2	3.5	
Ne_2	D∼T	90.2	79.1	80.7	58.7	
	T∼Q	96.5	96.2	98.6	81.8	
	Q∼5	103.6	104.8	102.9	92.1	102.6^h
	5∼6	102.0	102.3	102.6	96.5	
	$\bar{\Delta}_{abs}{}^g$	5.0	8.1	6.6	20.3	
			CCSD(T)			
He_2	D∼T	31.7	31.1	31.7	26.4	
	T∼Q	31.7	32.0	32.0	29.6	
	Q∼5	32.9	33.3	32.9	31.2	33.8^f
	5∼6	33.9	33.9	34.2	32.5	
	$\bar{\Delta}_{abs}{}^g$	1.3	1.3	1.3	3.9	
Ne_2	D∼T	114.4	101.9	103.5	78.0	
	T∼Q	123.4	123.1	125.6	105.5	
	Q∼5	131.7	133.2	131.5	118.2	130.4^h
	5∼6	129.5	130.2	130.2	123.3	
	$\bar{\Delta}_{abs}{}^g$	6.3	9.7	8.3	24.2	

[a] CP corrected SCF binding energy with aug-cc-pV6Z basis set plus correlation contribution obtained from eq 3 in the text. [b] CP corrected SCF binding energy with aug-cc-pV6Z basis set plus the correlation contribution obtained from eq 7. [c] Obtained from extrapolation of total energies by $1/X^3$ (eq 8). [d] Counterpoise corrected binding energies with aug-cc-pV(X+1)Z basis set. [e] Reference CBS limit binding energies. [f] From ref 15. [g] Average of the absolute deviations from $\Delta E_{ref}(\infty)$. [h] From ref 28.

of the presence of the highly accurate near-basis set limit results at these geometries, which were used as the reference basis set limit binding energies to evaluate the accuracy of the extrapolation schemes employed in this study. For consistency of the calculations, all energies of the fragments (monomers and dimers) were computed with the trimer centered basis sets at the aforementioned geometries. Only valence electrons were correlated in all ab initio electronic computations at the MP2, CCSD, and CCSD(T) levels with correlation consistent aug-cc-pVXZ (X = D, T, Q, 5, 6) basis sets, which were performed using Gaussian program packages.[27]

III. Results and Discussion

(1) Basis Set Limit Binding Energies of He_2 and Ne_2. In Table 1, we first compare the binding energies of He_2 and Ne_2 obtained through the computational and extrapolation procedures described in section II with the reference values for complete basis set (CBS) limit binding energies,[15,28] which were computed by linear R12 method with large uncontracted basis functions[29−37] for He_2 and by the methodology combining the large number of bond functions with the conventional atom-centered correlation consistent basis set (aug-cc-pV5Z+3s3p2d2f1g) to saturate the dispersion energy for Ne_2. It has to be noted, however, that although these reference values appear to be the most accurate results for these dimers to date and considered to be close to the exact CBS limits, probably within 0.1 μE_h for He_2 and a few tenth of μE_h for Ne_2,[38] the accuracy of the reference values for Ne_2 is slightly uncertain considering the discrepancies between the reference values and other results.[39,40] Our procedure to obtain the estimated binding energies $\Delta E_1(\infty)$ in Table 1 is as follows: first, MP2, CCSD, and CCSD(T) correlation energies of monomers and dimers with the trimer-centered aug-cc-pVXZ basis sets (X = D∼6) are computed, and then, assuming the correlation energies of monomer and dimer have the same basis set convergence behavior toward the respective basis set limit, the basis set limit of the dimer correlation energy is estimated for each basis set sequence X ∼ X + 1 (see eq 2). The employment of trimer centered basis sets at the aforementioned trimer geometries even for the monomers and dimers calculations were chosen to acheive consistency with the trimers calculations presented later. If one is only interested in the binding of the dimers, calculations with the dimer-centered basis set would produce the similar binding energies.[4] The key ingredient in this procedure is to employ the accurate basis set limt correlation energies of the monomers. While the basis set limit correlation energies for He were taken from Table 1 in ref 15, which are basically derived from the previous basis set limit Hartree−Fock, CCSD, and near-basis set limit MP2 results for He,[41−43] for Ne, we adopted the highly accurate correlation energy recently computed by Klopper[44] with a very large basis set (19s14p8d6f4g3h) by means of R12 methodology.[29−37] We also present the basis set limit binding energies estimated through the extrapolation of correlation and total energies by two-point $1/X^3$ ($\Delta E_2(\infty)$ and $\Delta E_3(\infty)$) formula and the conventional counterpoise (CP)[45] binding energies (ΔE_{CP}) with aug-cc-pVXZ basis set along with the averages of the absolute deviations, $\bar{\Delta}_{abs}$, of estimated binding energies from the reference basis set limits.

From the results in Table 1, it is clear that the extrapolation scheme exploiting the same convergence behavior of correlation energies toward the basis set limits for both the monomer and dimer generally yields the reliable and accurate estimates to the exact basis set limit binding energies, even for the extrapolation with small basis sets. For example, with DZ−TZ extrapolation, the estimated limits recover more than 90% of the exact basis set limit binding energies in most cases compared to the slow recovery ratio by the other extrapolation schemes. As the basis set becomes larger, the estimated basis set limits become similar, and in some cases, extrapolated results by $1/X^3$ appear to be closer to the exact limits than the extrapolation assuming the same convergence behavior of correlation energies of the monomer and dimer. This is understandable considering the approximate nature of the assumption inherent to the latter extrapolation scheme and the $1/X^3$ convergence behavior of the correlation energy near the basis set limit.[14,46] Although the two-point $1/X^3$ extrapolation of correlation or total energies appears to be able to yield the accurate results as the basis set increases, the results with smaller basis sets are not so reliable and accurate. However, both extrapolation schemes yield the much closer results to the basis set limits compared to the CP corrected binding energies. Besides the better accuracy of the extrapolation scheme exploiting the similar basis set convergence behavior for the monomer and dimer correlation energies than the simple two-point $1/X^3$ extrapolation schemes with smaller basis sets, it is interesting to note that extrapolation of total energies rather than correlation energies by $1/X^3$ formula appears to yield the equally or more accurate estimate to the exact basis set limits in most cases, especially for smaller basis sets. This must stem from the fact that the correlation consistent basis sets are built

TABLE 2: Basis Set Limit Binding Energy[a] Estimates ($\Delta E(\infty)$, in μE_h) and Three-Body Potential ($V_3(\infty)$ in μE_h) of He_3 and Ne_3

	X~X+1	$\Delta E_1(\infty)^b$	$V_3^{(1)}(\infty)$	$\Delta E_2(\infty)^c$	$V_3^{(2)}(\infty)$	$\Delta E_3(\infty)^d$	$V_3^{(3)}(\infty)$	$\Delta E_{CP}{}^e$	V_3^{CP}
				He_3					
MP2	D~T	41.2	−0.6	38.3	−0.3	39.7	−0.5	30.9	−0.7
	T~Q	40.5	−1.1	40.1	−1.3	39.9	−1.3	36.1	−0.9
	Q~5	42.6	0.0	42.4	0.2	42.3	−0.5	39.1	−0.7
	5~6	44.2	−1.4	43.9	−1.3	44.1	−0.9	41.2	−0.8
CCSD	D~T	54.6	−0.2	53.6	−0.2	54.9	−0.3	45.2	−0.4
	T~Q	54.3	−0.1	54.7	0.1	54.6	0.0	50.6	−0.2
	Q~5	56.5	−0.3	57.2	−0.2	57.0	−0.8	53.7	−0.5
	5~6	58.7	−0.5	59.0	−0.8	59.1	−0.3	56.0	−0.4
CCSD(T)	D~T	64.0	−0.6	62.8	−0.6	64.2	−0.8	53.3	−0.5
	T~Q	63.6	−0.2	64.1	−0.1	63.9	0.1	59.4	−0.2
	Q~5	66.0	−0.2	66.8	−0.2	66.7	−0.9	62.9	−0.5
	5~6	68.4	−0.6	68.7	−0.9	68.8	−0.4	65.4	−0.4
				Ne_3					
MP2	D~T	149.7	−1.1	123.8	−0.8	127.0	−0.8	88.5	−0.9
	T~Q	159.6	−1.2	152.1	−1.1	156.9	−0.7	128.0	−0.8
	Q~5	168.4	0.0	166.4	−0.2	163.1	−0.3	145.1	−0.5
	5~6	165.7	−0.8	164.6	−1.0	164.8	−0.6	153.4	−0.6
CCSD	D~T	178.8	1.4	157.0	1.2	160.1	1.3	116.4	1.0
	T~Q	191.7	1.3	190.9	1.5	195.7	1.5	162.2	1.4
	Q~5	205.2	2.0	207.4	2.2	203.9	1.9	182.6	1.6
	5~6	202.4	1.6	203.4	1.4	203.4	1.8	191.4	1.6
CCSD(T)	D~T	227.2	1.6	202.4	1.4	205.6	1.4	154.7	1.3
	T~Q	245.0	1.8	244.4	1.8	249.0	2.2	209.2	1.8
	Q~5	260.4	3.0	263.5	2.9	260.2	2.8	234.1	2.3
	5~6	257.6	1.4	259.0	1.4	259.3	1.1	244.7	1.9

[a] Binding energy for $X_2 + X \rightarrow X_3$ (X = He and Ne) [b] CP corrected SCF binding energy with aug-cc-pV6Z basis set plus correlation contribution obtained from eq 4 in the text. [c] CP corrected SCF binding energy with aug-cc-pV6Z basis set plus the correlation contribution obtained from eq 7. [d] Obtained from extrapolation of total energies by $1/X^3$ (eq 8). [e] CP corrected binding energies with aug-cc-pV(X+1)Z basis set.

in such a way that the basis functions of different angular momentum which contribute similarly to the correlation energy are added systematically as the cardinal number X increases. As a result, for correlation consistent energies with smaller basis sets which do not include sufficient number of diffuse (radial) basis functions, extrapolation of total energies rather than correlation energies could be more effective in such complexes. Similar basis set convergence behavior has been observed previously.[15,47]

(2) Binding Energies of Trimers and Three Body Potential. After having established that the new extrapolation scheme could provide reliable and accurate binding energies of rare gas dimers He_2 and Ne_2, binding energies of trimers (He_3 and Ne_3) from the dimer and monomer and three body potentials have been computed using the same methods as in Table 1, which are presented in Table 2. For binding energies and three body potentials of the trimers, although it is not possible at the present time to evaluate the accuracy of the estimated results because of the absence of the exact basis set limit results at these levels, the similarity between the results of trimer binding energies (and three body potentials) for different extrapolation schemes (different method) with largest basis sets, along with the observed accuracy of the estimated binding energies of the dimers in Table 1, suggests that extrapolation of the correlation energies of the trimer exploiting the basis set convergence behavior of the monomer correlation energies could also yield the reliable binding energy and three body potential estimates to the basis set limits with relatively small basis sets such as aug-cc-pVDZ and aug-cc-pVTZ. This is apparently more evident for Ne_3 than for He_3, which appears to signify the effectiveness of the extrapolation scheme to large clusters. It is interesting to note that, compared to a noticeable difference between the extrapolated and CP corrected binding energies ($\Delta E_i(\infty)$ and ΔE_{CP}) in Tables 1 or 2, the corresponding three body potential values $V_3{}^{(i)}(\infty)$ and $V_3{}^{CP}$ are pretty much similar each other in most cases. This must be caused by the cancellation of errors in the binding energies of the dimer and trimer in this kind of cluster, regardless of the method used to obtain the binding energies (see eq 5). For comparison, the CCSD(T) three body potential of He_3, $V_3{}^{(i)}(\infty)$, for 5Z-6Z extrapolation of $-0.4 \sim -0.9\ \mu E_h$ is in good agreement with the very accurate three body potential value of $-0.161\ \mu E_h$ using the extended group function model,[48] which corresponds to the full configuration interaction/complete basis set (FCI/CBS) limit, and previous CCSD(T) result of $-0.33\ \mu E_h$.[49] Although it is difficult to make a definite statement on the magnitude of the three body potential for Ne_3 because of the absence of supplemental theoretical or experimental data of three body potential at the above configuration, our present results in Table 2, along with the previous CCSD(T) result at the similar geometry,[49] suggest that the three body potential of Ne_3 would be positive in contrast to that of He_3, though the magnitudes for both species appear very small. In this case, considering the small magnitude of the obtained values for Ne_3, further investigations appear necessary to definitely settle the issue, especially employing the basis sets containing multiply augmented diffuse functions or bond functions, which were found important to describe the dispersion interaction in the rare gas clusters.[3,39,50]

(3) Hierarchical Approach toward the Basis Set and Electron Correlation Limit. One of the major goals of ab initio molecular orbital theory is to develop a model to estimate the molecular property (such as binding energy here) at the basis set and electron correlation limit from the results at the lower level of electron correlation than FCI level with limited number of basis functions in a systematic manner. To achieve this goal in practical calculations, the following conditions must be met: First, one should be able to compute the accurate basis set limit estimates at the lower level of electron correlation. Second, one must have the knowledge about the ratio between the basis set limits at the lower and FCI level (or be able to reproduce the ratio from the results with small basis sets). Here, we examine how this concept could be applied to the accurate evaluation of

TABLE 3: Ratio (γ_i) of the Estimated Basis Set Limit Binding Energies ($\Delta E_i(\infty)$, $i = 1$, 2, and 3) for DZ−TZ Extrapolation between Correlation Levels

	ratio	$\Delta E^{\mathrm{MP2}}/\Delta E^{\mathrm{CCSD}}$	$\Delta E^{\mathrm{MP2}}/\Delta E^{\mathrm{CCSD(T)}}$	$\Delta E^{\mathrm{CCSD}}/\Delta E^{\mathrm{CCSD(T)}}$
He_2	γ_1	0.746(28.7)[b]	0.640(33.4)	0.858(33.9)
	γ_2	0.712(29.9)	0.611(34.9)	0.859(33.9)
	γ_3	0.718(30.1)	0.618(34.9)	0.861(33.8)
	γ_{av}	0.732(29.1)	0.629(33.8)	0.860(33.9)
	γ_{CBS}[c]	0.738(29.0)	0.633(33.8)	0.858(33.8)
Ne_2	γ_1	0.824(100.2)	0.649(127.0)	0.788(129.4)
	γ_2	0.777(105.2)	0.604(135.5)	0.776(131.8)
	γ_3	0.782(105.0)	0.610(134.7)	0.780(131.6)
	γ_{av}	0.803(101.9)	0.630(129.9)	0.784(130.5)
	γ_{CBS}[c]	0.796(102.6)	0.627(130.4)	0.787(130.4)
He_3	γ_1	0.755(58.5)	0.644(68.6)	0.853(68.8)
	γ_2	0.715(61.4)	0.610(72.0)	0.854(69.1)
	γ_3	0.723(61.0)	0.618(71.4)	0.855(69.1)
	γ_{av}	0.739(59.4)	0.631(69.6)	0.854(69.1)
	γ_{CBS}[d]	0.744(59.0)	0.639(68.7)	0.859(68.7)
Ne_3	γ_1	0.837(197.9)	0.659(251.5)	0.787(257.2)
	γ_2	0.789(208.7)	0.612(269.1)	0.776(262.2)
	γ_3	0.793(207.8)	0.618(266.8)	0.779(261.2)
	γ_{av}	0.815(201.9)	0.638(257.9)	0.783(259.8)
	γ_{CBS}[d]	0.809(203.4)	0.636(259.0)	0.785(259.0)

[a] γ_i represents the ratio of $\Delta E_i(\infty)$ for DZ−TZ extrapolation between two correlation levels in Tables 1 and 2. γ_{av} is the average of γ_1 and γ_3. [b] Values in parentheses are the estimated basis set limit binding energies (in μE_h) at the higher (denominator) correlation level derived from the ratio γ_i and corresponding basis set limit estimates for 5Z−6Z extrapolation in Tables 1 and 2 at the lower (numerator) correlation level. For γ_{av}, the basis set limit estimates at the lower level were taken as $\Delta E_2(\infty)$ for 5Z−6Z extrapolation. [c] Ratio of $\Delta E_{\mathrm{ref}}(\infty)$ between two correlation levels. The values in parentheses are the reference CBS limit binding energy at the higher(denominator) correlation level in Table 1. [d] Ratio of $\Delta E_2(\infty)$ for 5Z−6Z extrapolation between two correlation levels. The values in parentheses are the basis set limit estimates $\Delta E_2(\infty)$ for 5Z−6Z extrapolation at the higher(denominator) correlation level in Table 2.

the binding energies of these rare gas clusters. Because FCI level calculations are not practical for these clusters with most of the basis sets employed here, we focus on obtaining the CCSD or CCSD(T) basis set limits from the results at the MP2 or CCSD level. The first condition, that is, to establish the basis set limit at the lower correlation level, can be performed by appropriate extrapolation of the results with large basis sets (such as the aug-cc-pV5Z and aug-cc-pV6Z set). To evaluate the ratio between the basis set limit binding energies at two different correlation levels, we examined the ratio between the estimates for DZ-TZ extrapolation, which is shown in Table 3 along with the ratio between the exact basis set limits. For trimers, because of the absence of the CBS limit results in the literature, the ratio between the CBS limit values at two levels was taken from the estimates $\Delta E_2(\infty)$ for 5Z-6Z extrapolation, which were considered to be closest to the CBS limit values (see the results for the dimers in Table 1). The values in parentheses are the estimated basis set limit binding energies at the higher correlation level (CCSD or CCSD(T) level) derived from the ratio and the corresponding lower (MP2 or CCSD) level basis set limit estimates with 5Z-6Z basis set. For He_2 and He_3, although the estimated basis set limits at the higher correlation level predicted by this procedure with $\Delta E_1(\infty)$ and $\Delta E_3(\infty)$ appear to be very close to the exact basis set limit binding energies in most cases, the agreement between the exact and estimated basis set limits in the case of Ne_2 and Ne_3 is not quite satisfactory. One way to resolve this problem is to use an averaged ratio of γ_1 and γ_3 as the γ_1 tends to be higher than γ_{CBS} and γ_3 is always lower than γ_{CBS} (γ_2 is too low). In Table 3, we also present the averaged ratio (γ_{av}) of γ_1 and γ_3 along with the CBS limit estimates (in parentheses) at the higher correlation level obtained with this ratio and basis set limit estimate $\Delta E_2(\infty)$ at the lower correlation level for 5Z-6Z set extrapolation. As the results show in Table 3, the agreement between the estimates and exact values in this case is excellent. All estimates appear to be within 1.0 μE_h for the dimers (He_2 and Ne_2) and He_3. Only in the case of Ne_3 does the differences between the exact and estimated CBS limit values appear to be larger than 1.0 μE_h in some cases but not to exceed 2.0 μE_h at most. It is not clear, however, whether this kind of procedure to estimate the basis set limit binding energy at the higher level of electron correlation from the results at the lower level could be generally applied to other weakly bound complexes, for which further studies appear necessary in the future.

TABLE 4: Estimated Basis Set Limit Binding Energies of Trimers ($\Delta E(\infty)$) Derived from the Ratios of Dimer Binding Energies between Correlation Levels

	$\Delta E(\infty)$[a]	CCSD[b]	CCSD(T)[c]	CCSD(T)[d]
He_3	$\Delta E_1(\infty)$	59.2(0.2)[e]	69.1(0.4)	68.4(0.3)
	$\Delta E_2(\infty)$	61.7(2.7)	71.8(3.2)	68.7(0.0)
	$\Delta E_3(\infty)$	61.4(2.4)	71.4(2.6)	68.6(0.1)
	$\Delta E_{\mathrm{av}}(\infty)$	60.0(1.0)	69.8(1.1)	68.6(0.1)
Ne_3	$\Delta E_1(\infty)$	201.2(2.2)	255.1(3.9)	256.7(2.3)
	$\Delta E_2(\infty)$	211.7(8.3)	272.7(13.7)	262.0(3.0)
	$\Delta E_3(\infty)$	210.8(7.4)	270.3(11.3)	260.9(1.9)
	$\Delta E_{\mathrm{av}}(\infty)$	204.9(1.5)	261.5(2.5)	259.6(0.6)

[a] $\Delta E_i(\infty)$ here represents the binding energy of the trimer derived from γ_i for the dimer in Table 3 and the corresponding basis set limit estimate of the trimer for 5Z−6Z extrapolation at the lower level in Table 2. $\Delta E_{\mathrm{av}}(\infty)$is the binding energy of the trimer derived from γ_{av} for the dimer in Table 3 and $\Delta E_2(\infty)$ of the trimer for 5Z−6Z extrapolation at the lower level in Table 2. [b] From the ratio for the dimer between MP2 and CCSD level. [c] From the ratio for the dimer between MP2 and CCSD(T) level. [d] From the ratio for the dimer between CCSD and CCSD(T) level. [e] Values in parentheses are absolute deviations from the reference CBS limits at respective correlation level, which were taken as $\Delta E_2(\infty)$ for 5Z−6Z extrapolation in Table 2 (see the text).

One more interesting feature found in these kinds of complexes in relation to the hierarchical model toward the basis set and correlation limit is that the ratios between the estimated binding energies at two given correlation levels for the dimers are similar to the corresponding ratios for the trimers. This suggests that, by using the ratio between the estimated basis set limit binding energies of the dimer at two correlation levels along with the (estimated) basis set limit binding energies of the trimer at the lower correlation level, one could further proceed to derive the basis set limit binding energies of the trimer at the higher correlation level. Therefore, for larger molecular clusters such as benzene or water clusters where employment of high level electron correlation treatment with a large basis set is severely limited in practical calculations, if the ratio (γ) between the basis set limit binding energies at two correlation levels, for example, MP2 and CCSD (or the CCSD(T)) level, could be known from dimer calculations with relatively small basis sets (such as DZ-TZ extrapolation here), one only needs to perform the MP2 calculations with large basis sets and subsequent extrapolation to estimate the accurate MP2 basis set limit binding energies of the dimer and trimer, which then could be used to deduce the binding energies of the dimer as well as trimer at the CCSD (or CCSD(T)) level using the ratio γ. Similar argument can be made for the results at the CCSD and CCSD(T) level. The estimated CCSD and CCSD(T) basis set limit binding energies of He_3 and Ne_3 deduced by this procedure using the ratios of dimers for DZ-TZ extrapolation in Table 3 are summarized in Table 4 along with the deviations of the deduced values from $\Delta E_2(\infty)$ for 5Z-6Z extrapolation in Table 3, which were taken as the reference CBS limits in the case of the trimers. Although the reference basis set limits adopted in Table 4 may be slightly different from the exact basis set limits, our procedure appears to be able to produce the quite reliable estimates to the exact basis set limit binding energies of He_3 and Ne_3 at the desired level of electron correlation, especially if one employs the ratios γ_1 and γ_{av} for the dimer results in Table 3.

IV. Summary and Conclusion

We have shown that the basis set limit binding energies and nonadditive three body potentials of He_3 and Ne_3 can be accurately estimated by the extrapolation of energies with correlation consistent aug-cc-pVXZ basis sets using the $1/X^3$ formula and a flexible extrapolation scheme which exploits the basis set convergence behavior of the monomer correlation energies for the convergence behavior of the cluster correlation energies. The latter extrapolation scheme was shown especially effective to obtain a reliable estimate to the basis set limit from computations with small basis sets. This confirms the usefulness of the assumption of this extrapolation scheme to the computation of binding energies of weakly bound clusters, especially large clusters. On the contrary, the better performance of the $1/X^3$ extrapolation scheme over the aforementioned extrapolation scheme with a large basis set in some cases shows the limitation of this method, which must stem from the approximate nature of the assumption adopted. We also have shown that, by utilizing the ratios between the estimated basis set limit binding energies at two different correlation levels with relatively small basis sets, it may be possible to estimate the basis set limit binding energy of the cluster at a high level of electron correlation from the binding energies estimated with large basis sets at low electron correlation level without actual computations at the high level with large basis sets.

These procedures can be summarized as follows. First, one estimates the accurate basis set limit binding energies of the cluster at the lower correlation level by applying the appropriate extrapolation scheme to the computed results (with large basis sets). Second, the approximate ratio between the basis set limit binding energies at the lower and higher correlation levels is computed using the extrapolated results with relatively small basis sets. For rare gas clusters, the ratio between MP2 and CCSD (or CCSD(T)) CBS limit binding energies could be reproduced most accurately by averaging the ratios with estimated binding energies by the $1/X^3$ extrapolation and the extrapolation based on the same convergence behavior of the monomer and cluster correlation energies with correlation consistent basis set. Finally, using this ratio and the basis set limit at the lower correlation level obtained in step 1, the basis set limit binding energy at the higher correlation level is computed. On the basis of this hierarchical procedure, using the MP2 basis set limit estimates $\Delta E_2(\infty)$ with aug-cc-pV5Z and aug-cc-pV6Z basis set in Table 1 and the ratio γ_{av} between the MP2 and CCSD(T) basis set limit estimates for DZ-TZ extrapolation in Table 3, the CCSD(T) basis set limit binding energies of He_2 and Ne_2 are estimated to be 33.8 (33.8) μE_h and 129.9 (130.4) μE_h, respectively, with the values in parentheses representing the reference basis set limits. The corresponding estimated CCSD(T) binding energies of He_3 and Ne_3 from the dimer and monomer by the same procedure are 69.6 (68.7) μEh and 257.9 (259.0) μE_h, where the reference CCSD(T) basis set limits of He_3 and Ne_3 in parentheses in this case correspond to the SCF binding energies with the aug-cc-pV6Z basis set combined with the $1/X^3$ extrapolated correlation contributions of the aug-cc-pV5Z and aug-cc-pV6Z set results. The magnitudes of the three body potentials of He_3 and Ne_3 near equilibrium were found to be negligible, though they may have opposite signs. In conclusion, the extrapolation method and hierarchical procedure described above to obtain the basis set and (eventually) correlation limit of the cluster binding energy from the results with limited electron correlation treatment and basis set size could provide an efficient path to study the structure and binding of the large weakly bound clusters as the extrapolation scheme exploiting the similar basis set convergence behavior of monomer and cluster correlation energies could be easily extended to the more complex clusters than dimers or trimers.

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