

On the Effectiveness of Function Counterpoise Method in the Calculation of He-He Interaction Energies

Jae Shin Lee

Department of Chemistry, College of Natural Sciences, Ajou University, Suwon, Kyungkido 442-749, Korea

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An accurate determination of interaction energies in weakly bound van der Waals complexes such as rare gas dimers and trimers is not an easy task. Due to highly diffusive nature of dispersion attraction which holds the monomers together in the complex, one usually has to employ a sophisticated theoretical model which incorporates high level electron correlation treatment with large and flexible basis set to properly describe the long range electronic motion in the complex. It is well known that one of the major obstacles in obtaining the accurate binding energies of weakly bound complexes such as van der Waals molecules and hydrogen-bonded complexes is so-called basis set superposition error (BSSE).¹ BSSE is unphysical (and relative) lowering of complex energy compared to the energies of the monomers which is caused by the "extra basis functions" other than the basis functions of the given monomer in the calculation of complex energy. In another respect, it is the consequence of finite (truncated) basis set in the calculation of energies of monomers and complex. As a result, the introduction of BSSE could increase the interaction energy compared to actual (experimental) value and its magnitude is known to be nonnegligible enough to prevent the accurate determination of interaction energies and potential energy surfaces of van der Waals molecules.² Accordingly, there have been numerous attempts and correction schemes to eliminate the BSSE in the calculation.³⁻⁹ The most commonly and widely used method to correct for BSSE is the function counterpoise (FCP) method originally proposed by Boys and Bernardi.³ In FCP scheme, the same basis functions are used in the calculation of monomer energies as in the calculation of the complex energies. Although there have been several studies and arguments questioning the validity of FCP method in the calculation of interaction energies of the complex,¹⁰⁻¹³ it is generally considered that counterpoise correction (CPC) is necessary for accurate determination of interaction energies of weakly bound complexes and CP corrected interaction energies would be closer to the experimental energies than uncorrected ones.¹⁴⁻¹⁷ However, there appear to be little systematic studies which could provide a general information on the validity of CPC as the basis set and electron correlation change in the calculation of interaction energies of the various complexes. This is understandable considering it is often very difficult to obtain an accurate well depth from experimental data or estimate the basis set limit of interaction energies for very weakly bound complexes with full correlation treatment. In this paper, we examine the variation of magnitude of CPC with basis set,

electron correlation and internuclear distance of the complex (molecular geometry). We choose He₂ as our model system. Though simple, this system provides an ideal venue to examine the effects of various factors such as basis set and electron correlation on calculated interaction energies of van der Waals complexes to the full extent as the high level *ab initio* calculations can be performed relatively easily and highly accurate experimental (or *ab initio*) energies are available for comparison.

The theoretical model employed in this study is Moller-Plesset perturbation theory at second order up to the fourth order (MP2,MP3,MP4)¹⁸⁻²⁰ with the augmented correlation-consistent basis set aug-cc-pVxZ (x=D,T,Q,5)²¹ and 6-311++G type basis sets with multiple polarization and diffuse functions.²² The correlation-consistent basis sets were designed to properly account for the electron correlation effect in atoms and molecules and, coupled with highly correlated methods, they were found highly successful in describing the interaction energies of weakly bound molecules.^{15-17,23} One of the most important aspects of the correlation-consistent basis sets is that they enable one to estimate the complete basis set (CBS) limit through extrapolation of energies in a simple exponential manner.^{24,25} Since the effect of CPC on the binding energy could depend on internuclear separation (*R*_{He-He}), we calculated the binding (interaction) energies for He₂ at three different internuclear distances: (a) at equilibrium; *R*(He-He) = 3.0 Å (experimental 2.969 Å) (b) shorter than equilibrium (*R*(He-He) = 2.7 Å) (c) longer than equilibrium (*R*(He-He) = 4.0 Å). The interaction energies (*E*) in the supermolecular approach are computed as the difference between the energies of complex and monomers. In the FCP scheme, the interaction energy is calculated as follows;

$$\Delta E = E(\text{He}_2) - 2E'(\text{He})$$

Here, *E'* represents the energy of He atom calculated with the dimer basis set.

In Table 1 interaction energies for He₂ with and without CPC are presented along with estimated CBS limiting values at three internuclear distances. Here, the interaction energies at the CBS limit were estimated from the total electronic energies at the CBS limit (*E*_{CBS}) which were obtained by using the formula *E*_{CBS} = *E*(*x*) - *Ae*^{-*Bx*} where *E*(*x*) is the energy with aug-cc-pVxZ (x = T, Q, 5) basis set (*A* and *B* are fitting parameters). In the last column interaction energies of He₂ based on the HFD-B3-FCI1 potential of He₂ are also given for comparison.²⁶ This potential was obtained by fitting the

Table 1. He-He interaction energies (in microhartrees) with and without counterpoise correction

R(He-He)		6-311++G(d,p)	6-311++G(3df,3pd)	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z	CBS ^a	Theory/Expt. ^b
2.7 Å ⁰	MP2	58.6(72.4)	18.8(36.4)	4.6(43.4) ^c	9.3(20.9)	8.8(14.8)	8.5(11.3)	8.3	
	MP3	57.7(72.1)	10.4(27.0)	-4.4(34.4)	-1.5(8.5)	-2.3(1.9)	-3.5(-1.9)	-4.9	-14.5
	MP4	58.3(72.9)	7.7(24.1)	-7.2(31.2)	-6.0(4.0)	-6.9(-2.7)	-8.4(-6.6)	-10.1	
3.0 Å ⁰	MP2	0.9(11.1)	-24.9(8.7)	-35.8(-6.8)	-21.5(-16.3)	-22.0(-18.6)	-21.7(-19.9)	-21.0	
	MP3	-0.4(10.2)	-30.3(-14.3)	-40.2(-12.4)	-27.6(-23.2)	-28.3(-25.9)	-28.6(-27.4)	-28.8	-34.6
	MP4	-0.4(10.6)	-32.1(-16.1)	-41.5(-14.3)	-30.1(-25.7)	-30.9(-28.5)	-31.4(-30.0)	-31.8	
4.0 Å ⁰	MP2	-6.0(-2.4)	-11.4(-5.8)	-10.4(-5.8)	-8.7(-6.5)	-7.6(-6.6)	-7.1(-6.9)	-6.8	
	MP3	-6.4(-2.8)	-12.6(-7.0)	-10.8(-7.0)	-9.9(-7.7)	-8.7(-8.1)	-8.4(-8.2)	-8.4	-9.3
	MP4	-6.5(-2.9)	-13.0(-7.2)	-10.9(-7.3)	-10.4(-8.2)	-9.1(-8.5)	-9.0(-8.6)	-9.2	

^a Total electronic energies with aug-cc-pVxZ (x=T,Q,5) basis sets were extrapolated to estimate CBS limit for exponential behavior. Interaction energies were then calculated by the differences of the total electronic energies of dimer and monomers. ^b Values in this column represent the values of HFD-B potential of Aziz *et al.* (ref. 26) at respective internuclear separation. ^c Values in parentheses are counterpoise corrected interaction energies.

highly accurate *ab initio* points including full configuration interaction (FCI) points in the intermediate region and found to be the most accurate one than any other (experimental or theoretical) He-He potentials present at this time.²⁷ It appears that the convergent behavior of interaction energies with basis set and the effect of CPC on them vary according to electron correlation and molecular geometry, though the correlation change from MP2 to MP4 does not significantly change the general converging behavior of the interaction energies. In Fig. 1 the interaction energies with basis set at MP4 level are plotted for three internuclear separations. One of the most interesting results in Table 1 and Figure 1 is that the uncorrected interaction energies are closer to the estimated CBS limits (and "true" energies) than the CP corrected interaction energies in most cases, regardless of the type of basis set, especially for R(He-He) = 2.7 and 3.0 Å. This is especially true for MP4 electron correlation treatment with the basis sets larger than aug-cc-pVDZ (in the case of correlation-consistent basis sets). On the contrary, the effect of CPC on the interaction energies appears to become more effective as the internuclear distance increases, especially for MP2 and MP3 level. The poor performance of CP corrected interaction energies compared to uncorrected ones should be the direct consequence of surprising results in Table 1 and Figure 1 that the magnitude of interaction energies at equilibrium or shorter internuclear distances are often less than the estimated CBS limiting values. In such cases, of course, CPC would make interaction energies farther apart from the estimated CBS limit. This is very interesting because in usual supermolecular approach one generally could expect larger interaction energies by BSSE compared to actual (BSSE-free) interaction energies. Our results clearly show that the interaction energy could be more strongly affected by the intrinsic property of the basis set (such as optimization procedure) rather than BSSE. This may be related to the fact that the basis functions are usually optimized for atoms rather than molecules. The optimized basis sets for atoms may not describe the complex state as well as it does the dissociated (atomic) state. In this respect it is interesting to note that the enlargement of the interaction energies by BSSE

compared to the estimated CBS limit appears to be more noticeable for the calculations with smaller basis sets such as aug-cc-pVDZ set (except 6-311++G(d,p)). This can be understood considering that the basis sets in such cases are still far from converged and contributions to the total energy from the basis functions centered on the other monomer would be relatively larger compared to the case with larger (more converged) basis sets. However, as shown in the case of 6-311++G(d,p) set, if the basis set does not include appropriate polarization functions (and diffuse functions), other deficiencies rather than BSSE appear to be a dominant factor in the calculation of interaction energies. This also appears to be related to the relative effectiveness of CP method at R(He-He) = 4.0 Å. At large internuclear distance, though the absolute magnitude of BSSE would be smaller than at shorter internuclear distances, the calculated energy of the complex (He₂) could be much closer to the CBS energy than at shorter distance as the basis set could be well suited for molecular configurations near dissociation. This could increase the interaction energies and make CPC more effective in correcting for BSSE. The increase of the electron correlation from MP2 to MP4 appears to reduce the BSSE, thereby causing the interaction energies even at R(He-He) = 4.0 Å to be less than the estimated CBS interaction energies in some cases. Therefore it would be essential to employ a proper electron correlation method to estimate the effect of BSSE and the validity of CP method in correcting for BSSE in the determination of the interaction energy of the weakly bound complex.

As an intermediate conclusion, we can summarize our results as follows; the use of CP procedure in correcting for BSSE for the calculation of accurate interaction energy requires a careful investigation on the dependence of BSSE upon basis set, electron correlation and molecular geometry. A simple CPC on interaction energies could yield more erroneous results than the uncorrected interaction energies with respect to actual (experimental) energies. This could become more evident as the internuclear separations decrease. This implies that the intrinsic property of basis set originating from optimization procedure rather than BSSE

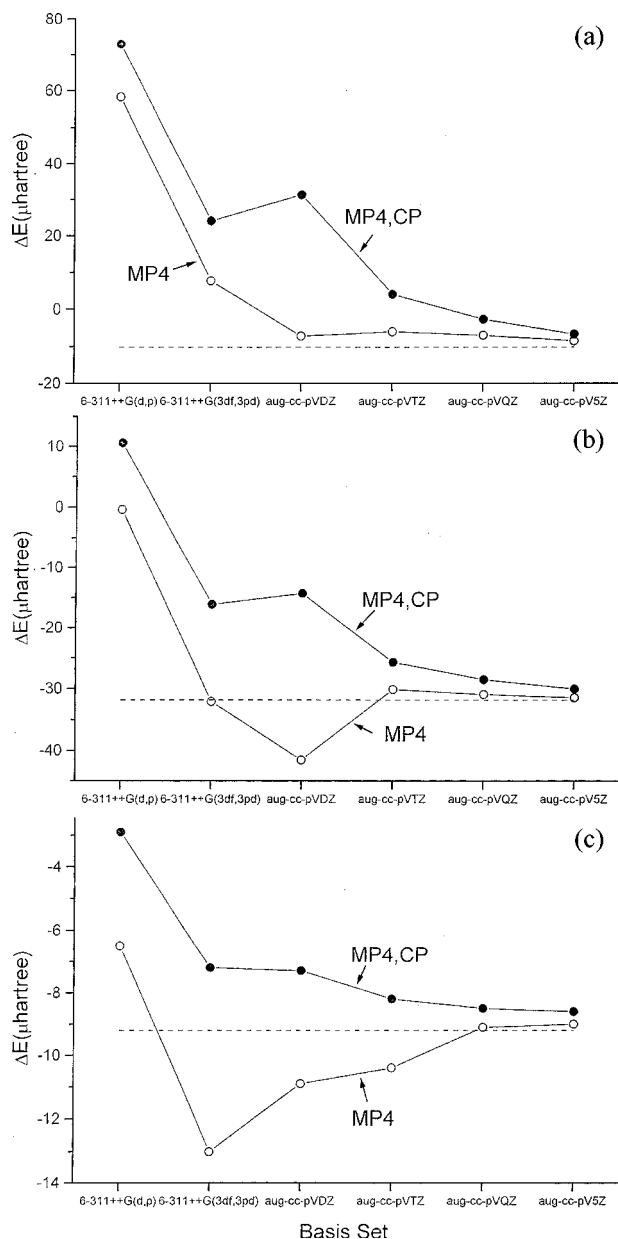


Figure 1. He-He interaction energies (ΔE) with (●) and without (○) counterpoise correction at MP4 level at different internuclear separation. The dashed line represents the estimated complete basis set limit (see the text). (a) $R(\text{He-He}) = 2.7 \text{ \AA}$. (b) $R(\text{He-He}) = 3.0 \text{ \AA}$. (c) $R(\text{He-He}) = 4.0 \text{ \AA}$.

could play a major role in determining the interaction energies of the complex, which becomes more evident as the internuclear distances between monomers are decreased. Our results are in accord with the recent study on some hydrogen-bonded systems where the uncorrected binding energies were found to be closer to the CBS limiting values than the CP corrected binding energies.²⁸ In this sense the previous success of CP method in reproducing the relatively accurate interaction energies for van der Waals molecules may be attributed in part to the larger internuclear separations between interacting partners.¹⁴⁻¹⁷ Further study on

other weakly bound systems is under way to explore the generality of our conclusions.

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