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Accurate ab initio determination of binding energies for rare-gas dimers by basis set extrapolation

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Abstract To investigate the electron correlation effect on the binding energies of very weakly bound complexes at highly correlated levels, an extrapolation scheme exploiting the convergent behavior of the binding energy *differences* between two correlation levels with the correlation-consistent basis set aug-cc-pVXZ was explored. The scheme is based on extrapolating the binding energy differences between the lower and higher correlation levels (such as second-order Møller–Plesset perturbation theory (MP2) and the single and double coupled-cluster method with perturbative triple correction CCSD(T) level), by X^{-3} for relatively small basis set calculations to estimate the corresponding basis set limit, which is then added to the complete basis set(CBS) limit binding energy at the lower correlation level to derive the CBS limit binding energy at the higher level. Test results on rare-gas dimers Rg_2 (Rg is He, Ne, Ar) show that the CCSD(T) CBS limit binding energies estimated by this scheme with aug-cc-pVXZ and aug-cc-pV($X+1$)Z basis sets are more accurate than the CBS limit estimated by direct extrapolation of correlation energies by X^{-3} with aug-cc-pV($X+1$)Z and aug-cc-pV($X+2$)Z basis sets in most cases, which signifies the utility of the proposed extrapolation scheme as the level of electron correlation treatment increases. The nonnegligible discrepancy in the well depth near equilibrium between the experimental and the full connected single, double, and triple coupled-cluster method (CCSDT) CBS limit estimate obtained by this procedure in the case of Ar_2 suggests that the previous semiempirical potential may be too attractive near equilibrium compared with the actual one.

Keywords: Basis set extrapolation – Complete basis set limit binding energies – Rare-gas dimers – Ar_2

1 Introduction

Rare-gas clusters are among the most difficult systems to study theoretically. A proper description of weak dispersion interaction between the closed-shell rare-gas atoms requires a high level of electron correlation treatment and this becomes an even more difficult task owing to the fact that a very large one-electron basis set is needed to expand the wavefunction of the system at high-level ab initio theory. As a result, an appropriate expansion of the wavefunction in such systems requires various excited configurations, including single, double and often triple excitations (as well as quadruple and higher-order excitations in some cases) and a basis set containing high angular momentum polarization functions and diffuse functions.

The hierarchical structure of the ab initio molecular orbital theory is now well known. Starting from the Hartree–Fock level, which is roughly an N^4 computational procedure (where N is the number of basis functions), the computational demand with electron correlation treatment increases to approximately N^5 at the second-order Møller–Plesset perturbation theory (MP2) level [1, 2, 3, 4] and approximately N^6 and approximately N^7 at the single and double excitation coupled cluster (CCSD) level [5, 6, 7, 8] and the single and double excitation coupled cluster method with noniterative triples corrections [CCSD(T)] level [9], respectively. This suggests that the computational demand rapidly increases with electron correlation treatment, especially as the basis set becomes larger and it is much easier to compute the energies near the CBS (complete basis set) limit at the lower correlation level (such as MP2) than at the higher correlation level [such as CCSD(T)]. Therefore, if there exists systematic convergent behavior for the *energy differences* between two correlation levels with basis set and one can identify the

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appropriate extrapolation formula which can provide a reliable estimate of the energy difference between two correlation levels at the CBS limit, one could estimate the CBS limit energy at the higher correlation level from the corresponding CBS limit result at the lower level (along with the estimated CBS limit energy difference between two correlation levels) without actual computation at the higher correlation level with a huge basis set close to the basis set limit. Ever since the advent of correlation-consistent basis sets by Dunning and coworkers [10, 11, 12, 13, 14, 15] more than a decade ago, for which systematically convergent behavior of correlation energy has been observed, although there have been numerous studies and suggestions about basis-set extrapolation formulas for atomic or molecular correlation (or total) energy at the specific correlation level [16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27], study of the basis set convergence of energy differences between two correlation levels appears scarce. Therefore, we focus here on exploring the basis set convergence behavior of energy differences between two correlation levels, especially differences in binding energies of rare-gas complexes, rather than basis set convergence of correlation energies themselves, although the convergence behavior of the former would be certainly related to the convergence behavior of the latter.

Among various theoretical methods developed to investigate the electron correlation effect on atomic and molecular properties, one of the most effective and accurate theoretical methods for the study of van der Waals systems is the CCSD(T) method [9]. By effectively incorporating the triple contributions to CCSD method in a perturbative manner, this method not only reduces the computational time scale to approximately the N^7 from approximately the N^8 scale at the full CCSDT level [28, 29] but an accurate result is also obtained when a proper basis set is employed, in good agreement with experimental results in most cases. However, for the obvious reason, the higher-order correlation effect beyond the CCSD(T) level, which could be critical in understanding the finer details of the potential energy surface of very weakly bound clusters such as rare-gas dimers, is in general less well known. The purpose of this article is to develop an effective scheme to facilitate the accurate computation of molecular properties at such a highly correlated level as CCSD(T) or CCSDT level and, as a model case, investigate the electronic binding energies of rare-gas dimers He_2, Ne_2, and Ar_2 at the CCSDT and higher correlation levels, which could guide further experimental investigation on these dimers in the future. Since the use of a very large basis set is required in elucidating the *intrinsic* accuracy of a given electron correlation method, which is often not possible in practice, we here examine the reliability of various extrapolation methods to estimate the CBS limit binding energy and the *difference* between the lower correlation level (such as MP2) and a higher correlation level [such as CCSD(T) or CCSDT] exploiting the systematic convergent behavior of a correlation-consistent basis set.

This paper is organized as follows. In Sect. 2 we explain the theoretical approach and computational procedures employed in this study. The results and discussion are presented in Sect. 3. The summary and conclusion is in Sect. 4.

2 Theoretical approach

It is known that the asymptotic behavior of the correlation energy with the correlation-consistent basis set cc-pVXZ or aug-cc-pVXZ [where X is D(2), T(3), Q(4), 5, 6] converges to approximately X^{-3} as the basis set limit is approached [18, 20, 21]. Although the appropriate extrapolation formula to yield the exact basis set limit correlation energies in the case of small basis sets such as cc-pVDZ and cc-pVTZ could be different according to the correlation level [22, 25, 27] it is important to recognize that the focus here is to find the CBS limit difference between the binding energies of the complex at two correlation levels, not the binding energies themselves. This suggests that one would need an extrapolation formula which not only yields reasonably accurate CBS limit binding energy estimates at both correlation levels but also could cancel out errors occurring from the fragment and complex correlation energy estimates. To express this point clearly, let $\delta^{1,2}(X)$ represent the difference between binding energies of complex AB at correlation level 1, $\Delta E^{AB}_{tot1}(X)$, and level 2, $\Delta E^{AB}_{tot2}(X)$, with the aug-cc-pVXZ basis set, that is,

$$\delta^{1,2}(X) = \Delta E^{AB}_{tot1}(X) - \Delta E^{AB}_{tot2}(X).$$

As the Hartree–Fock contributions to the binding energies are common to both $\Delta E^{AB}_{tot1}(X)$ and $\Delta E^{AB}_{tot2}(X)$, this equation can be rewritten as

$$\begin{aligned}\delta^{1,2}(X) &= \Delta E^{AB}_{corr1}(X) - \Delta E^{AB}_{corr2}(X)\\ &= \left[E^{A}_{corr1}(X) + E^{B}_{corr1}(X) - E^{AB}_{corr1}(X)\right]\\ &\quad - \left[E^{A}_{corr2}(X) + E^{B}_{corr2}(X) - E^{AB}_{corr2}(X)\right], \end{aligned} \tag{1}$$

where $\Delta E^{AB}_{corr}(X)$ is the correlation energy contribution to the binding energy at the respective correlation level with $E^{A}_{corr}(X)$ [or $E^{B}_{corr}(X)$] and $E^{AB}_{corr}(X)$ representing the correlation energy of the fragment and complex, respectively. If one employs the estimated basis set limit binding energies [$\Delta E^{AB}_{corr,est}(\infty)$] in Eq. (1), the corresponding equation shall be written as

$$\delta^{1,2}_{est}(\infty) = \Delta E^{AB}_{corr1,est}(\infty) - \Delta E^{AB}_{corr2,est}(\infty). \tag{2}$$

If one defines ρ as the difference in δ between the estimated, $\delta^{1,2}_{est}(\infty)$, and exact (reference), $\delta^{1,2}_{ref}(\infty)$, CBS limit value,

$$\begin{aligned}\rho &= \delta^{1,2}_{\mathrm{est}}(\infty) - \delta^{1,2}_{\mathrm{ref}}(\infty)\\ &= \left[\Delta E^{\mathrm{AB}}_{\mathrm{corr1,est}}(\infty) - \Delta E^{\mathrm{AB}}_{\mathrm{corr1,ref}}(\infty)\right]\\ &\quad - \left[\Delta E^{\mathrm{AB}}_{\mathrm{corr2,est}}(\infty) - \Delta E^{\mathrm{AB}}_{\mathrm{corr2,ref}}(\infty)\right], \qquad (3)\end{aligned}$$

which can be rewritten as

$$\begin{aligned}\rho &= \left[E^{\mathrm{A}}_{\mathrm{corr1,est}}(\infty) - E^{\mathrm{A}}_{\mathrm{corr1,ref}}(\infty)\right]\\ &\quad + \left[E^{\mathrm{B}}_{\mathrm{corr1,est}}(\infty) - E^{\mathrm{B}}_{\mathrm{corr1,ref}}(\infty)\right]\\ &\quad - \left[E^{\mathrm{AB}}_{\mathrm{corr1,est}}(\infty) - E^{\mathrm{AB}}_{\mathrm{corr1,ref}}(\infty)\right]\\ &\quad + \left[E^{\mathrm{A}}_{\mathrm{corr2,est}}(\infty) - E^{\mathrm{A}}_{\mathrm{corr2,ref}}(\infty)\right]\\ &\quad + \left[E^{\mathrm{B}}_{\mathrm{corr2,est}}(\infty) - E^{\mathrm{B}}_{\mathrm{corr2,ref}}(\infty)\right]\\ &\quad - \left[E^{\mathrm{AB}}_{\mathrm{corr2,est}}(\infty) - E^{\mathrm{AB}}_{\mathrm{corr2,ref}}(\infty)\right].\end{aligned}$$

As clearly seen in the previous expression, ρ would vanish if the differences between the estimated and reference basis set limit correlation energies for fragments and the complex at the respective correlation level become equal. Assuming that the exact basis set limit correlation contribution to the binding energy at the (lower) correlation level 1 (which is usually assigned to the MP2 level in this study) $\Delta E^{\mathrm{AB}}_{\mathrm{corr1,ref}}(\infty)$ is (or could be) known, the major task here would be to find an appropriate extrapolation formula which can minimize ρ. For the higher correlation level (level 2), CCSD(T), CCSDT, and full configuration interaction (FCI) (in the case of $\mathrm{He_2}$) levels were employed in this study. The basis set limit total binding energy of the complex at correlation level 2, $\Delta E^{\mathrm{AB}}_{\mathrm{tot2,est}}(\infty)$, is then computed as

$$\Delta E^{\mathrm{AB}}_{\mathrm{tot2,est}}(\infty) = \Delta E^{\mathrm{AB}}_{\mathrm{tot1,ref}}(\infty) + \delta^{1,2}_{\mathrm{est}}(\infty). \qquad (4)$$

Although various extrapolation methods could be used to compute $\delta^{1,2}_{\mathrm{est}}(\infty)$ in Eq. (2), we focused our study on the performance of two-point X^{-3} extrapolation formula [18, 20, 21] as this extrapolation method was shown to yield an accurate estimate of the CBS limit difference between binding energies at the MP2 and CCSD(T) levels despite the simplicity of the formula. For comparison we also examined the performances of "direct" extrapolation schemes which fit two or three successive correlation energies with correlation-consistent basis sets $E_{\mathrm{corr}}(X)$ of fragments and the complex by $E_{\mathrm{corr}}(X) = E_{\mathrm{corr}}(\infty) + AX^{-3}$ [18, 20, 21, 30] or $E_{\mathrm{corr}}(\mathrm{X}) = E_{\mathrm{corr}}(\infty) + A\mathrm{e}^{-BX}$ [16] and $E_{\mathrm{corr}}(\mathrm{X}) = E_{\mathrm{corr}}(\infty) + AX^{-3} + BX^{-4}$ [18, 31] in estimating the CBS limit binding energies of these dimers. The results obtained by direct extrapolation of correlation energies using these formulas will be compared with the results obtained by extrapolating the binding energy differences between two correlation levels and utilized to check the accuracy of the CCSDT binding energies obtained using our suggested procedure through Eq. (4).

A more frequently used approach to correct for the basis set truncation error (BSTE) at the higher correlation level with the specified aug-cc-pVXZ basis set is to approximate the BSTE at the higher correlation level as the BSTE at the lower correlation level with the same basis set and add the latter BSTE to the computed binding energy at the higher correlation level:

$$\Delta E^{\mathrm{AB}}_{\mathrm{tot2,est}}(\infty) = \Delta E^{\mathrm{AB}}_{\mathrm{tot2}}(X) + (\mathrm{BSTE})_1, \qquad (5)$$

where

$$(\mathrm{BSTE})_1 = \Delta E^{\mathrm{AB}}_{\mathrm{tot1,ref}}(\infty) - \Delta E^{\mathrm{AB}}_{\mathrm{tot1}}(X). \qquad (6)$$

Although this "lower level correction (such as MP2 correction) term" was found useful to improve the computed binding energies at the higher level with small basis sets, making them closer to the basis set limit or experimental binding energy in many cases [32, 33], it is not clear whether this kind of substitution of BSTEs between two correlation levels would be appropriate for very weakly bound systems such as rare-gas dimers where the degree of electron correlation could significantly affect the magnitude of the computed binding energy of the complex.

For the reference CBS limit binding energies of $\mathrm{He_2}$ at the lower correlation level (level 1) and the reference CBS limit binding energy differences between two correlation levels, we adopted the highly accurate MP2-R12 and CCSD(T)-R12 results of Klopper [34] and Klopper and Noga [35] as well as the almost exact quantum Monte Carlo result of Anderson [36] corresponding to FCI/CBS limit. For $\mathrm{Ne_2}$ and $\mathrm{Ar_2}$, the MP2 and CCSD(T) near basis set limit binding energies of Cybulski and Toczylowski [37] (S.M. Cybulski, private communication), who employed a very large basis set consisting of an aug-cc-pV5Z basis set augmented by bond functions (33221), were adopted. All computed binding energies were corrected by the counterpoise (CP) method [38] for basis set superposition error. Initially the core electrons were frozen and later activated when investigating the core-correlation effect on the computed binding energies. Ab initio computations were performed with Gaussian98 [39] as well as with Gamess [40] and ACESII [41] program packages. For comparison with previous studies, the interatomic distances of $\mathrm{He_2}$, $\mathrm{Ne_2}$, and $\mathrm{Ar_2}$ were set to 5.6 au, 3.1 Å, and 7.1 au (=3.7572 Å), respectively, which are close to the equilibrium geometries of these dimers (the minima of semiempirical potentials of $\mathrm{Ne_2}$ and $\mathrm{Ar_2}$ [42, 43] correspond to bond distances of 3.093 and 3.757 Å, respectively).

3 Results and discussion

In Table 1 we first present the differences, $\delta(X)$, between the binding energies at the MP2 and higher correlation levels [CCSD(T), CCSDT, and FCI levels in the case of $\mathrm{He_2}$] with the aug-cc-pVXZ (X is D, T, Q, 5, 6) basis set

Table 1. Basis set convergence of binding energy difference (δ(X), in μE_h) between the MP2 and higher (CCSD(T), CCSDT, FCI) correlation level.

	X[a]	$\delta(X)$[b]		
		CCSD(T)	CCSDT	FCI
He_2	D(2)	9.0	9.8	9.9
	T(3)	11.4 (12.4)[c]	12.4 (13.4)	12.4 (13.5)
	Q(4)	11.8 (12.1)	12.8 (13.1)	
	5	12.0 (12.2)	13.0 (13.2)	
	6	12.1 (12.3)		
	CBS	12.4[d]		13.4[e]
Ne_2	D(2)	17.9	18.2	
	T(3)	33.5 (40.1)	34.7 (41.6)	
	Q(4)	41.5 (47.3)	43.2 (49.4)	
	5	45.5 (49.7)		
	6	46.8 (48.6)		
	CBS	48.7[f]		
Ar_2	D(2)	−85.5	−85.2	
	T(3)	−73.7 (−68.7)	−77.4 (−74.1)	
	Q(4)	−71.5 (−69.9)	−76.1 (−75.2)	
	5	−71.2 (−70.9)		
	CBS	−70.7[f]		

[a] Aug-cc-pVXZ basis set

[b] $\delta(X) = \Delta E_{\mathrm{higher}}(X) - \Delta E_{\mathrm{MP2}}(X)$ where $\Delta E_{\mathrm{MP2}}(X)$ and $\Delta E_{\mathrm{higher}}(X)$ represent the binding energies at the MP2 and higher (CCSD(T), CCSDT, FCI) levels than the MP2.

[c] Values in parentheses represent the extrapolated estimates of $\delta(X-1)$ and $\delta(X)$ by X^{-3}.

[d] From Ref. 34 and Ref. 35.

[e] From Ref. 34 and 36.

[f] Based on the results from Ref. 37 and from S.M. Cybulski (private communication)

for He_2, Ne_2, and Ar_2 along with the corresponding differences, $\delta_{\mathrm{ref}}(\infty)$, at the CBS limit. We also present the extrapolated results of $\delta(X{-}1)$ and $\delta(X)$ by X^{-3} [$\delta_{\mathrm{est}}(\infty)$, in parentheses] for comparison. From the convergence behavior of $\delta(X)$ with basis set in Table 1 it is clear that, although $\delta(X)$ approaches the CBS limit value as the basis set is increased as expected, use of large basis sets is necessary to correctly evaluate the effect of the electron correlation on the binding energies, especially in the case of Ne_2 and Ar_2. In this respect, it is interesting to observe that the effect caused by raising the electron correlation treatment from the CCSD(T) to the CCSDT level on the binding energy of Ar_2 can only be correctly manifested with a basis sets larger than the aug-cc-pVDZ set. However, it is also important to note that despite the difference in the higher-order correlation effect beyond the MP2 level on the binding energies of the dimers, $\delta(X)$ as a whole appears to exhibit similar convergent behavior with basis set. Therefore, if one could identify an appropriate basis set extrapolation formula for $\delta(X)$, the basis set limit binding energy at the higher correlation level could be predicted with the basis set limit binding energy at the lower level using Eq. (4). The X^{-3} extrapolated results for $\delta(X)$ given as an example of such an extrapolation scheme to estimate $\delta_{\mathrm{est}}(\infty)$ are quite impressive compared with the unextrapolated $\delta(X)$ results. At the CCSD(T) level where the reference CBS limits are known, it appears that the extrapolated results with aug-cc-pVDZ–aug-cc-pVTZ (or aug-cc-pVTZ–aug-cc-pVQZ basis set in the case of Ne_2) are close to the CBS limit within 1–2 μE_h, which correspond to about 1% of total binding energies for these dimers. This kind of accuracy is only achievable with the aug-cc-pV5Z (or larger) basis set for conventional calculations. Although the accuracy of the extrapolated estimates at the CCSDT level cannot be confirmed at this point owing to the absence of the corresponding reference CBS limit results, the similar basis set convergence behavior of δ(X) at the CCSD(T) and CCSDT levels shown in Table 1 suggests that the CCSDT extrapolated estimates may have similar accuracy as the corresponding CCSD(T) extrapolated estimates. This will be indirectly confirmed later by the comparison of CCSDT extrapolated estimates with experimental results.

Table 2 compares the various CCSD(T) CBS limit binding energy estimates for which different procedures were employed to estimate the CBS limit correlation contribution to the binding energy. While $\Delta E_1(\infty)$ and $\Delta E_2(\infty)$ are the CBS limit estimates obtained by direct extrapolation of CCSD(T) correlation energies $E_{\mathrm{corr}}(X)$ with three successive correlation–consistent basis sets(-such as aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ sets) by $E_{\mathrm{corr}}(X) = E_{\mathrm{corr}}(\infty) + Ae^{-BX}$ [16] and $E_{\mathrm{corr}}(X) = E_{\mathrm{corr}}(\infty) + AX^{-3} + BX^{-4}$ extrapolation functions, respectively, the correlation contribution to $\Delta E_3(\infty)$ is obtained by two-point X^{-3} extrapolation [18, 21] of CCSD(T) correlation energies with aug-cc-pVXZ and aug-cc-pV($X+1$)Z basis sets. For $\Delta E_4(\infty)$, the CCSD(T) binding energy is obtained by Eq. (4) with the X^{-3} extrapolated estimates of the binding energy differences, $\delta_{\mathrm{est}}(\infty)$, between the MP2 and CCSD(T) levels and the reference MP2 CBS limit binding energy. Finally, $\Delta E_5(\infty)$ represents the CCSD(T) binding energy obtained by Eq. (5), that is, in this case the CCSD(T) binding energy with aug-cc-pVXZ is corrected by the known BSTE at the MP2 level as shown in Eq. (6) to account for the BSTE in CCSD(T) calculations. In all cases the self consistent-field contribution to the binding energy was taken as the near Hartree–Fock limit values with aug-cc-pV5Z + (33221) basis from Ref. [37] and from S.M. Cybulski (private communication).

From the results in Table 2 it is clear one can get a much more reliable and accurate estimate of the CCSD(T) CBS limit binding energy by extrapolation of binding energy differences $\delta(X)$ between the MP2 and CCSD(T) levels compared with direct extrapolation of correlation energies at the CCSD(T) level, especially for small basis set extrapolation such as aug-cc-pVDZ and aug-cc-pVTZ sets. In general, the CCSD(T) basis set limits estimated by this method with aug-cc-pVDZ and aug-cc-pVTZ basis sets are better than the corresponding CBS limit estimate obtained with basis sets containing up to aug-cc-pVQZ and aug-cc-pV5Z basis sets by direct extrapolation of CCSD(T) correlation energies except for Ne_2, where basis set convergence is unusually slow (the CP binding energy with the aug-cc-pVTZ basis set in the case of Ne_2 only amounts to 58% of the CBS

Table 2. CCSD(T) CBS limit binding energy estimates [$\Delta E_i(\infty)$, $i = 1–5$, in μE_h) by various extrapolation methods.

	X[a]	$\Delta E_1(\infty)$[b]	$\Delta E_2(\infty)$[c]	$\Delta E_3(\infty)$[d]	$\Delta E_4(\infty)$[e]	$\Delta E_5(\infty)$[f]	$\Delta E_{ref}(\infty)$
He_2	T(3)			30.8	33.8	32.8	33.8[g]
	Q(4)	30.7	31.6	31.8	33.5	33.2	
	5	31.8	34.0	32.9	33.6	33.4	
	6	34.5	35.2	34.2	33.7	33.5	
	$\overline{\Delta}_{abs}$[h]	1.9	1.3	1.6 (1.1)	0.2 (0.2)	0.6 (0.4)	
Ne_2	T(3)			100.5	121.8	115.2	130.4[i]
	Q(4)	124.1	130.9	122.9	129.0	123.2	
	5	129.8	137.2	132.0	129.6	127.2	
	6	126.6	129.4	130.5	130.3	128.5	
	$\overline{\Delta}_{abs}$[h]	3.6	2.8	9.8 (3.1)	2.8 (0.8)	6.9 (4.1)	
Ar_2	T(3)			380.2	443.2	438.2	441.2[i]
	Q(4)	420.7	445.9	429.0	442.0	440.4	
	5	441.1	464.2	451.3	441.0	440.7	
	$\overline{\Delta}_{abs}$[h]	10.3	13.9	27.8 (11.2)	1.0 (0.5)	1.4 (0.7)	

[a] X represents the cardinal number of the largest aug-cc-pVXZ basis set used in the extrapolation

[b] The correlation contribution to $\Delta E_1(\infty)$ is obtained by extrapolation of correlation energies of fragments and complex with aug-cc-pV(X−2)Z, aug-cc-pV(X−1)Z, and aug-cc-pVXZ basis sets by $E_{corr}(X) = E_{corr}(\infty) + Ae^{-BX}$

[c] The correlation contribution to $\Delta E_2(\infty)$ is obtained by extrapolation of correlation energies of fragments and the complex with aug-cc-pV(X−2)Z, aug-cc-pV(X−1)Z, and aug-cc-pVXZ basis sets by $E_{corr}(X) = E_{corr}(\infty) + AX^{-3} + BX^{-4}$

[d] The correlation contribution to $\Delta E_3(\infty)$ is obtained by extrapolation of correlation energies of fragments and the complex with aug-cc-pV(X−1)Z and aug-cc-pVXZ basis sets by $E_{corr}(X) = E_{corr}(\infty) + AX^{-3}$

[e] The correlation contribution to $\Delta E_4(\infty)$ is obtained according to Eq. (4) with the CBS limit binding energy difference between the MP2 and CCSD(T) levels estimated through the extrapolation of $\delta(X-1)$ and $\delta(X)$ by X^{-3} and the reference CBS limit MP2 binding energies.

[f] The correlation contribution to $\Delta E_5(\infty)$ is obtained according to Eq. (5) in the text. The $(BSTE)_{MP2}$ is computed using the reference MP2 CBS limit binding energy in Ref. 34

[g] From Ref. 35

[h] Mean absolute deviation. Values in *parentheses* are the corresponding mean absolute deviations to $\Delta E_1(\infty)$ and $\Delta E_2(\infty)$ with the first data (corresponding to X = T) excluded from the data set

[i] Based on the results from Ref. 37

limit compared with 78% for the He_2 and 69% for the Ar_2 cases). This demonstrates the effectiveness of the simple X^{-3} extrapolation formula to cancel the energy differences for fragments and the complex between the estimates and references (Eq. 3), despite the fact that the individual CBS limit correlation energies of fragments or the complex are not accurately estimated by X^{-3} formula when basis sets are small as shown in the results of $\Delta E_3(\infty)$. Table 2 also shows that although the MP2 limit correction method, $\Delta E_5(\infty)$, could be effective in many cases to correct for the BSTE in the CCSD(T) calculation, the method is not always reliable in yielding the accurate CBS limit at the CCSD(T) level, especially when the basis set employed is not sufficiently large. Although it is obvious that direct extrapolation of CCSD(T) correlation energies with small basis sets using the formulas adopted here would not always yield the accurate and reliable basis set limits, extrapolation by $AX^{-3} + BX^{-4}$ with DTQ basis sets appears to yield the most accurate estimates with the basis sets of a given size. However, as the basis set becomes larger and the basis function space becomes saturated, the correlation energies with correlation-consistent basis sets follow asymptotic X^{-3} behavior as expected. The difference between the estimated and reference CBS limit results at the CCSD(T) level will be exploited to check the accuracy of the various extrapolated estimates at the CCSDT level in Table 3 later.

Table 3 shows the CCSDT CBS limit estimates corresponding to Table 2 along with the exact and experimental (semiempirical) binding energies for these dimers. The binding energies (and the values in the parentheses) in the column of $\Delta E_6(\infty)$ represent the CCSDT CBS limit binding energy estimates obtained by extrapolating the energy differences between the CCSD(T) and CCSDT levels with aug-cc-pVXZ (and d-aug-cc-pVXZ) basis sets by X^{-3}, which were then added to the reference CBS limit CCSD(T) binding energies in Table 2. These values, which are generally in very good agreement with the exact quantum Monte Carlo (in the case of He_2) or experimental results (in the case of Ne_2 and Ar_2), should be considered as the closest results to the exact CCSDT CBS limit binding energies of these dimers. The results with a doubly augmented correlation-consistent basis set [d-aug-cc-pVXZ (X is D, T, Q)] [12] were included to confirm the accuracy of the extrapolated results with aug-cc-pVXZ basis sets as these kinds of multiply augmented basis sets were found often necessary for accurate description of very weak molecular interactions such as the interactions in rare-gas dimers [12, 44, 45]. Interestingly, the estimated CCSDT CBS limits with aug-cc-pVXZ basis sets are very similar to the corresponding results with d-aug-cc-pVXZ basis sets if the CBS limits are estimated according to Eq. (4); the differences between them do not exceed 0.7 μE_h at most. Therefore, the extrapolation scheme exploiting the fast convergence of the binding energy differences between two correlation levels with basis set also appears to diminish the requirement of using multiply augmented basis sets for weak interaction. The accuracy of the estimated results by this method (Eq. 4) can also be confirmed by comparing these results with the other estimates in Table 3. For $\Delta E_2(\infty)$, which exhibits close agreement of the estimates with the reference CBS limit results for DTQ basis set extrapolation (TQ5 extrapolation in case of He_2) at the CCSD(T) level, if one assumes the same difference between the estimated and reference CBS limit binding energies at the CCSD(T) and CCSDT levels, one would obtain 34.8 μE_h for He_2 (with TQ5 basis sets), 132.6 μE_h for Ne_2 (with DTQ basis sets) and 435.9 μE_h for Ar_2 (with DTQ basis sets), respectively. Similar results could be obtained for the other CBS limit estimates in Table 3 if the corrections for the estimates and reference CBS limit results at the CCSD(T) level are made to the estimated CCSDT results. Therefore, the values in the $\Delta E_6(\infty)$ column in

Table 3. CCSDT CBS limit binding energy estimates $\{\Delta E_i(\infty), i = 1\text{–}6$, in $\mu E_h\}$ by various methods.

	X[a]	$\Delta E_1(\infty)$[b]	$\Delta E_2(\infty)$[c]	$\Delta E_3(\infty)$[d]	$\Delta E_4(\infty)$[e]	$\Delta E_5(\infty)$[f]	$\Delta E_6(\infty)$[g]	Exp.[h]
He_2	T(3)			32.1	34.8	33.8	34.9 (34.8)	34.7
	Q(4)	31.5	32.6	32.5	34.5	34.3	34.8 (34.8)	
	5	32.9	35.0 (34.8)[i]	34.1	34.6	34.4	34.8	
Ne_2	T(3)			102.2	123.3	116.4	131.8 (132.5)	
	Q(4)	126.4	133.1 (132.6)[i]	125.2	131.1	124.9	132.3 (132.6)	133.8
Ar_2	T(3)		–	374.8	437.8	434.5	436.1 (436.3)	
	Q(4)	415.6	440.6 (435.9)[i]	437.7	436.7	435.8	435.9 (435.5)	453.6

[a] X represents the cardinal number of the largest aug-cc-pVXZ basis set used in the extrapolation and computation

[b] The correlation contribution to $\Delta E_1(\infty)$ is obtained by extrapolation of correlation energies of fragments and the complex with aug-cc-pV(X−2)Z, aug-cc-pV(X−1)Z, and aug-cc-pVXZ basis sets by $E_{\mathrm{corr}}(X) = E_{\mathrm{corr}}(\infty) + Ae^{-BX}$

[c] Thecorrelation contribution to $\Delta E_2(\infty)$ is obtained by extrapolation of correlation energies of fragments and the complex with aug-cc-pV(X−2)Z, aug-cc-pV(X−1)Z, and aug-cc-pVXZ basis sets by $E_{\mathrm{corr}}(X) = E_{\mathrm{corr}}(\infty) + AX^{-3} + BX^{-4}$

[d] The correlation contribution to $\Delta E_3(\infty)$ is obtained by extrapolation of correlation energies of fragments and the complex with aug-cc-pV(X−1)Z and aug-cc-pV XZ basis sets by $E_{\mathrm{corr}}(X) = E_{\mathrm{corr}}(\infty) + AX^{-3}$

[e] $\Delta E_4(\infty)$ is obtained according to Eq. (4) with the CBS limit binding energy difference between the MP2 and CCSDT levels estimated through the extrapolation of $\delta(X{-}1)$ and $\delta(X)$ by X^{-3} and the reference CBS limit MP2 binding energies.

[f] $\Delta E_5(\infty)$ is obtained according to Eq. (5)

[g] $\Delta E_6(\infty)$ is obtained according to Eq. (4) with the CBS limit binding energy difference between the CCSD(T) and CCSDT levels estimated through the extrapolation of $\delta(X{-}1)$ and $\delta(X)$ by X^{-3} and the reference CBS limit CCSD(T) binding energies from Ref. [35](He_2) and Ref. [37](Ne_2, Ar_2). The values in *parentheses* correspond to the estimated CCSDT CBS limits whend-aug-cc-pV XZ (X is D,T,Q) basis sets were employed instead of aug-cc-pVXZ basis sets

[h] Experimental or exact theoretical results. For He_2, this value corresponds to the quantum Monte Carlo result in Ref. [36]. For Ne_2 and Ar_2, these values correspond to the semiempirical results in Ref. [42] and Ref. [43], respectively

[i] Values in *parentheses* represent the corrected values by the differences between the estimated and reference CBS limit binding energies at the CCSD(T) level in Table 2

Table 3 appear to provide reliable CCSDT CBS limit binding energies for these dimers.

One interesting finding from Table 3 is that while the CCSDT CBS limit binding energies for He_2 and Ne_2 are closer to the experimental results than the CCSD(T) CBS limits, the opposite trend is observed in the case of Ar_2. Since other factors such as core-correlation and relativistic effects as well as higher-order correlation effects beyond CCSDT treatment on the binding energies could affect the actual magnitude of the binding energy, it is necessary to examine the effect of these factors to compare our theoretical results with the experimental values. Therefore, except for He_2, where these factors could be ignored, the following investigations were performed for Ne_2 and Ar_2. First, the core–core and core–valence correlation effect on the binding energy was estimated by calculating the CCSD(T) binding energy with all electrons being correlated employing the aug-cc-pCVQZ basis set, which contains the tight core-correlating functions as well as the valence-optimized aug-cc-pVQZ basis set. This resulted in a 0.1 μE_h decrease and a 4.2 μE_h increase of the binding energies for Ne_2 and Ar_2, respectively, with respect to the frozen-core results with the aug-cc-pVQZ basis set. These results are in good agreement with the previous CCSD(T) estimate of a 0.2 μE_h decrease and a 3.6 μE_h increase by Wilson and Dunning, who employed d-aug-cc-pwCVQZ basis sets in their all-electron correlated (LM shell-electron correlation only for Ar_2) calculation [44]. Second, the relativistic effect on the binding energy was estimated by computing the differences in the first-order Darwin and mass-velocity terms in the Cowan–Griffith Hamiltonian [46] for the monomers and dimer at the all-electron correlated CCSD(T) level with the aug-cc-pCVTZ basis set, which resulted in 0.01 and 3.6 μE_h increases in the binding energy. Thus, combining these corrections with the valence-electron correlated CCSDT basis set limit binding energy of Ne_2 and Ar_2, which were taken as the values in parentheses in the $\Delta E_6(\infty)$ column in Table 3, we obtain 132.5 and 443.3 μE_h. These results are still 1.3 and 10.3 μE_h smaller than the semiempirical values for Ne_2 and Ar_2, respectively. One may be inclined to think that the remaining difference between the theoretical and experimental results is caused by the higher-order correlation effect beyond CCSDT. Since the coupled-cluster calculation employing the full quadruple excitation operator, CCSDTQ, is not practically possible for these dimers at the present time, an approximate method to investigate the effect of quadruple excitations on the binding energies of Ne_2 and Ar_2 was adopted. For this purpose, the binding energies were computed using the CCSDT(Q_f) method [47] with the aug-cc-pVTZ basis set, which employs the noniterative factorized inclusion of connected quadruple to the CCSDT method. The quadruple excitation effect via CCSDT(Q_f) on the binding energies of Ne_2 and Ar_2 along with the core-correlation effect and relativistic corrections are all collected in Table 4. Surprisingly, the results in Table 4 suggest that further excitation beyond CCSDT would decrease the binding energies for Ne_2 and Ar_2 rather than increase them, which would make the discrepancy between the theoretical and the experimental results slightly larger than the value at the CCSDT level. Similar reductions of

Table 4. Core-correlation (*CORE*), relativistic (*REL*), and quadruple excitation (*QUAD*) effect on the binding energies (in microhartrees).

	CORE[a]	REL[b]	QUAD[c]
Ne_2	−0.1	0.0	−1.7
Ar_2	+4.2	+3.6	−2.5

[a] The difference in binding energies between frozen-core CCSD(T)/aug-cc-pVQZ and all-electron CCSD(T)/aug-cc-pCVQZ results (see the text)
[b] Relativistic corrections were performed with the Cowan–Griffin Hamiltonian in Ref. [46] at the CCSD(T)/aug-cc-pCVTZ level with all electrons correlated (see the text)
[c] Difference in binding energies between frozen-core CCSDT and CCSDT(Q_f) levels with the aug-cc-pVTZ basis set

binding energies from the CCSD(T) result were observed when the CCSD(TQ_f) approximate quadruple treatment method was employed. Although there is a possibility that the approximation adopted in the CCSDT(Q_f) method, such as forced factorization, could yield a somewhat inaccurate quadruple excitation effect in this case, considering the negligible difference in binding energies between the CCSDT and CCSDTQ(FCI) levels in the case of He_2 (Table 1), there is also a possibility that the semiempirical well depths of Ne_2 and Ar_2 near equilibrium in Refs. [42, 43] could be deeper than the true well depths.

4 Summary and conclusion

In this paper, an extrapolation approach exploiting the convergent behavior of the correlation energy differences between correlation levels with correlation-consistent basis sets aug-cc-pV*XZ* has been developed to facilitate the evaluation of the high-order excitation effect on the binding energies of very weakly bound complexes. Compared with the individual correlation energies of the fragments and the complex which deviate significantly from X^{-3} asymptotic formula for small basis set extrapolation either at the MP2 level or at the CCSD(T) level [22, 27], the binding energy difference between the MP2 and CCSD(T) (or CCSDT) levels in the case of rare-gas dimers (He_2, Ne_2, and Ar_2) is shown to quickly converge to X^{-3} even with small basis sets such as aug-cc-pVDZ and aug-cc-pVTZ. This enables one to estimate the CBS limit binding energies at the CCSD(T) (or CCSDT) level with only the MP2 limit results of these dimers without near basis set limit computation with a huge basis set at the CCSD(T) (or CCSDT) level. For small basis set calculations, the estimated CBS limit binding energies by this procedure are shown to be much closer to the exact CBS limit binding energies than the corresponding results obtained by direct extrapolation of correlation energies of the fragments and the complex or the MP2 limit correction method, which approximates the BSTE at the CCSD(T) level by the corresponding BSTE at the MP2 correlation level.

The CCSDT CBS limit binding energy estimates of Ne_2 and Ar_2 obtained by this procedure with d-aug-cc-pVTZ and d-aug-cc-pVQZ basis sets, after corrections for core-correlation and relativistic effects, amount to 132.5 (133.8) and 443.3 (453.6) μE_h, respectively, with the values in parentheses representing the experimentally derived results. These results are in accord with a recent study on Ar_2 [48] which found the CCSDT CBS limit binding energy near equilibrium, after corrections for core-correlation and relativistic effects, appears to be still smaller than the semiempirical well depth by 1 cm^{-1}(approximately 5 μE_h). Since the employment of an approximate treatment method for the T_4 cluster operator such as CCSDT(Q_f) and CCSD(TQ_f) [47] points toward the negative quadruple excitation effect on the binding energy, our study suggests a possibility that the semiempirical well depth of Ar_2 [43] could be deeper than the true well depth of this dimer near equilibrium, although there is also a possibility that the quadruple excitation effect by the aforementioned approximate correlation methods may not accurately represent the true quadruple excitation effect and the higher-order effect beyond quadruple excitations may be nonnegligible in this weakly bound dimer. Further study on the Ar_2 dimer appears necessary in the future to settle the issue. It would be interesting to examine whether the concept of extrapolating the differences in correlation energies between two correlation levels by the simple X^{-3} formula would be equally effective and applicable to other weakly bound systems and molecular properties other than the binding energy (such as the dipole moment and the polarizability). Further investigations of other weakly bound dimers, such as $(CO)_2$, $(NO)_2$, and $(C_6H_6)_2$, are in progress to examine the general applicability of the procedure developed in this study.

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