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REGULAR ARTICLE

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

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Abstract In this work we comment on an extrapolation scheme presented by Lee in *Theoretical Chemistry Accounts*, which is based on an extrapolation of energy differences instead of actual energies. In particular, we show that a very similar scheme had been introduced already in 1999, and used to estimate the MP5, CCSDT and FCI complete basis set limits of He_2.

Keywords Helium dimer · Correlation consistent basis sets · Basis set extrapolation

1 Introduction

In a recent article in *Theoretical Chemistry Accounts* [1] Lee presented an extrapolation scheme that exploits the convergence behaviour of the energy differences between the different levels of theory when using the augmented correlation consistent basis sets, and used this scheme to estimate the complete basis set (CBS) limits at the coupled cluster including single, double, and perturbative triples (CCSD(T)) and coupled cluster including single, double, and full triples (CCSDT) levels of theory for the interaction energies of the rare-gas dimers He_2, Ne_2 and Ar_2. In this scheme, the CBS interaction energies at the higher level (CCSD(T) or CCSDT) are estimated by adding to the CBS interaction energy at the lower level (taken to be second-order Møller-Plesset perturbation theory — MP2) the extrapolated difference between the interaction energies at the higher and lower levels computed using relatively small basis sets, thereby avoiding large basis set calculations at the higher level.

The author seems to be unaware that a very similar scheme has been applied previously by us [2] to estimate the MP5 (fifth-order Møller–Plesset perturbation theory), CCSDT and FCI (full configuration-interaction) CBS limits of He_2, using the augmented and doubly augmented correlation consistent basis sets (aug-cc-pVXZ and d-aug-cc-pVXZ, respectively, with X = D, T, Q, 5 and 6 [3–5]). As calculations employing the largest basis sets were not feasible for the most sophisticated methods (MP5, CCSDT and FCI), reliable estimates of the MP5, CCSDT and FCI CBS limits were obtained by exploiting the rapid convergence of the differences between the MP5/MP4, CCSDT/CCSD(T) and FCI/CCSDT interaction energies, computed with the smaller basis sets. In addition, the fast convergence with basis set of the full triples and connected quadruples corrections to the CCSD(T) energies was utilised to compute an estimated FCI/CBS potential energy curve for He_2. This potential energy curve was later found to be in excellent agreement with Anderson's "exact" quantum Monte Carlo (QMC) results [6].

Though the two extrapolation schemes differ in their details, they are based on a common perception: the energy differences between two correlation methods converge more rapidly than the actual energies. (This has also been observed recently for the MP2-CCSD(T) Ar_2 interaction energy differences [7].) The extrapolation scheme can be expressed in the following general form:

$$\Delta E_{\text{level}\,2}(\infty) = \Delta E_{\text{level}\,1}(\infty) + \delta^{1,2}(\infty) \tag{1}$$

where $\Delta E_{\text{level}\,n}(\infty)$ is the CBS limit at theory level n ($n = 1, 2$; 1 = lower, 2 = higher), and $\delta^{1,2}$ is the extrapolated difference between the binding energies at correlation levels 1 and 2. In the preferred extrapolation scheme in Lee's paper (Eq. (4) in Ref. [1]), $\Delta E_{\text{level}\,1}(\infty)$ is taken to be the highly accurate MP2-R12 result of Klopper [8], whereas $\delta^{1,2}(\infty)$ was obtained by extrapolation of the differences between the MP2 and CCSD(T) (or CCSDT) interaction energies computed with aug-cc-pV5Z and aug-cc-pV6Z, using the two-point X^{-3} extrapolation formula of Helgaker et al. [9, 10]. In our 1999 paper [2], we used an exponential extrapolation formula to estimate the CBS limits of the MP4/d-aug-cc-pVXZ and CCSD(T)/d-aug-cc-pVXZ results (with X = Q, 5, 6), yielding $\Delta E_{\text{level}\,1}(\infty)$. The correction $\delta^{MP4,MP5}(\infty)$ was estimated by

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Comment to the article "Accurate ab initio determination of binding energies for rare-gas dimers by basis set extrapolation" by J.S. Lee, Theor Chem Acc (2005) 113: 87–94

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Table 1 CBS interaction energy estimates (in K) by various extrapolation schemes

	$\Delta E_{\mathrm{level2}}(\infty)$		
	CCSD(T)	CCSDT	FCI
Lee (Eq. 4)[a]	10.64	10.99	
Van Mourik and Dunning[b]	10.68	10.98	11.00
Exact	10.67[c]	n/a	-10.998 ± 0.005[d]

[a] From Ref. [1]. To keep consistency with our 1999 paper, we used the conversion factor 1 E_h=315777 K

[b] From Ref. [2]. The CCSD(T) limit is obtained by direct extrapolation of the d-aug-cc-pVTZ – d-aug-cc-pV6Z interaction energies, see also Ref. [5]. The CCSDT limit is obtained using the extrapolation scheme described above

[c] CCSD(T)-R12 result from Klopper and Noga [11]

[d] Most recent QMC result by Anderson [6]. Note that the QMC result taken to be the "exact" value for the He_2 interaction energy in Lee's paper (10.98 K or 34.77 μE_h) has been superseded by this value. Also note that the correct reference to Anderson's 2001 QMC result (Ref. 36 in Lee's paper) should be Anderson JB (2001) J Chem Phys 115:4546

extrapolation of the MP4/MP5 energy differences computed with the singly augmented basis sets (aug-cc-pVDZ – aug-cc-pVQZ) to yield the limiting value of the aug-cc-pVXZ energy difference, which was subsequently multiplied by the ratio of the d-aug-cc-pVTZ and aug-cc-pVTZ differences. Similar procedures were employed to estimate the CCSDT and FCI limits.

Table 1 compares the CBS interaction energy limits obtained with the different extrapolation procedures. We obtained CCSD(T) and CCSDT limiting values of 10.68 and 10.98 K, whereas the corresponding values obtained by Lee are 10.64 and 10.99 K, respectively. Thus, whereas the CCSDT limiting values are very similar, Lee's estimate of the CCSD(T) CBS limit is significantly smaller than ours (and further from the "exact" CCSD(T)-R12 result of Klopper and Noga [11]). Klopper demonstrated that the X^{-3} extrapolation used by Lee tends to overestimate the attraction in He_2 [12]; using the aug-cc-pV5Z and aug-cc-pV6Z basis sets, Klopper obtained an X^{-3}-extrapolated CBS limit of 10.80 K for the He_2 interaction energy at 5.6 a_0. In Lee's extrapolation scheme, this overestimate of the X^{-3} extrapolation is likely cancelled to a large extent by extrapolating the interaction energy differences instead of the actual energies. It should be noted that our extrapolation scheme makes use of the doubly augmented basis sets, whereas Lee used the singly augmented sets, which could be a possible explanation for the discrepancy between the two CCSD(T) CBS limits. We did not attempt to estimate the aug-cc-pVXZ CBS limits with our extrapolation procedure, as the aug-cc-pVXZ interaction energies are not as well described as the d-aug-cc-pVXZ results by the exponential fitting function used [5]. For the CCSDT CBS limits Lee found that the results obtained with the aug-cc-pVXZ basis sets are very similar to the corresponding results computed with the d-aug-cc-pVXZ basis sets. In this case, the CBS limits predicted by Lee's and our extrapolation scheme are indeed very similar.

In conclusion, whereas the rapid convergence of the energy differences computed at different levels of theory with the correlation consistent basis sets can be extremely useful to estimate CBS limits at high levels of theory, caution is advised in over-reliance on the computed results, particularly for highly challenging systems like He_2. We have shown here that quantitatively different CBS limits can be obtained even if very similar extrapolation schemes are employed. As Klopper has remarked, "it is very difficult, whether impossible, to extrapolate the helium pair potential to the limit of a complete basis within the accuracy needed to improve significantly on existing, directly computed potentials" [12].

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