

Can the Counterpoise Correction for Basis Set Superposition Effect Be Justified?

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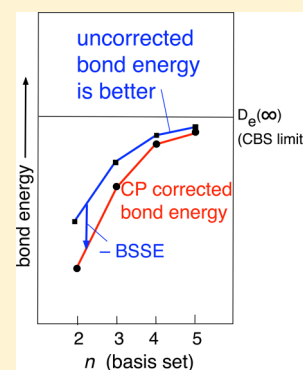
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S Supporting Information

ABSTRACT: The basis set superposition effect (BSSE) is a simple concept, and its validity is almost universally accepted. So is the counterpoise method to correct for it. The idea is that the basis set is biased toward the dimer because each monomer in the dimer can “use” the basis functions on the other monomer, which it cannot in a simple monomer calculation. This hypothesis can only be tested if basis set free benchmark numbers are available for monomers and dimer. We are testing the hypothesis on a few systems (in this paper Be_2) that are small enough that sufficiently accurate benchmark numbers (basis set free, or close to basis set limit; full CI or close to full CI) are available or can be obtained. We find that the answer to the title question is negative: the standard basis sets of quantum chemistry appear to be biased toward the atom in the sense that basis set errors are *larger* for the dimer than the monomer. Applying the counterpoise correction increases the imbalance by reducing the already smaller basis set error of the monomer even further. Counterpoise corrected bond energies then deviate more from the basis set limit numbers than uncorrected bond energies. These conclusions hold both at the Hartree–Fock level and (much stronger) at the correlated (CCSD(T), full CI) levels. So the answer to the title question is No.



I. INTRODUCTION

The basis set superposition effect (BSSE) is an intuitively highly plausible concept. Maybe the first application of an approach in this spirit has been for Hartree–Fock (HF) level calculation of a protonation energy by Jansen and Ros.¹ Subsequently the counterpoise correction (CPC) procedure was advocated by Boys and Bernardi² and extensively discussed and applied by Liu and McLean.^{3,4} It is the notion that when performing calculations on a dimer composed of two atoms or two molecular fragments, the basis set for one fragment in the dimer is actually somewhat better than for the stand alone fragment: in the dimer the fragment can utilize to some extent the additional basis functions that are brought in by the basis set on the other fragment. Therefore the binding energy will be exaggerated. An obvious way to correct for this BSSE is the performance of the monomer calculations in the full dimer basis set, the so-called Boys–Bernardi CPC method.² Some debate has been going on whether one should use in the CPC fragment basis the full set of basis functions on the other fragment, or only the virtual orbitals on that fragment. It is commonly accepted that the full basis should be used.⁵ By now BSSE and the need to use the CPC method is universally accepted. In particular when the interaction is small compared to the total energies of the fragments, as in weakly bound complexes (in particular dispersion bound systems), basis set effects are important. Nevertheless, critical discussions continue to appear,^{6–9} and it has also often been observed that CPC does not always improve the interaction

energy compared to a known benchmark result or a very good estimate based for instance on extrapolation to the CBS.^{10,11} In that case it has sometimes been argued that since we “know” that CPC is the proper thing to do, we should not let ourselves be deterred by such unhappy outcomes. In other words, even if the facts do not corroborate the intuitive notion of an error incurred by the BSSE phenomenon, we should not yield to the facts.

We try to take here an unprejudiced view: can we test the hypothesis that there is an error due to the BSSE that should be corrected by the CPC? (We define BSSE as basis set superposition *effect* to avoid bias in this discussion.) This can be done if we have basis set limit results available. Those can be obtained at several levels: HF and various correlated levels. The HF level is by far the easiest. It is possible to obtain basis set free results from some alternative methods that do not use basis set expansion. Here we will use the method and program devised by Kobus.¹² We will systematically compare the non-CPC and CPC results in a series of basis sets, at different distances between two monomers. The correlated level is much more difficult. In the first place we are dealing now with two effects: the basis set incompleteness, and the possible configuration incompleteness in the configuration interaction (CI) treatment. It is highly advantageous if we can eliminate the last problem by doing full configuration interaction (FCI) calculations up to the largest

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basis set we wish to test. This can be done in the He₂ dimer. The (dispersion) energy in this system has been investigated to very high accuracy, so benchmark numbers are available. Moreover, this system has been the model system for BSSE discussions.⁵ We have published results for correlated calculations in this system.¹³ In the He₂ system the interaction energy (van der Waals well depth of ca. 34 μE_H) is very small compared to the total energy of the dimer (and of two monomers), which is about 5.80 E_H . This system is a good example of the balancing act that has to be performed when the interaction energy is evaluated with finite basis sets. The total dimer energy (from FCI calculations) varies in the series of aug-cc-pVXZ, $X = 2-5$ basis sets as -5.77913994, -5.80170487, -5.80547332, -5.80643453. Even from QZ to SZ the jump is still around a thousand μE_H , while we are interested in the tiny interaction energy of 34 μE_H . A small imbalance in the accuracy of these basis sets for monomers versus dimer will hugely affect the reliability of the interaction energy calculation. Does CPC help to get this balance right? For He₂ it does not.¹³

Thorough testing of the hypothesis that an error in bond energies is incurred by the BSSE has been hampered by the dearth of reliable “hard data” (basis set free or basis set limit) for (correlated) interaction energies. The next useful system is the Be₂ dimer. It has received an enormous amount of interest, mostly because of the peculiar shape of the interaction energy curve.^{3,14–34} This has been explained from the intricate nature of the bonding in this system, which is a combination of dispersion energy and weak chemical bonding effects (basically donor–acceptor interaction between occupied 2s and empty 2p orbitals). These chemical bonding effects cause its binding energy of about 4000 μE_H (ca. 2.5 kcal/mol) to be already 2 orders of magnitude larger than the dispersion only interaction energy of He₂ of 34 μE_H . In this sense Be₂ is a much more typical representative of the systems for which usually the noncovalent interactions are studied, such as the S22 set,³⁵ which combine dispersion interaction and weak chemical bonding (donor–acceptor) effects such as π – π stacking. Accurate benchmark numbers for Be₂ are available from the work by Szalewicz et al.,^{25,26} which have been obtained from a combination of the most accurate calculations with elaborate testing to experimental results for the vibrational states.³⁶ We are able to do FCI calculations in a series of basis sets up to cc-pV6Z and aug-cc-pVSZ if we only correlate the 4 valence electrons and take the two 1s orbitals as inactive space. Doing CCSD(T) calculations, we can correlate all electrons up to basis sets of cc-pV6Z or aug-cc-pVSZ quality. We will discuss how this enables us, using well-known extrapolations to the basis set limit, to establish complete basis set limit (CBS) numbers to sufficient precision to achieve unambiguous conclusions regarding the magnitude and the effect of the BSSE and the CPC method. Of course, since we can generate exact, basis set free, data at the HF level, testing of BSSE for HF calculations is straightforward.

II. PROBLEM DEFINITION

We are interested in the errors coming from using finite basis set expansions. We will therefore not consider relativistic effects and non Born–Oppenheimer effects, which would be relevant for a comparison with experiment. For the latter we refer, for Be₂, to refs 25, 26, 37, and 38. Ideally we should use complete basis sets at any level we consider (HF, CCSD(T), FCI) to obtain benchmark numbers, but since those calculations are not feasible we will resort to some of the standard extrapolation procedures^{39–44} of estimating basis set limit values, see next

section. We test those procedures against some available basis set free benchmarks to assess their accuracy. Assuming that accurate complete basis set (CBS) numbers have been obtained, we can give definitions and describe the problem at hand as follows. The interaction energy of two monomers (subsystems) A and B obtained in a basis set denoted X is defined as

$$\begin{aligned}\Delta E^{\text{level}}(X) &= E_D^{\text{level}}(X) - E_A^{\text{level}}(X) - E_B^{\text{level}}(X) \\ &\equiv D^{\text{level}}(X) - A^{\text{level}}(X) - B^{\text{level}}(X) \quad \text{or} \\ &D^{\text{level}}(X) - 2M^{\text{level}}(X) \quad \text{if } A = B = M\end{aligned}\quad (1)$$

where “D” stands for “dimer” and “level” stands for the theoretical level used to account for the correlation energy: all-electron (AE) CCSD(T), or FCI, or valence-only (VO) CCSD(T) or FCI, or just HF. In general, equations we will omit this superscript. To avoid too many super- and subscripts we denote the energy of the dimer with just D and that of the monomers with just A or B , or for two equal monomers, with just $2M$. As can be seen from (eq 1) energies for the dimer AB and both monomers have to be evaluated separately to obtain the interaction energy (the supermolecule approach). Since in practical applications satisfying the completeness of the basis is impossible we are always working with finite basis sets. We are concerned with the possible errors that arise from basis set incompleteness. In Figure 1 we have drawn diagrams of the energy levels for some finite basis X compared to the basis set limit energy levels (denoted CBS), picturing two different situations for the relative magnitudes of the basis set errors of monomers and of dimer.

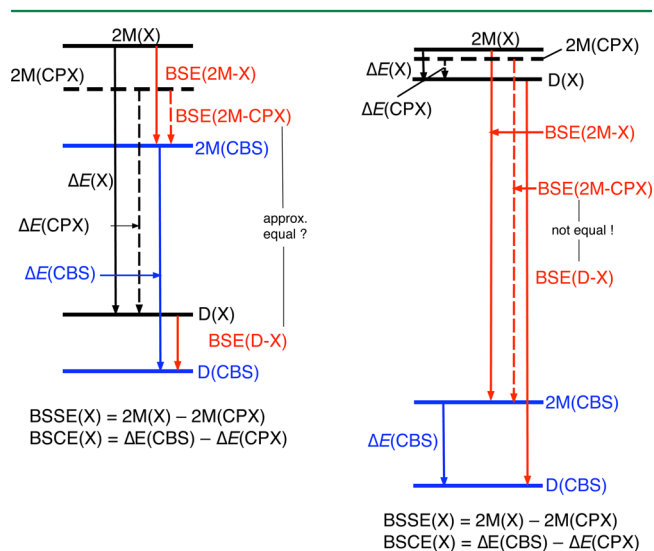


Figure 1. Level diagram for the energies of two identical monomers and the dimer calculated at some correlation level (or just HF) within the basis set X . The energies are compared to those of the CBS (blue) and the basis set error BSE (red: difference of the energy in CBS limit and in basis X) is defined for both dimer and monomers. The counterpoise corrected energy in basis X (CPX) is obtained by calculating a monomer in the full basis of both monomers (i.e., the dimer basis). In panel (a) the situation is pictured of a relatively small BSE compared to the bonding energy, and a larger BSE for the monomers than for the dimer. In panel (b) the more realistic situation is depicted of a relatively large BSE compared to the bonding energy, and a larger BSE for the dimer than for the two monomers.

The diagrams can be applied at any level of correlation treatment (or just HF). We define the basis set error (BSE) as the difference of the CBS number and the number obtained with basis set X ; there is obviously such an error for both the monomers and the dimer

$$\begin{aligned} \text{BSE}(\text{level}, D, X) &= D^{\text{level}}(\text{CBS}) - D^{\text{level}}(X) \\ \text{BSE}(\text{level}, 2M, X) &= 2(M^{\text{level}}(\text{CBS}) - M^{\text{level}}(X)) \end{aligned} \quad (2)$$

Panel a of Figure 1 depicts the situation in which the BSE is larger for the two monomers than for the dimer. This is generally expected, on the basis of the argument that the dimer can employ around each monomer the basis functions of the other monomer. This is supposed to lead to an imbalance in the treatment of the monomers and dimers, called the basis set superposition error. One can counter this by the so-called counterpoise technique: calculate the energy lowering of each monomer if the basis functions of the other monomer are added. The basis set superposition error is often just defined as this effect. There have been some arguments whether only the unoccupied orbitals in the given basis on the other monomer should be used, or all its basis functions, but the general feeling is that the whole basis set should be used.^{2,5} In very large basis sets this might obviously lead to an overcompleteness problem, but with basis sets used in practice this is not yet a problem. So the energy of a monomer A , or both monomers, in the counterpoise corrected basis is defined as

$$\begin{aligned} A(\text{CPX}) &= A(X\{\text{AB}\}) \quad \text{and} \\ 2M(\text{CPX}) &= 2[M(X\{\text{MM}\})] \end{aligned} \quad (3)$$

With $\{\text{AB}\}$ and $\{\text{MM}\}$ we indicate that the basis set on both monomers is used for the calculation of one monomer. We denote this henceforth as basis CPX. We have depicted in Figure 1a the ideal situation that the CPC reduces the BSE of $2M$ so much that it becomes almost equal to the BSE of the dimer D . Then the BSE of $2M$ and of D would cancel, and the CBS interaction energy is already obtained with the finite basis X . Of course perfect equality of the counterpoise corrected BSE for the monomers and the BSE of the dimer will not occur, but it is assumed that at least the CPC will bring the BSE of the monomers much closer to the BSE of the dimer, making $\Delta E(\text{CPX}) = D(X) - 2M(\text{CPX})$ a more realistic approximation to $\Delta E(\text{CBS}) = D(\text{CBS}) - 2M(\text{CBS})$.

Dunning¹¹ calls the basis set error that still consists for the CP corrected bond energy (the difference in the BSE of the counterpoise corrected monomers and the BSE of the dimer) the basis set completeness error BSCE. The signs of the error terms are defined as follows

$$\Delta E(X) = D(X) - 2M(X) \quad (\text{uncorrected bond energy})$$

$$\text{BSSE}(X) = 2M(X) - 2M(\text{CPX}) \quad (\text{positive})$$

$$\begin{aligned} \Delta E(\text{CPX}) &= D(X) - 2M(\text{CPX}) = \Delta E(X) + \text{BSSE}(X) \\ & \quad (\text{CP corrected bond energy}) \end{aligned}$$

$$\text{BSE}(D, X) = D(\text{CBS}) - D(X);$$

$$\text{BSE}(2M, X) = 2M(\text{CBS}) - 2M(X)$$

$$(\text{BSEs are negative})$$

$$\begin{aligned} \text{BSE}(2M, \text{CPX}) &= 2M(\text{CBS}) - 2M(\text{CPX}) \\ &= \text{BSE}(2M, X) + \text{BSSE}(X) \end{aligned}$$

$$\begin{aligned} \Delta E(\text{CBS}) &= D(\text{CBS}) - 2M(\text{CBS}) = D(X) + \text{BSE}(D, X) \\ & \quad - 2M(X) - \text{BSE}(2M, X) = \Delta E(X) + \Delta \text{BSE}(X) \\ & \rightarrow \Delta \text{BSE}(X) \quad (\text{error of the uncorrected bond energy}) \end{aligned}$$

$$\begin{aligned} \Delta E(\text{CBS}) &= D(\text{CBS}) - 2M(\text{CBS}) = D(X) + \text{BSE}(D, X) \\ & \quad - 2M(\text{CPX}) - \text{BSE}(2M, \text{CPX}) = \Delta E(\text{CPX}) + \Delta \text{BSE}(\text{CPX}) \\ & \rightarrow \Delta \text{BSE}(\text{CPX}) \quad (\text{error of the CP corrected bond energy}) \end{aligned}$$

$$\begin{aligned} \Delta E(\text{CBS}) - \Delta E(\text{CPX}) &\equiv \text{BSCE}(X) \\ & \quad (\text{error of CP corrected bond energy}) \end{aligned}$$

$$\begin{aligned} \Delta \text{BSE}(\text{CPX}) &= \text{BSE}(D, X) - \text{BSE}(2M, \text{CPX}) = \text{BSCE}(X) \\ & \quad (\text{error of CP corrected bond energy}) \end{aligned}$$

$$\begin{aligned} \Delta \text{BSE}(X) &= \text{BSE}(D, X) - \text{BSE}(2M, X) = \Delta E(\text{CBS}) \\ & \quad - \Delta E(X) = \text{BSCE}(X) + \text{BSSE}(X) \\ & \quad (\text{error of the uncorrected bond energy}) \end{aligned}$$

$$\begin{aligned} \Delta \text{BSE}(\text{CPX}) &= \Delta \text{BSE}(X) - \text{BSSE}(X) \\ & \quad (\text{CPC adds } -\text{BSSE} \text{ to error of the uncorrected bond energy}) \end{aligned} \quad (4)$$

Note that BSSE is always positive and the BSEs are all negative, due to the variation principle. Figure 1 pictures the ΔE s as negative, which will usually be the case, but they can of course be positive. The sign of BSCE depends on the relative magnitude of the BSEs of dimer and monomers. Now the assumptions embodied in Figure 1a often prove to be incorrect. The situation is most of the time not like the one of Figure 1a but rather like the one of Figure 1b. In the first place, the BSE is often, particularly in medium size basis sets, larger than the interaction energy, or at least of the same order of magnitude, in particular in the cases where the interaction energy is small (noncovalent interactions), which are exactly the cases where accuracy matters and where the BSSE has been an important issue. We gave the extreme example of He_2 in the introduction; Be_2 will provide other examples. With the large BSEs, compared to $\Delta E(X)$ and $\Delta E(\text{CBS})$, the issue of proper balance becomes also more intricate. In the second place, more importantly and more disturbingly, one often sees a *larger* BSE in the dimer than in the monomers, as also depicted in Figure 1b. Maybe that is not surprising. In the dimer a lot more is going on than in the atoms. There are chemical bonding effects, with types of correlation (such as left right correlation along the bond axis) that are absent in the atom. The dispersion interaction, which is the focus of much of the BSSE discussion, is precisely a typical dimer phenomenon, again a correlation that is absent in the atom. Maybe also the fact that the basis sets of quantum chemistry are atom centered means that there is a bias to higher accuracy in the atomic calculations. It is therefore maybe not surprising that we have found in the prototype He_2 case that the BSE was larger in the dimer (see ref 13). We will demonstrate here that this state of affairs also applies in the more realistic case of Be_2 , with its mix of dispersion and chemical bonding effects and much larger total interaction energy.

Table 1. Convergence of the HF Level Energies with the Basis Set for Be Atom^a

X	VXZ	aVXZ	CVXZ	aCVXZ
2	-14.5723376310	-14.5723803114	-14.5723382052	-14.5723803211
3	-14.5728734682	-14.5728753567	-14.5728734834	-14.5728755576
4	-14.5729681272	-14.5729691860	-14.5729681573	-14.5729692154
5	-14.5730120389	-14.5730125092	-14.5730120423	-14.5730125121
6	-14.5730207477			
CBS(5p)	-14.5730157473			
CBS(4p) ^b	-14.5730324636	-14.5730115941	-14.5730095528	-14.5730115398
CBS(3p) ^c	-14.5730229022	-14.5730496710	-14.5730499619	-14.5730497354
Exact ^d		-14.5730232039		

^aAll energies are given in hartree. ^bX = 3, 4, 5, 6 points are used in the case of cc-pVXZ, for the remaining basis sets X = 2, 3, 4, 5 points are used. ^cX = 4, 5, 6 points are used in the case of cc-pVXZ, for the remaining basis sets X = 3, 4, 5 points are used. ^dResult from numerical HF procedure of Kobus.¹²

III. METHODOLOGICAL DETAILS: VALIDATION OF EXTRAPOLATIONS TO THE CBS LIMIT

In this section we establish that we can obtain CBS limit numbers for the correlated energies to sufficient numerical precision that we can discuss BSE in the various basis sets, at the various levels of correlated treatment. As will be seen in the next section, from DZ to 5Z basis sets the BSEs range for all-electron correlated calculations from about 30000 μE_H to about 2000 μE_H . In the present section we will show that the numerical precision with which we can obtain the BSEs (the “error bars” on the BSEs) are a few tens of μE_H . VO FCI calculations have somewhat lower BSEs, ranging from 4600 (DZ) to 200 (5Z) and 100 μE_H (6Z). The error bars in that case are also lower, they are estimated at a couple of μE_H . The precision is more than sufficient to reliably discuss the BSEs, as a function of distance and of basis set, and in particular the effect of CPC on the BSE, see section IV.

HF level energy and correlation energy pose different demands on the basis set and have different convergence rates so it is justified and even advantageous to treat them separately. At the HF level, we can obtain benchmark numbers from basis set free techniques. We will use the method and programs of Kobus¹² for Be atom and Be dimer. There is also a correlated benchmark number available for the Be atom.³⁷ These independent basis set free HF and correlated benchmarks afford an estimate of the accuracy of the applied basis set extrapolation techniques.

In our investigation we have used four series of correlation consistent polarized X zeta (X being the so-called cardinal number) basis sets of Prascher et al.⁴⁵ Two series of basis sets were employed for VO correlation, namely cc-pVXZ with X = 2, 3, 4, 5, 6 (denoted VXZ) and aug-cc-pVXZ with X = 2, 3, 4, 5 (aVXZ). In all-electron (AE) calculations two series of corresponding core–valence basis sets were used, namely, cc-pCVXZ with X = 2, 3, 4, 5 (CVXZ) and aug-cc-pCVXZ with X = 2, 3, 4, 5 (aCVXZ). Additionally, to enhance saturation of the dimer basis, a set of bond functions of Partridge was used,⁴⁶ composed of uncontracted [6s6p6d3f1g1h] functions (MB95) positioned at the bond midpoint.

All calculations were performed using the GAMESS-US program package,⁴⁷ FCI calculations employed the ORMAS code.⁴⁸ We report in the tables the energies to two decimal places in μE_H . We have made sure that such numerical precision is achieved in the calculations. Several numerical thresholds were tightened, in particular: integral evaluation threshold 10^{-30} , SCF convergence threshold 10^{-8} , integral transformation threshold 10^{-10} , precision of Davidson diagonalization in CI 10^{-8} , CCSD amplitude convergence threshold 10^{-8} . As will be seen below, the

“error bars” on the CBS limit numbers, which constitute our reference values, are larger than this numerical precision.

A. CBS Limit for HF Calculations. Since the first step in the conventional calculations accounting for correlation is the HF SCF we turn our attention to the basis set convergence of the HF energy and estimate HF limit values. Since benchmark basis set free HF energies are available, also for the dimer, this only serves to test extrapolation procedures to obtain an estimate of the CBS values. To obtain this limit from finite basis set calculations at the HF level we employ the following exponential fit

$$E^{\text{HF}}(X) = E_{\text{CBS}}^{\text{HF}} + \alpha \exp^{-\beta X} \quad (5)$$

which is the so-called Dunning–Feller empirical extrapolation formula.^{39–42} In eq 5 $E^{\text{HF}}(X)$ are the HF energies as determined in the basis sets of cardinality X, α , β and $E_{\text{CBS}}^{\text{HF}}$ (the estimate of the CBS value of the HF energy) are obtained from a suitable fitting procedure. In our case the numerical fit was performed using the curve fitting package from Python’s SciPy library.⁴⁹

Be Atom. Results of the finite basis set HF calculations together with the CBS extrapolated values for the Be atom are collected in Table 1 and compared to the basis set free calculation. As could have been anticipated, inclusion of core functions has a negligible influence on the HF energy since the differences between the results in VXZ and CVXZ as well as between aVXZ and aCVXZ are below 1 μE_H . Atomic total energies are also not sensitive to the presence of diffuse functions, in this case the differences between nonaugmented and augmented sets are at the level of 1 μE_H for the larger basis sets. Comparing the energies from the largest basis sets it can be noted that all basis sets with X = 5 underestimate the exact value by 11 μE_H and going to X = 6 for VXZ reduces the difference to 2.5 μE_H , which marks an excellent performance. Surprisingly the CBS values extrapolated according to eq 5 do not improve the agreement with the benchmark value compared to the largest basis set results, except for the VXZ basis, where a 6Z result is available. Four point extrapolation (X = 2, 3, 4, 5) in the cases aVXZ, CVXZ, and aCVXZ gives energies roughly of the same accuracy as the corresponding X = 5 sets. Going to three point extrapolation, where sets with X = 3, 4, 5 are taken, overestimates the energy by 26 μE_H . In the VXZ series the 6Z basis achieves already an accuracy of 2.5 μE_H and the five-point (X = 2, 3, 4, 5, 6) and four-point (X = 3, 4, 5, 6) extrapolations actually slightly worsen that agreement to 7.5 and 9.2 μE_H respectively. Only three-point extrapolation reduces the error substantially to 0.3 μE_H which is an order of magnitude smaller than the value in V6Z and 2 orders of magnitude smaller compared to basis sets with X = 5. These atomic extrapolations show that with basis sets up to

Table 2. Convergence of the HF Level Energies with the Basis Set for Be Dimer at Equilibrium Internuclear Separation^a

X	VXZ	aVXZ	CVXZ	aCVXZ	CVXZ+MB95
2	−29.1322987785	−29.1326987054	−29.1323320241	−29.1327308211	−29.1329300268
3	−29.1337749163	−29.1338083766	−29.1337978125	−29.1338265964	−29.1338554441
4	−29.1340309055	−29.1340556214	−29.1340376444	−29.1340605254	−29.1340612817
5	−29.1341443009	−29.1341533088	−29.1341461163	−29.1341545472	−29.1341555356
6	−29.1341692835				
CBS(5p)	−29.1341546294				
CBS(4p) ^b	−29.1341981701	−29.1341631665	−29.1341363647	−29.1341611249	−29.1341624547
CBS(3p) ^c	−29.1341763428	−29.1342171159	−29.1342356881	−29.1342177326	−29.1342351512
Exact ^d			−29.1341759449		

^aAll energies are given in hartree. ^bX = 3, 4, 5, 6 points are used in the case of cc-pVXZ, for the remaining basis sets X = 2, 3, 4, 5 points are used. ^cX = 4, 5, 6 points are used in the case of cc-pVXZ, for the remaining basis sets X = 3, 4, 5 points are used. ^dResult from numerical HF procedure of Kobus.¹²

Table 3. Convergence of the (VO and AE) Correlation Energies with the Basis Set for Be Atom^a

X	VO		AE			
	VXZ	aVXZ	CVXZ		aCVXZ	
	FCI	FCI	CCSD(T)	FCI	CCSD(T)	FCI
2	−0.0445050438	−0.0445219035	−0.0794811580	−0.0794940093	−0.0795465879	−0.0795596019
3	−0.0455540325	−0.0455799151	−0.0894657703	−0.0894929639	−0.0894912997	−0.0895186366
4	−0.0459826592	−0.0459903615	−0.0926787765	−0.0927120458	−0.0926882390	−0.0927214678
5	−0.0460656734	−0.0460690974	−0.0934942304	−0.0935254940	−0.0934984883	−0.0935297157
6	−0.0461011340					
CBS ^b	−0.0461498436	−0.0461517056	−0.0943497886	−0.0943789478	−0.0943485859	−0.0943777135
exact ^c			−0.0943332547			

^aAll energies are given in hartree. ^bTwo point extrapolation according to formula 7 where two basis sets with the largest cardinal numbers were used from each set. ^cExact correlation energy is obtained by subtracting the numerical HF value from the ECGF(6000) result.³⁷

5Z we achieve accuracy in the order of 10 μE_H either from the largest basis set or from extrapolation.

Be₂ Dimer. We have performed similar tests of the HF total energy convergence for Be dimer at the experimentally deduced equilibrium internuclear separation of $R(\text{Be}-\text{Be}) = 4.6366 \text{ au}$.³⁶ The results are shown in Table 2. With respect to core functions a similar conclusion as for Be atom can be drawn in the case of the dimer: a few μE_H effect in the larger ($X = 4, 5$) bases. Diffuse functions have a slightly larger impact on the energy. Inclusion of the aug functions lowers the dimer energy by around 25 μE_H in $X = 4$ and by around 10 μE_H in $X = 5$. It is worth noting that adding the midbond set has the same effect on the HF energy as adding the aug functions. The errors with respect to the reference value, for basis sets with $X = 5$ are 32, 23, 30, 21, and 20 μE_H for VSZ, aVSZ, CVSZ, aCVSZ and CVSZ+MB95 respectively. CBS extrapolated energies offer an improvement only when a diffuse basis set (aVXZ, aCVXZ) or bond midpoint functions (CVXZ+MB95) are used together with 4 point extrapolation ($X = 2, 3, 4, 5$). When three point extrapolation is used the discrepancy with respect to the benchmark is larger (40–60 μE_H). The series with a 6Z function achieves notably higher accuracy. The energy in the V6Z is only 6.7 μE_H above the benchmark value, and three point extrapolation based on $X = 4, 5, 6$ reduces the error to the value of 0.4 μE_H .

We can conclude that as far as HF energies are concerned the 5Z basis sets can yield a precision of about 20 μE_H and extrapolation does not improve this. The 6Z basis is clearly superior (6.7 μE_H) and allows for more successful extrapolation (to 0.4 μE_H). These tests provide information on the efficacy of extrapolation techniques. We will however use in this work the basis set free benchmark numbers we can calculate with the methods and programs of ref 12.

B. CBS Limit for Correlated Calculations. We will now proceed to establish CBS limit numbers for the correlation energy at various levels (VO FCI, AE CCSD(T)) by examining the convergence of the correlation energy defined in the usual way as the difference between HF and post-HF treatment at some level in the given basis X

$$E_{\text{corr}}^{\text{level}}(X) = E^{\text{level}}(X) - E^{\text{HF}}(X) \quad (6)$$

Correlation energies obtained in the series of correlation-consistent basis sets will then be extrapolated to the CBS limit using the 2 point extrapolation technique proposed by Helgaker et al.^{43,44} according to the formula

$$E_{\text{corr}}(\text{CBS}) = \frac{X^3 E_X - (X-1)^3 E_{X-1}}{X^3 - (X-1)^3} \quad (7)$$

where X and $X-1$ denote a pair of basis sets with subsequent cardinalities and E_X , E_{X-1} their respective correlation energies. We can examine the convergence of the correlation energy at some level and the performance of the CBS extrapolation technique for the Be atom for which a very accurate nonrelativistic Born–Oppenheimer energy, obtained with 6000 explicitly correlated Gaussian functions (ECGF(6000)), is available.³⁷ Unfortunately accurate correlated benchmark energies are not yet available for the Be dimer; therefore, we will have to resort to the extrapolation techniques to obtain the CBS results for the energy of Be₂ at the correlation levels to be investigated at the relevant distances, which can be added to the basis set free HF energies of the dimer at those distances to obtain our best CBS estimates of the total dimer energies.

Since in our discussion of basis set effects we would like to exclude any method related errors such as configuration basis

Table 4. Convergence of the VO Correlation Energies with the Basis Set for Be Dimer at Equilibrium Internuclear Separation^a

X	VXZ		aVXZ	
	CCSD(T)	FCI	CCSD(T)	FCI
2	−0.1006245329	−0.1018156424	−0.1009784529	−0.1022212373
3	−0.1047828536	−0.1059553512	−0.1051595256	−0.1063464496
4	−0.1062511383	−0.1073462078	−0.1064207465	−0.1075274600
5	−0.1066997691	−0.1077648534	−0.1067608859	−0.1078266562
6	−0.1068704347	−0.1079158272		
CBS ^b	−0.1071048655	−0.1081232088	−0.1071177535	−0.1081405670

^aAll energies are given in hartree. ^bTwo point extrapolation according to formula 7 where two basis sets with the largest cardinal numbers were used from each set.

inconsistency as defined by Liu and McLean,⁴ our method of choice is FCI. Unfortunately FCI calculations in the all electron (AE) dimer case are only possible for the smallest basis set and they are prohibitively expensive for larger ones. We will therefore only apply FCI for VO calculations, where two (one) inner orbitals are kept doubly occupied in all the determinants constituting the Be dimer (atom) FCI expansion. In the AE dimer case we turned to coupled cluster expansion with single and double excitations with the perturbative correction for triples (CCSD(T)).

Be Atom. In Table 3 finite basis set correlation energies obtained for Be atom from VO-FCI, AE-CCSD(T), and AE-FCI and their corresponding CBS values from the two-point extrapolation are collected and compared to the benchmark ECGF(6000) correlation energy obtained from the total energy of ref 37 by subtracting the basis set free HF energy. The second and third columns compare VO-FCI correlation energies for the Be atom in the series of VXZ and aVXZ basis sets respectively. (With two valence electrons, FCI is equivalent to CCSD.) It can be noted that for all the cardinal numbers the augmentation of the basis has little effect: the aVXZ results differ by at most a few tens of μE_H from VXZ, with the largest difference for triple- ζ (26 μE_H) and the smallest difference for quintuple- ζ (3 μE_H). Remarkably, despite the fact that the VO-CBS values were obtained with different cardinal pairs from two different series of basis sets ($X = 5, 6$ for VXZ and $X = 4, 5$ for aVXZ) the CBS extrapolated values of the correlation energies differ only by 2 μE_H , which gives confidence in the extrapolation procedure. Although we do not have a basis set free benchmark number available for the VO correlation energy to test the extrapolated value, it appears that a few μE_H is a fair estimate of the accuracy of our extrapolated CBS value for the VO correlation energy. This is adequate accuracy in view of the BSEs for the VO correlated energy ranging from 4600 μE_H (17900 for dimer) for DZ basis to 200 for basis 5Z, see next section.

For the all-electron correlation energy of Be atom a benchmark number is available by subtracting the basis set free HF energy from the total energy with 6000 explicitly correlated Gaussians (ECG6000) of ref 37. The all-electron correlation energies (about twice as large as the VO correlation energies because now four electrons are correlated) at both CCSD(T) and FCI level exhibit higher sensitivity to the presence of diffuse functions than VO energies, see Table 3. This effect is largest for $X = 2$ where the difference ($E_{\text{corr}}^{\text{CCSD(T)/FCI(aCV2Z)}} - E_{\text{corr}}^{\text{CCSD(T)/FCI(CV2Z)}}$) is around $-65 \mu E_H$ and diminishes with basis set size to reach the value of around $-4 \mu E_H$ in the largest $X = 5$ basis. The difference between all-electron FCI and CCSD(T) correlation energies is, for the atom, rather minor (not for the dimer, see below). The difference between the two correlation treatments is smallest for the smallest basis set ($-13 \mu E_H$ for $X = 2$) and grows with

increasing cardinal number to reach $-31 \mu E_H$ for $X = 5$. The CCSD(T) error with respect to FCI is independent of the presence of augmented functions. When AE CCSD(T)/FCI correlation in the largest available basis sets are compared to the benchmark they are both still some 800 μE_H too positive. Application of the extrapolation procedure is quite effective, it reduces this discrepancy by an order of magnitude. FCI CBS values in both CVXZ and aCVXZ bases overestimate the benchmark correlation by around 45 μE_H and for CCSD(T) this overestimate is 16 μE_H . The agreement of our extrapolated CBS values for both CCSD(T) and FCI is an order of magnitude better than with the largest basis set, and establishes the error bars on these values to be about 50 μE_H . It should be noted that the better agreement between CCSD(T) and reference correlation than between FCI and reference correlation should be considered accidental. The AE-CCSD(T) calculations do not have to converge to the exact correlation energy, and the difference of the AE-CCSD(T) extrapolated value with the benchmark correlation energy as well as with the FCI extrapolated value is within the errors bars of the extrapolation procedure anyway. For the sake of consistency we have chosen to use the extrapolated AE-CCSD(T) correlation energy as the basis set limit number for the calculation of the monomer BSE(X) in the AE-CCSD(T) calculations in the various basis sets X . Since the basis set errors (BSE) range at the all-electron level from 31 000 (basis DZ) to 1720 (basis 5Z) μE_H (see next section) the choice between benchmark value or extrapolated value is irrelevant.

Be₂ Dimer. As in the basis convergence study for HF, we have chosen the equilibrium distance to examine convergence properties and CBS values of the dimer correlation energy. Table 4 collects the results of the VO-CCSD(T) and VO-FCI in the series of VXZ and aVXZ basis sets. The first striking observation is the relatively large difference between VO-FCI and VO-CCSD(T) which is more than 1000 μE_H and appears to be quite insensitive to increasing cardinal number and the presence of diffuse functions in the aVXZ set. If it is contrasted with the AE calculations for Be atom, where also four electrons were correlated and the difference between AE-FCI and AE-CCSD(T) was only 13 (DZ) to 31 (5Z) μE_H , one can see how much more important is the inclusion of higher excitations for the dimer than for the atom. The VO-FCI CBS extrapolated energies differ from VO-CCSD(T) CBS by 1018 μE_H and 1022 μE_H in VXZ and aVXZ respectively. Differences between results obtained with and without diffuse functions range from 377 ($X = 2$) to 61 ($X = 5$) μE_H for CCSD(T) and from 406 ($X = 2$) to 62 ($X = 5$) μE_H for FCI and further reduce after extrapolation is performed to 13 μE_H and 17 μE_H for VO-CCSD(T) and VO-FCI respectively. In view of the large discrepancy between CCSD(T) and FCI results we will discuss for the VO correlation

calculations just the FCI results, and use the extrapolated VO-FCI correlation energy from the VXZ bases, which go up to $X = 6$, as the CBS limit value for VO correlation. Although no basis set free VO benchmark value is available for the VO-FCI correlation energy (and neither for the VO-CCSD(T) correlation energy), the relatively small error between CBS energies extrapolated from the two different basis sets (VXZ and aVXZ) using different cardinal pairs provides confidence that the CBS VO-FCI correlation energy is close (within $20 \mu E_H$) to the true basis set limit.

Turning now to the all-electron correlation energy, acquiring a highly accurate value is virtually impossible since AE-FCI calculations because of their steep scaling are only feasible for the smallest CV2Z set. Therefore in the all-electron calculations we will be limited to only the CCSD(T) correlation level, which may differ substantially from FCI (see previous paragraph). Our BSSE study is thus limited to this correlation level, and we need to establish a CBS limit value of the dimer correlation energy at this level. Results of AE-CCSD(T) calculations are presented in Table 5. The enhancement in the correlation energy caused by

Table 5. Convergence of the AE-CCSD(T) correlation Energies with the Basis Set for Be Dimer at Equilibrium Internuclear Separation^a

X	CVXZ	aCVXZ	CVXZ+MB95
2	-0.1709363553	-0.1715301913	-0.1810234852
3	-0.1928426651	-0.1931746332	-0.1952924715
4	-0.1999643292	-0.2001280312	-0.2005329282
5	-0.2018618254	-0.2019219576	-0.2020576624
CBS ^b	-0.2038526411	-0.2038041099	-0.2036573835

^aAll energies are given in hartree. ^bTwo point extrapolation according to formula 7 where two basis sets with the largest cardinal numbers were used from each set.

the presence of diffuse functions (aCVXZ with respect to CVXZ) varies from around $600 \mu E_H$ for $X = 2$ to $60 \mu E_H$ for $X = 5$. As expected, and as observed before, when the CVXZ basis set becomes more saturated the influence of aug functions becomes less important. CBS extrapolations from CVXZ and aCVXZ result in energies only $50 \mu E_H$ apart. We choose the CBS value extrapolated from the aCVXZ series as the CBS limit value for the dimer correlation energy at the AE CCSD(T) level of theory for use in the BSE calculations of the next section.

We have added in Table 5 a further series of basis sets, the standard CVXZ and aCVXZ sets augmented with a set of 95 midbond functions⁴⁶ which we will use to discuss a case where the basis set for the dimer has been very much extended so as to correct for the deficiency of the “normal” atomic basis sets for the description of molecular correlation effects. Especially for the smallest basis set the influence of the MB95 set on the correlation energy is dramatic. For $X = 2$ the difference between CVXZ with and without MB95 is 10 mH ! The midbond functions apparently effectively compensate for the lack of higher angular momentum functions that are centered on the nuclear positions.⁵⁰ However, these basis sets do not show the same regular trends as the CVXZ and aCVXZ basis sets. For instance the influence of aug functions shows irregular behavior along the series, with the smallest effect ($13 \mu E_H$) at the DZ basis and a maximum effect of $544 \mu E_H$ at the 4Z basis. Also, although the correlation energies are all larger than with the basis sets lacking bond midpoint functions, the irregular behavior of these basis sets make the extrapolation somewhat questionable. It leads for the aCVXZ+MB95 series to

an about $650 \mu E_H$ smaller CBS limit value for the correlation energy than from the aCVXZ basis series. Since apparently the inclusion of the MB95 set changes the convergence pattern and energy increments of the series considerably, so that the correlation-consistency of the whole set is distorted, the value extrapolated from the aCVXZ+MB95 series does not seem to be a reliable CBS limit value for the dimer correlation energy at AE CCSD(T) level.

For reference purposes we list in Table 6 the numbers we have actually used as (approximate) CBS values, both the basis set free

Table 6. Be Atom and Dimer HF Basis Set Free Energies, and the VO-FCI Correlation and AE-CCSD(T) Correlation Energies (Both Extrapolated CBS Limit Values) Used as the Benchmark Approximate Basis Set Free Values^a

R(Be–Be)	exact HF ^b	$E_{\text{corr}}^{\text{VO-FCI } c}$	$E_{\text{corr}}^{\text{AE-CCSD(T) } d}$
3.00	-29.0204121180	-0.1368607252	-0.2348033793
4.00	-29.1201074860	-0.1171235483	-0.2132425632
4.64	-29.1341759449	-0.1081232088	-0.2038041099
5.00	-29.1376959774	-0.1042018155	-0.1998726645
6.00	-29.1424126012	-0.0977166697	-0.1936393733
7.00	-29.1445364969	-0.0949611607	-0.1911083797
8.00	-29.1454847254	-0.0936613887	-0.1899297244
10.00	-29.1459862338	-0.0926596076	-0.1890249882
12.00	-29.1460412260	-0.0924031179	-0.1887937038
15.00	-29.1460462295	-0.0923231803	-0.1887188556
atom	-14.5730232039	-0.0461498436	-0.0943485859

^aAll values in atomic units. ^bNumerical HF results obtained using the program of Kobus. ^cExtrapolated from the VXZ set using $X = 5, 6$. ^dExtrapolated from aCVXZ using $X = 4, 5$.

HF values for Be atom and dimer, and the extrapolated CBS limit values for the correlation energies at both VO-FCI and AE-CCSD(T) level for the atom and dimer.

IV. RESULTS: BASIS SET ERRORS IN HF AND CORRELATED CALCULATIONS AND ADVERSE EFFECT OF THE CPC

Since the basis set error of the dimer, BSE(D) as well as the CPC BSSE will exhibit a dependence on the internuclear separation, 10 internuclear distances were selected at which the BSEs and BSSEs are catalogued, providing a discrete representation of the potential energy curve. Two internuclear distances are in the short-range part: 3.0 and 4.0 Bohr; the experimentally determined equilibrium distance of 4.6366;³⁶ and 7 distances in the mid- and long-range part, 5.0, 6.0, 7.0, 8.0, 10.0, 12.0, and 15.0 Bohr.

Discussion of basis set errors will be divided into three parts. Errors at the HF level are first treated, next the correlated level will be presented. Finally we comment on the effect of bond midpoint functions.

A. Basis Set Errors for the Dimer Binding Energy and the BSSE at the HF Level. HF level and correlated BSEs and interaction energies can be separated according to

$$\begin{aligned} \Delta E^{\text{level}}(X) &= D^{\text{HF}}(X) - A^{\text{HF}}(X) - B^{\text{HF}}(X) + D_{\text{corr}}^{\text{level}}(X) \\ &\quad - A_{\text{corr}}^{\text{level}}(X) - B_{\text{corr}}^{\text{level}}(X) \\ &= \Delta E^{\text{HF}}(X) + \Delta E_{\text{corr}}^{\text{level}}(X) \end{aligned} \quad (8)$$

Table 7 presents the results for binding energy calculations at the HF level, with the cc-pVXZ ($X = D, T, Q, 5, 6$) series of basis sets.

Table 7. HF Basis Set Errors (BSEs) for Beryllium Dimer and Two Beryllium atoms in the Series of cc-pVXZ ($X = D, T, Q, S, 6$) Basis Sets^a

$R(\text{Be}-\text{Be})$ (au)	basis	BSE(D)	BSE(2M)	BSE(2M, CP)	BSSE	$\Delta\text{BSE} = \text{error}$ uncorr	$\Delta\text{BSE}(\text{CP}) = \text{error CP}$ corr	$E_{\text{int}}^{\text{HF}}$	$\text{CP} E_{\text{int}}^{\text{HF}}$	$E_{\text{int}}^{\text{exactHF}}$
R = 3.00	D	-6955.31	-1371.15	-1334.06	37.09	-5584.16	-5621.25	131218.45	131255.54	125634.29
	T	-1905.47	-299.47	-296.00	3.47	-1606.00	-1609.47	127240.29	127243.76	
	Q	-228.28	-110.15	-107.75	2.40	-118.13	-120.53	125752.41	125754.82	
	S	-52.55	-22.33	-20.63	1.70	-30.22	-31.91	125664.50	125666.20	
	6	-11.80	-4.91	-4.76	0.15	-6.89	-7.04	125641.18	125641.33	
R = 4.00	D	-2491.17	-1371.15	-1337.21	33.93	-1120.02	-1153.96	27058.95	27092.88	25938.92
	T	-609.43	-299.47	-297.09	2.38	-309.96	-312.34	26248.88	26251.27	
	Q	-173.42	-110.15	-108.22	1.93	-63.27	-65.20	26002.19	26004.12	
	S	-37.68	-22.33	-21.15	1.18	-15.35	-16.52	25954.27	25955.45	
	6	-8.25	-4.91	-4.81	0.10	-3.34	-3.44	25942.26	25942.36	
R = 4.64	D	-1877.17	-1371.15	-1338.32	32.82	-506.02	-538.84	12376.48	12409.31	11870.46
	T	-401.03	-299.47	-297.17	2.31	-101.56	-103.86	11972.02	11974.33	
	Q	-145.04	-110.15	-108.43	1.72	-34.89	-36.61	11905.35	11907.07	
	S	-31.64	-22.33	-21.31	1.02	-9.31	-10.34	11879.78	11880.80	
	6	-6.66	-4.91	-4.83	0.08	-1.75	-1.83	11872.21	11872.29	
R = 5.00	D	-1725.20	-1371.15	-1338.76	32.39	-354.05	-386.44	8704.48	8736.87	8350.43
	T	-357.73	-299.47	-297.50	1.97	-58.26	-60.23	8408.69	8410.66	
	Q	-134.46	-110.15	-108.46	1.70	-24.31	-26.00	8374.74	8376.44	
	S	-28.87	-22.33	-21.39	0.94	-6.54	-7.48	8356.97	8357.91	
	6	-6.08	-4.91	-4.84	0.08	-1.16	-1.24	8351.59	8351.67	
R = 6.00	D	-1518.80	-1371.15	-1344.73	26.42	-147.65	-174.07	3781.46	3807.88	3633.81
	T	-317.25	-299.47	-297.74	1.73	-17.78	-19.50	3651.58	3653.31	
	Q	-117.61	-110.15	-108.81	1.34	-7.46	-8.80	3641.27	3642.61	
	S	-24.34	-22.33	-21.59	0.74	-2.01	-2.75	3635.81	3636.56	
	6	-5.27	-4.91	-4.85	0.07	-0.36	-0.43	3634.17	3634.23	
R = 7.00	D	-1405.93	-1371.15	-1349.84	21.30	-34.78	-56.08	1544.69	1566.00	1509.91
	T	-307.70	-299.47	-297.93	1.54	-8.23	-9.77	1518.14	1519.68	
	Q	-112.27	-110.15	-109.01	1.14	-2.11	-3.25	1512.02	1513.16	
	S	-22.79	-22.33	-21.76	0.57	-0.46	-1.04	1510.37	1510.95	
	6	-5.04	-4.91	-4.86	0.05	-0.13	-0.18	1510.04	1510.09	
R = 8.00	D	-1347.73	-1371.15	-1352.18	18.97	23.42	4.45	538.26	557.23	561.68
	T	-303.79	-299.47	-298.30	1.17	-4.32	-5.49	566.00	567.17	
	Q	-111.35	-110.15	-109.33	0.82	-1.19	-2.01	562.88	563.70	
	S	-22.13	-22.33	-21.89	0.44	0.20	-0.25	561.49	561.93	
	6	-4.97	-4.91	-4.87	0.04	-0.05	-0.09	561.74	561.78	
R = 10.00	D	-1348.89	-1371.15	-1357.81	13.34	22.26	8.92	37.92	51.26	60.17
	T	-298.69	-299.47	-298.56	0.91	0.78	-0.13	59.39	60.31	
	Q	-109.90	-110.15	-109.60	0.55	0.26	-0.30	59.92	60.47	
	S	-22.04	-22.33	-22.00	0.33	0.29	-0.03	59.88	60.21	
	6	-4.90	-4.91	-4.89	0.03	0.01	-0.01	60.16	60.19	
R = 12.00	D	-1359.84	-1371.15	-1360.89	10.25	11.31	1.06	-6.13	4.12	5.18
	T	-298.54	-299.47	-298.87	0.60	0.93	0.33	4.25	4.85	
	Q	-109.53	-110.15	-109.78	0.38	0.62	0.24	4.56	4.94	
	S	-21.93	-22.33	-22.07	0.26	0.40	0.14	4.78	5.04	
	6	-4.84	-4.91	-4.89	0.02	0.07	0.05	5.11	5.13	
R = 15.00	D	-1369.70	-1371.15	-1369.86	1.28	1.45	0.17	-1.27	0.01	0.18
	T	-299.03	-299.47	-299.12	0.35	0.44	0.09	-0.26	0.09	
	Q	-109.80	-110.15	-109.88	0.27	0.36	0.08	-0.18	0.09	
	S	-22.05	-22.33	-22.14	0.19	0.28	0.09	-0.10	0.09	
	6	-4.82	-4.91	-4.90	0.01	0.10	0.08	0.08	0.09	

^aAll values are given in $\mu\text{hartree}$. $\Delta\text{BSE} = \text{BSE}(\text{D}) - \text{BSE}(2\text{M})$ is the basis set error in the (uncorrected) dimer binding energy, $\Delta\text{BSE}(X) = \Delta E(\text{CBS}) - \Delta E(X)$. $\Delta\text{BSE}(\text{CP})$ are the errors in the dimer binding energy that remain after CPC of the monomer energies, $\Delta E(\text{CBS}) - \Delta E(\text{CPX})$.

The binding energies are all repulsive, because of Pauli repulsion between the closed shells, although the Pauli repulsion is counteracted by chemical bonding effects. In this case dimer and monomer BSEs are evaluated with respect to the numerical HF values from the procedure of Kobus.¹² The BSE of the monomers is of course constant at all distances. It diminishes

rapidly though the series $X = \text{D}-6$. For $R \leq 7.00$ bohr, that is, except for very long distances, the $\text{BSE}(\text{D})$ is always larger than the $\text{BSE}(2\text{M})$. At longer distances, where the binding energy becomes small, the BSEs for dimer and monomers of course approach each other. At shorter distances, for instance around the equilibrium distance of 4.64 bohr, the BSE of the dimer is

Table 8. VO FCI Basis Set Errors (BSEs) for Beryllium Dimer and Two Beryllium Atoms in the Series of cc-pVXZ ($X = D, T, Q, 5, 6$) Basis Sets^a

$R(\text{Be-Be})$ (au)	basis	BSE(D)	BSE(2M)	BSE(2M,CP)	BSSE	$\Delta\text{BSE} = \text{error uncorr}$	$\Delta\text{BSE (CP)} = \text{error CP corr}$	$E_{\text{int}}^{\text{FCI}}$	$^{\text{CP}}E_{\text{int}}^{\text{FCI}}$	$E_{\text{int}}^{\text{exact}}$
R = 3.00	D	-17905.04	-4660.75	-4233.71	427.03	-13244.29	-13671.32	94317.54	94744.58	81073.25
	T	-5404.12	-1491.09	-1195.65	295.44	-3913.03	-4208.47	84986.28	85281.72	
	Q	-1287.85	-444.52	-366.00	78.53	-843.33	-921.86	81916.58	81995.11	
	5	-546.72	-190.67	-149.32	41.35	-356.05	-397.40	81429.30	81470.66	
	6	-297.78	-102.33	-84.86	17.47	-195.45	-212.92	81268.70	81286.17	
R = 4.00	D	-9917.17	-4660.75	-4443.94	216.81	-5256.43	-5473.24	6371.49	6588.30	1115.06
	T	-3128.86	-1491.09	-1326.87	164.23	-1637.76	-1801.99	2752.82	2917.05	
	Q	-1014.48	-444.52	-401.57	42.96	-569.96	-612.92	1685.02	1727.98	
	5	-437.36	-190.67	-167.79	22.88	-246.69	-269.58	1361.75	1384.64	
	6	-239.55	-102.33	-92.59	9.74	-137.22	-146.96	1252.28	1262.02	
R = 4.64	D	-8184.73	-4660.75	-4497.14	163.60	-3523.99	-3687.59	-429.07	-265.47	-3953.06
	T	-2568.89	-1491.09	-1384.36	106.74	-1077.79	-1184.53	-2875.27	-2768.53	
	Q	-922.04	-444.52	-416.73	27.79	-477.52	-505.31	-3475.54	-3447.75	
	5	-390.00	-190.67	-174.76	15.91	-199.33	-215.24	-3753.73	-3737.82	
	6	-214.04	-102.33	-96.31	6.02	-111.71	-117.73	-3841.35	-3835.33	
R = 5.00	D	-7619.35	-4660.75	-4521.11	139.64	-2958.61	-3098.25	-593.09	-453.45	-3551.70
	T	-2380.14	-1491.09	-1407.68	83.42	-889.05	-972.47	-2662.65	-2579.23	
	Q	-881.80	-444.52	-422.90	21.63	-437.27	-458.90	-3114.42	-3092.80	
	5	-371.77	-190.67	-178.40	12.27	-181.10	-193.37	-3370.60	-3358.33	
	6	-204.51	-102.33	-97.63	4.70	-102.18	-106.88	-3449.52	-3444.82	
R = 6.00	D	-6552.59	-4660.75	-4567.36	93.38	-1891.85	-1985.23	108.67	202.05	-1783.18
	T	-2060.58	-1491.09	-1448.48	42.61	-569.49	-612.10	-1213.69	-1171.07	
	Q	-767.43	-444.52	-431.69	12.84	-322.91	-335.75	-1460.27	-1447.43	
	5	-326.04	-190.67	-184.23	6.44	-135.37	-141.81	-1647.81	-1641.36	
	6	-179.87	-102.33	-99.94	2.39	-77.54	-79.93	-1705.64	-1703.24	
R = 7.00	D	-5725.95	-4660.75	-4587.84	72.91	-1065.21	-1138.11	-86.36	-13.45	-1151.56
	T	-1886.52	-1491.09	-1468.98	22.11	-395.42	-417.54	-756.14	-734.03	
	Q	-690.02	-444.52	-437.26	7.26	-245.50	-252.76	-906.06	-898.80	
	5	-293.87	-190.67	-187.14	3.53	-103.20	-106.73	-1048.36	-1044.83	
	6	-161.92	-102.33	-101.22	1.11	-59.59	-60.69	-1091.98	-1090.87	
R = 8.00	D	-5164.06	-4660.75	-4601.36	59.38	-503.31	-562.69	-296.71	-237.33	-800.02
	T	-1750.68	-1491.09	-1474.39	16.70	-259.59	-276.29	-540.43	-523.73	
	Q	-638.95	-444.52	-440.95	3.58	-194.43	-198.01	-605.59	-602.01	
	5	-273.56	-190.67	-188.84	1.83	-82.89	-84.72	-717.13	-715.30	
	6	-150.47	-102.33	-101.80	0.53	-48.14	-48.67	-751.88	-751.35	
R = 10.00	D	-4754.77	-4660.75	-4638.27	22.47	-94.02	-116.49	-205.73	-183.25	-299.75
	T	-1562.16	-1491.09	-1482.56	8.53	-71.06	-79.60	-228.68	-220.15	
	Q	-520.76	-444.52	-442.96	1.56	-76.23	-77.80	-223.51	-221.95	
	5	-231.09	-190.67	-189.95	0.72	-40.42	-41.14	-259.33	-258.61	
	6	-125.88	-102.33	-102.13	0.20	-23.54	-23.75	-276.20	-276.00	
R = 12.00	D	-4680.59	-4660.75	-4654.54	6.21	-19.85	-26.05	-78.40	-72.20	-98.25
	T	-1504.72	-1491.09	-1488.46	2.64	-13.63	-16.26	-84.62	-81.99	
	Q	-461.41	-444.52	-443.80	0.73	-16.89	-17.61	-81.36	-80.64	
	5	-201.05	-190.67	-190.32	0.35	-10.38	-10.73	-87.87	-87.52	
	6	-108.51	-102.33	-102.25	0.08	-6.17	-6.26	-92.07	-91.99	
R = 15.00	D	-4664.62	-4660.75	-4660.08	0.67	-3.87	-4.54	-19.44	-18.78	-23.31
	T	-1493.46	-1491.09	-1490.94	0.15	-2.37	-2.52	-20.95	-20.79	
	Q	-447.32	-444.52	-444.41	0.11	-2.80	-2.91	-20.52	-20.41	
	5	-192.34	-190.67	-190.58	0.09	-1.67	-1.76	-21.64	-21.56	
	6	-103.36	-102.33	-102.30	0.03	-1.03	-1.06	-22.29	-22.25	

^aAll values are given in $\mu\text{hartree}$. $\Delta\text{BSE} = \text{BSE(D)} - \text{BSE(2M)}$ is the basis set error in the (uncorrected) dimer binding energy, $\Delta\text{BSE}(X) = \Delta E(\text{CBS}) - \Delta E(X)$. $\Delta\text{BSE(CP)}$ are the errors in the dimer binding energy that remain after CPC of the monomer energies, $\Delta E(\text{CBS}) - \Delta E(\text{CPX})$.

considerably larger than that of the monomer, for all basis sets, but most markedly for the smaller basis sets. This underlines our contention that the atom centered basis sets are biased toward the atom. The CPC then makes the imbalance worse since it reduces the BSE of the monomers further. However, the BSSE is very small, so this effect is quite small. At all distances and for all

basis sets the BSSE is one to 2 orders of magnitude smaller than the BSEs for both dimer and monomers. This is the same as saying that the BSE(2M,X) and the counterpoise corrected BSE(2M,CPX) are very similar, and both are considerably smaller than the BSE(D) . The BSSE is even quite small compared to the difference between the BSE(D) and BSE(2M) .

Table 9. All-Electron CCSD(T) Basis Set Errors (BSEs) for Beryllium Dimer and Two Beryllium Atoms in the Series of cc-pCVXZ ($X = D, T, Q, 5$) Basis Sets^a

R(Be–Be) (au)	basis	BSE(D)	BSE(2M)	BSE(2M,CP)	BSSE	$\Delta BSE = \text{error}$ uncorr	$\Delta BSE(\text{CP}) = \text{error}$ CP corr	$E_{\text{int}}^{\text{CCSD(T)}}$	$E_{\text{int}}^{\text{CP-CCSD(T)}}$	$E_{\text{int}}^{\text{exact}}$
R = 3.00	D	–44434.18	–31104.85	–29775.99	1328.87	–13329.33	–14658.19	92857.41	94186.27	79528.08
	T	–14221.17	–10065.07	–9695.04	370.03	–4156.10	–4526.13	83684.18	84054.21	
	Q	–4701.92	–3449.71	–3358.05	91.66	–1252.21	–1343.86	80780.29	80871.95	
	S	–2329.85	–1731.03	–1687.85	43.19	–598.81	–642.00	80126.90	80170.09	
R = 4.00	D	–36761.93	–31104.85	–30528.38	576.47	–5657.08	–6233.55	7050.61	7627.08	1393.53
	T	–12081.61	–10065.07	–9917.33	147.74	–2016.53	–2164.28	3410.07	3557.81	
	Q	–4140.47	–3449.71	–3401.43	48.28	–690.76	–739.04	2084.29	2132.57	
	S	–2053.78	–1731.03	–1708.28	22.75	–322.74	–345.49	1716.27	1739.02	
R = 4.64	D	–34711.68	–31104.85	–30758.79	346.06	–3606.82	–3952.88	370.35	716.41	–3236.48
	T	–11339.58	–10065.07	–9954.52	110.56	–1274.50	–1385.06	–1961.97	–1851.42	
	Q	–3978.08	–3449.71	–3418.58	31.13	–528.37	–559.50	–2708.11	–2676.97	
	S	–1972.11	–1731.03	–1715.22	15.81	–241.08	–256.89	–2995.40	–2979.59	
R = 5.00	D	–34034.39	–31104.85	–30841.81	263.04	–2929.53	–3192.58	104.47	367.52	–2825.06
	T	–11054.04	–10065.07	–9967.97	97.10	–988.97	–1086.07	–1836.10	–1738.99	
	Q	–3910.09	–3449.71	–3425.07	24.64	–460.37	–485.01	–2364.69	–2340.05	
	S	–1936.98	–1731.03	–1718.63	12.40	–205.95	–218.35	–2619.11	–2606.71	
R = 6.00	D	–32869.97	–31104.85	–30952.57	152.29	–1765.11	–1917.40	456.72	609.01	–1308.40
	T	–10595.90	–10065.07	–10010.14	54.93	–530.83	–585.76	–777.57	–722.63	
	Q	–3755.91	–3449.71	–3436.19	13.52	–306.20	–319.72	–1002.20	–988.68	
	S	–1857.32	–1731.03	–1724.29	6.74	–126.29	–133.03	–1182.11	–1175.36	
R = 7.00	D	–32056.59	–31104.85	–30981.47	123.38	–951.74	–1075.12	50.44	173.83	–901.30
	T	–10409.17	–10065.07	–10041.99	23.08	–344.10	–367.18	–557.20	–534.12	
	Q	–3669.65	–3449.71	–3441.61	8.10	–219.93	–228.04	–681.36	–673.26	
	S	–1818.26	–1731.03	–1727.17	3.87	–87.23	–91.09	–814.07	–810.20	
R = 8.00	D	–31525.84	–31104.85	–31003.49	101.36	–420.99	–522.35	–249.88	–148.52	–670.87
	T	–10292.98	–10065.07	–10052.09	12.98	–227.90	–240.89	–442.97	–429.98	
	Q	–3619.27	–3449.71	–3445.71	4.01	–169.56	–173.56	–501.31	–497.31	
	S	–1798.87	–1731.03	–1728.96	2.08	–67.83	–69.91	–603.04	–600.96	
R = 10.00	D	–31172.43	–31104.85	–31064.92	39.93	–67.58	–107.51	–200.06	–160.13	–267.64
	T	–10131.95	–10065.07	–10057.55	7.53	–66.88	–74.40	–200.76	–193.24	
	Q	–3519.32	–3449.71	–3448.11	1.60	–69.61	–71.21	–198.03	–196.43	
	S	–1768.10	–1731.03	–1730.27	0.76	–37.07	–37.83	–230.57	–229.81	
R = 12.00	D	–31121.31	–31104.85	–31094.95	9.90	–16.46	–26.36	–74.89	–64.99	–91.35
	T	–10080.13	–10065.07	–10061.77	3.30	–15.05	–18.35	–76.30	–73.00	
	Q	–3467.81	–3449.71	–3448.94	0.78	–18.10	–18.87	–73.25	–72.48	
	S	–1743.43	–1731.03	–1730.67	0.36	–12.39	–12.75	–78.96	–78.60	
R = 15.00	D	–31108.59	–31104.85	–31104.09	0.76	–3.73	–4.50	–17.77	–17.01	–21.51
	T	–10067.69	–10065.07	–10064.73	0.34	–2.61	–2.95	–18.89	–18.55	
	Q	–3452.69	–3449.71	–3449.58	0.13	–2.98	–3.11	–18.52	–18.40	
	S	–1733.07	–1731.03	–1730.95	0.09	–2.03	–2.12	–19.47	–19.38	

^aAll values are given in $\mu\text{hartree}$. $\Delta BSE = BSE(D) - BSE(2M)$ is the basis set error in the (uncorrected) dimer binding energy, $\Delta BSE(X) = \Delta E(\text{CBS}) - \Delta E(X)$. $\Delta BSE(\text{CP})$ are the errors in the dimer binding energy that remain after CPC of the monomer energies, $\Delta E(\text{CBS}) - \Delta E(\text{CPX})$.

For instance, already at the triple- ζ basis set the BSSE at R_e is a mere $2.3 \mu E_H$, to be compared to BSE(D) and BSE(2M) of -401.0 and $-299.5 \mu E_H$ respectively, and to an interaction energy of $11870.5 \mu E_H$. So applying the CPC has a very small effect, but it is an adverse effect. The errors in the uncorrected bond energies are consistently slightly smaller, for all distances and basis sets until 7.00 bohr. In all those cases the BSEs are small compared to the binding energy anyway, and the difference in the BSEs of dimer and monomers is 1 to 2 orders of magnitude smaller still. Only in the tail of the energy curve, at distances ≥ 8 bohr, where the errors in both corrected and uncorrected binding energies are very small indeed, there is no longer a consistent trend to smaller error for uncorrected energies.

From the table for HF calculations with the aug-cc-pVXZ ($X = 2-5$) basis sets (see Table I in the Supporting Information) one

can see that the augmentation of the basis with a set of diffuse functions makes the BSEs only little smaller. The BSSE is slightly larger since the diffuse functions on the other monomer are a bit more effective in lowering the energy of a monomer. However, the changes due to augmentation of the basis are insignificant, the bias in the basis set remains toward the atoms, and all trends are the same.

B. Basis Set Errors for the Dimer Binding Energy and the BSSE at Correlated Level. We now turn to the correlated calculations. The BSEs and the BSSE are then considerably larger than in the HF calculations, but the trends will prove to be all exactly the same. The discussion is split into a VO part, where FCI calculations are still feasible, and an all electron part where only CCSD(T) results are available.

Table 10. All-Electron CCSD(T) Basis Set Errors (BSEs) for Beryllium Dimer and Two Beryllium Atoms in the Series of cc-pCVXZ+MB95 (X = D, T, Q, 5) Basis Sets^a

R(Be–Be) (au)	basis	BSE				BSSE		ΔBSE		E_{int}			
		dimer	2 M NOCP	2 M MBCE	2 M FCP	MBCE	FCP	2 M NOCP	2 M MBCE	2 M NOCP	2 M MBCE	2 M FCP	exact
R = 3.00	D	–23459.99	–31104.85	–21704.43	–21499.11	9400.42	9605.74	7644.87	–1755.55	71883.22	81283.63	81488.96	79528.08
	T	–8950.99	–10065.07	–8035.30	–7906.62	2029.77	2158.45	1114.09	–915.68	78414.00	80443.76	80572.45	1393.53
R = 4.00	D	–23749.06	–31104.85	–22877.49	–22737.71	8227.36	8367.15	7355.79	–871.57	–5962.26	2265.11	2404.89	1956.23
	T	–8850.69	–10065.07	–8365.85	–8288.00	1699.22	1777.07	1214.38	–484.84	179.15	1878.37	1956.23	–3236.48
R = 4.64	D	–24026.54	–31104.85	–23586.04	–23422.76	7518.81	7682.09	7078.31	–440.50	–10314.79	–2795.98	–2632.69	–2882.91
	T	–8832.14	–10065.07	–8547.52	–8478.58	1517.55	1586.49	1232.93	–284.62	–4469.41	–2951.86	–3100.57	–3079.53
R = 5.00	Q	–3385.84	–3449.71	–3249.94	–3228.90	199.77	220.81	63.87	–135.90	–3300.34	–3100.30	–3139.30	–3130.86
	S	–1766.86	–1731.03	–1669.68	–1661.24	61.35	69.79	–35.82	–97.17	–105.61	–3200.65	–3139.30	–2610.83
R = 6.00	D	–24270.64	–31104.85	–24056.41	–23849.96	7048.45	7254.89	6834.22	–214.23	–420.68	–9659.28	–2404.39	–2825.06
	T	–8823.11	–10065.07	–8636.47	–8567.37	1428.60	1497.70	1241.96	–186.64	–4067.02	–2638.42	–2569.32	–2706.08
R = 7.00	Q	–3366.23	–3449.71	–3266.29	–3247.24	183.42	202.47	83.48	–99.94	–2908.55	–2725.13	–2743.46	–1163.20
	S	–1748.12	–1731.03	–1674.27	–1666.52	56.76	64.51	–17.09	–73.85	–2807.97	–2751.22	–2743.46	–1308.40
R = 8.00	D	–26582.87	–31104.85	–26842.45	–26526.22	4262.40	4578.63	4521.98	259.58	–56.65	–5423.28	–844.65	–901.30
	T	–9128.94	–10065.07	–9192.62	–9105.56	872.46	959.51	936.13	63.67	–23.38	–1837.43	–964.97	–877.91
R = 10.00	Q	–3342.72	–3449.71	–3345.88	–3327.34	103.83	122.37	106.99	3.16	–15.38	–1008.29	–904.46	–885.92
	S	–1701.18	–1731.03	–1696.62	–1691.65	34.42	39.38	29.86	–4.56	–9.52	–931.16	–896.74	–891.77
R = 12.00	D	–27832.37	–31104.85	–28109.99	–27812.27	2994.86	3292.58	3272.49	277.63	–20.09	–3943.36	–948.50	–670.87
	T	–9467.67	–10065.07	–9536.37	–9461.00	528.70	604.07	597.40	68.70	–6.67	–1268.27	–739.57	–664.20
R = 15.00	Q	–3365.91	–3449.71	–3370.82	–3360.67	78.89	89.04	83.80	4.91	–5.24	–754.67	–675.78	–665.63
	S	–1703.47	–1731.03	–1704.93	–1700.74	26.10	30.29	27.56	1.46	–2.73	–698.43	–672.33	–668.14
R = 15.00	D	–29361.75	–31104.85	–29584.47	–29360.58	1520.38	1744.27	1743.10	222.72	–1.17	–2010.74	–490.36	–266.47
	T	–9800.98	–10065.07	–9830.63	–9801.21	234.44	263.87	264.09	29.65	0.22	–531.73	–297.30	–267.87
R = 15.00	Q	–3404.16	–3449.71	–3409.05	–3403.98	40.66	45.73	45.55	4.89	–0.18	–313.19	–272.53	–267.46
	S	–1714.49	–1731.03	–1716.92	–1715.01	14.11	16.03	16.55	2.44	0.52	–284.19	–270.08	–268.16
R = 15.00	D	–30230.29	–31104.85	–30337.05	–30230.90	767.80	873.95	874.57	106.76	0.62	–965.92	–198.11	–91.97
	T	–9905.32	–10065.07	–9932.19	–9905.55	132.88	159.53	159.75	26.87	0.23	–251.10	–118.22	–91.58
R = 15.00	Q	–3425.17	–3449.71	–3427.84	–3425.15	21.87	24.56	24.54	2.67	–0.02	–115.89	–94.02	–91.33
	S	–1721.32	–1731.03	–1722.79	–1721.68	8.24	9.36	9.71	1.47	0.36	–101.06	–92.82	–91.71
R = 15.00	D	–30805.20	–31104.85	–30821.60	–30804.34	283.25	300.51	299.65	16.40	–0.86	–321.16	–37.91	–20.64
	T	–10007.98	–10065.07	–10013.23	–10007.76	51.84	57.31	57.10	5.26	–0.21	–78.60	–26.76	–21.29
R = 15.00	Q	–3438.26	–3449.71	–3439.05	–3438.00	10.66	11.71	11.45	0.79	–0.26	–32.96	–22.30	–21.24
	S	–1726.99	–1731.03	–1727.52	–1726.92	3.52	4.11	4.04	0.53	–0.07	–25.55	–22.03	–21.44

^aAll values are given in $\mu\text{hartree}$.

VO Correlation. Table 8 (and Table II in the Supporting Information) present basis set errors and interaction energies for VO-FCI in the series of VXZ and aVXZ sets respectively. Basis set errors were calculated with respect to the benchmark energy obtained by adding the CBS limit for the VO-FCI correlation energy to the basis set free HF energy

$$E_{\text{VO}}^{\text{CBS}}(S) = E^{\text{exactHF}}(S) + E_{\text{VO-corr}}^{\text{CBS-FCI}}(S) \quad (9)$$

where S denotes the system (Be dimer or atom), $E^{\text{exactHF}}(S)$ is the exact HF energy, and $E_{\text{VO-corr}}^{\text{CBS-FCI}}(S)$ is the VO-FCI correlation energy extrapolated from the VXZ series of basis sets as described in the previous section. (We also need the extrapolated CBS number because there is not a basis set free benchmark VO correlation energy for the atom.) The energy for a VO-FCI calculation in basis set X for either monomer or dimer has an implicit HF error for basis set X , but we do not split the total BSE into a HF part and a correlation part. It is not clear whether it would be justified to do so, and it is not necessary since the total BSE at the correlated level is so much larger than the BSE at the HF level (compare Tables 7 and 8) that it would not affect the discussion. Although the magnitudes of the terms for VO-FCI in Table 8 are much larger than for the HF case, the trends are all the same as in HF. The BSEs are not only much larger than in the HF case, the difference between the D and 2M BSEs has also considerably increased, the BSE(D) being always considerably larger than the BSE(2M) (the ΔBSE are all negative). In this case there is no exception, not even at very long distance, although of course the BSE(D) and BSE(2M) approach each other when R becomes long. The expected stronger bias of the basis set toward the atoms in the correlated case is thus fully corroborated. Again, the CPC procedure improves the atomic basis set further, so the bias increases, and the errors for the CP corrected bond energies are all larger than for the uncorrected bond energies. The error is obtained by comparing the calculated bond energies with basis X , uncorrected or CP corrected, with the benchmark value obtained from the VO correlated CBS values of the energies of the dimer and the atoms. We note again that compared to total error in the calculated bond energies the BSSE is small, although percentagewise it is somewhat larger than in the HF case (now ca. 10% of the BSE(D) and BSE(2M) at R_e). The CPC does deteriorate the bond energies, even if only little (the error resulting from applying CPC goes from 4% to 0.4% of the bond energy from DZ to 5Z basis).

All these findings apply equally well to the series of aug-cc-pVXZ ($X = \text{D, T, Q, 5}$) basis sets, for which the results are shown in Supporting Information, Table II. Understandably, the augmented basis sets have slightly smaller BSEs and the CPCs are somewhat larger. In this case in the outer tail (distances 10 Bohr and beyond) the BSE(D) and BSE(2M) are getting very close, and the BSE(D) is sometimes a bit smaller than the BSE(2M) (but now we are talking about effects at the level of a couple of μE_H).

All-Electron Correlation. Table 9 displays the results for all-electron CCSD(T) calculations in the cc-pCVXZ, $X = \text{D, T, Q, 5}$ series of basis sets. The Supporting Information contains CCSD(T) calculations in the series of augmented basis sets, aug-cc-pCVXZ (Supporting Information, Table II). The benchmark for the all-electron calculations is evaluated according to the expression

$$E_{\text{AE}}^{\text{CBS}}(S) = E^{\text{exactHF}}(S) + E_{\text{AE-corr}}^{\text{CBS-CCSD(T)}}(S) \quad (10)$$

where $E_{\text{AE-corr}}^{\text{CBS-CCSD(T)}}(S)$ is the CBS CCSD(T) correlation energy extrapolated from two basis sets with highest cardinality from the aCVXZ series, see discussion in previous section. (For the atom we use the AE-CCSD(T) extrapolated value, which is very close to the benchmark fully correlated Be atom energy of ref 37 anyway.)

The BSEs are considerably larger than in the VO-FCI calculations. Most importantly, again the BSE(D) is (much) larger than the BSE(2M), so also at this level of theory we have to conclude that the basis sets are biased toward the atoms. This behavior persists through the (small) BSEs at long distances; there is no exception. The BSEs are so large, as well as their difference, that the bond energies in the smaller basis sets are very poor. For the DZ basis at R_e there is even a reversal of sign: the BSE in the dimer is so much larger than in the monomers that the bonding is lost. Of course the CPC makes things worse, and the basis set errors for the CP corrected bond energies are all larger than the uncorrected errors. The magnitude of the BSSE is small compared to the BSEs, but not so small compared to the difference ΔBSE (which is the basis set error for the bond energy). The CPC accordingly has an adverse effect on the calculated bond energies, ranging, in percentages of the benchmark value of the bond energy of $-3236.5 \mu\text{E}_\text{H}$, from 10.7% for DZ through 3.4% for TZ to 0.5% for 5Z. Since the values for the bond energy that are actually calculated in the various basis sets (the $\Delta E(X)$) are much different from the benchmark value (in particular in the smaller basis sets of course), the adverse effect of applying the CPC on those poor bond energies becomes much larger: 93.4% for DZ through 5.6% for TZ to 0.5% again for 5Z. Applying the BSSE correction becomes worse when the basis set becomes smaller!

From the Supporting Information, Table III for the all-electron CCSD(T) calculations with the aug-cc-pVXZ ($X = 2-5$) basis sets in the Supporting Information one can see that the augmentation of the basis with a set of diffuse functions makes the BSEs somewhat smaller and the BSSE slightly larger. The bias in the basis set remains strongly toward the atoms, and all trends are the same as with the nonaugmented cc-pVXZ series of basis sets. Because the BSSE has become somewhat larger, its adverse effect also increases somewhat: from 19% (of benchmark bond energy) for DZ to 0.6% for 5Z at R_e (and 153.6% for DZ to 8.6% for TZ and 0.6% for 5Z of the basis set bond energies $\Delta E(X)$).

C. Effect of Bond Midpoint Functions. We have presented evidence that the standard quantum chemical basis sets have larger basis set errors when applied to interactions between atoms than when applied to just atoms, for the HF and several correlated levels. This of course does not need to hold for all types of basis set. It should be possible to improve upon the basis set in the molecule, so that the balance in BSEs becomes better. This would even be very desirable if it could be done in a systematic fashion. We report an investigation of bond midpoint functions, which is documented in Table 10. The bond midpoint functions are the ones from Partridge and Bauschlicher⁴⁶ which have been mentioned already in section III. The set is composed of 95 uncontracted [6s6p6d3f1g1h] functions (denoted MB95) positioned at the bond midpoint. One can apply two types of CPC, one with only the MB95 set added to a monomer basis (leaving monomer basis set error denoted 2M MBCP in Table 10) and the other one with both the basis set of the other monomer plus the MB95 set added (denoted 2M FCP in Table 10). The first observation is that the bond midpoint set of functions lowers the BSE(D) so much that it becomes smaller than BSE(2M): the ΔBSE in the NOCP case have all turned

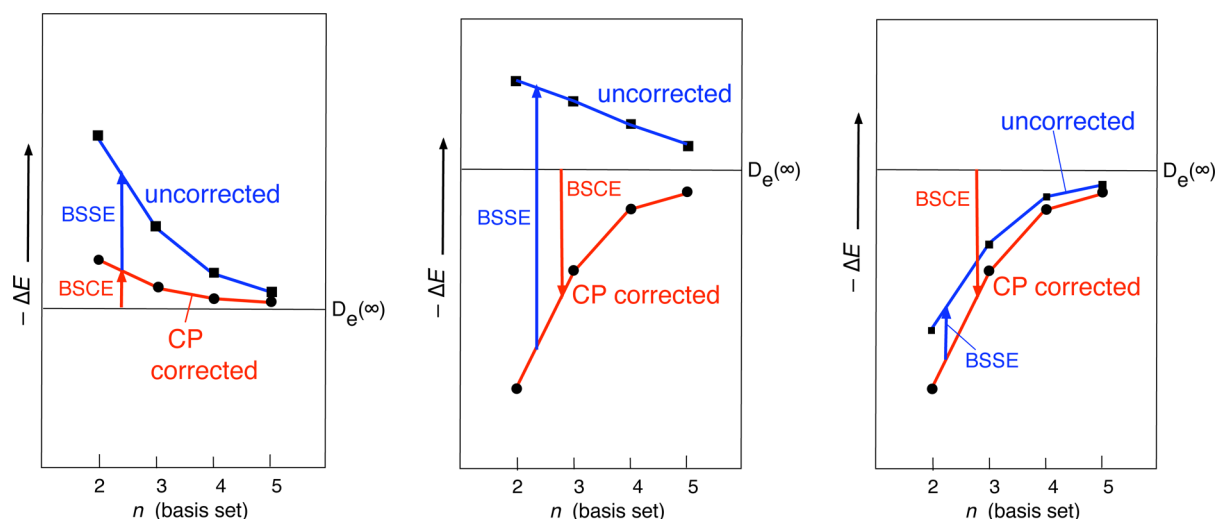


Figure 2. Behavior of the positive bonding energies $-\Delta E(X)$ (uncorrected) and $-\Delta E(CPX)$ (CP corrected) as a function of basis set size ($D_e(\infty) = -\Delta E(\text{CBS})$). (a): Naively expected behavior on the basis of assumed smaller basis set error in the dimer because of the BSSE, and the reduction of the error by CPC (indicated by the contribution $-\text{BSSE}$, see eq 11). (b): Occasional behavior as depicted in Figure 4 of ref 11 [Reprinted from ref 11. Copyright 2000 American Chemical Society] and He_2 with d-aug and t-aug bases.¹⁰ (c): Actual behavior in Be_2 (present work) and He_2 with aug-cc-pVXZ bases¹³ and many other cases.¹⁰ The arrows indicate the sign of correction terms, up is positive, down is negative: $-\Delta E(\text{CPX}) = D_e(\infty) + \text{BSCE}(X)$ and $-\Delta E(X) = -\Delta E(\text{CPX}) + \text{BSSE}$.

positive except for the ΔBSE for CVSZ for $R = 4.64$, and $R = 5.0$. So here the dimer basis set, with the inclusion of the bond midpoint functions, has indeed become in almost all cases “better” than the pure atomic basis sets for the monomers (as has often been erroneously assumed to be already the case without bond midpoint functions because of the BSSE effect). Now CPC might improve the balance, unless of course it overshoots. The CPC with only the MB95 set sometimes improves the balance, in the sense that ΔBSE becomes smaller in that case. We have made the smallest entry out of the three ΔBSE at a given distance and basis set bold, and observe that in a number of cases the $\Delta\text{BSE}(\text{MBCP}, X)$ is better than the uncorrected $\Delta\text{BSE}(\text{NOCP}, X)$. Then correspondingly the calculated interaction energy is closer to the “exact” one; the best interaction energies are also made bold. Sometimes the addition of the other monomer functions in the CP calculation makes the error smaller, mostly at longer distances. This confirms the general finding that the CPC is generally all right at very long distances, where it is very small, but where the bond energies are also very small.¹³ There are also cases where the NOCP ΔBSE is the best. However, in those cases the NOCP ΔBSE is not so much better than the MBCP ΔBSE , while on the other hand in the cases where MBCP ΔBSE is better, it is sometimes a lot better than NOCP ΔBSE .

The columns comparing ΔBSE values in Table 10 when no CP or different CP schemes are used clearly show that the balance between dimer and monomer BSEs crucially depends not only on the basis set quality but also on the distance. For the short and intermediate distances ($R = 4.64, 5.0, 6.0, 7.0, 8.0$) there is a transparent distinction between two cases, namely “small” (DZ and TZ) and “large” (QZ and SZ) basis sets. The same behavior is observed for the near equilibrium separations ($R = 4.64, 5.0$) where ΔBSE is the smallest when MBCP is used for the “small” sets and no CPC for “large” sets. Going to intermediate distances ($R = 6.0, 7.0, 8.0$) smallest ΔBSE s are obtained with FCP for “small” basis sets and with MBCP for “large” sets. Beyond those separations ($R = 10.0, 12.0, 15.0$) consistently better results are obtained using the full counterpoise scheme.

If any recommendation could be extracted from this example, it would be that with bond midpoint functions the CPC method in either the MBCP form or the FCP form appears to be a more balanced approach than just omitting any CPC. Actually, the FCP ΔBSE is always much improved over the ΔBSE of the AE CCSD(T) calculations in the same series of basis sets but without bond midpoint functions in Table 9. The same cannot be said for the NOCP ΔBSE of the MB95 calculations.

The overall conclusion is that it is wise to try to correct for the imbalance in performance of the standard basis sets for molecules (interaction energies) compared to atoms. That cannot be done with the standard counterpoise procedure, it “corrects” in the wrong direction. The addition of bond midpoint functions applies improvement of the basis set just where it is needed, in the interaction energy calculation. It makes the BSEs for dimer and atoms much more equal. In the case at hand, it is then advantageous to apply the CPC, at least with the bond midpoint functions, to the atomic calculations. Many more investigations are necessary to devise a systematic approach with bond midpoint functions.

V. DISCUSSION OF THE CPC PROCEDURE. THE ISSUE OF DIFFUSE BASIS FUNCTIONS

We follow in this discussion and in the figures the convention of using positive bonding energies $D_e(X) = -\Delta E(X)$ and $D_e(\text{CPX}) = -\Delta E(\text{CPX})$ for the uncorrected and CP corrected bonding energies, respectively, and $D_e(\infty) = -\Delta E(\text{CBS})$ for the basis set limit value (note that here the ΔE s were all negative, except for the repulsive HF ΔE s), and we use the definitions of $\text{BSCE}(X)$ and $\text{BSSE}(X)$ eq 4, see ref 11,

$$-\Delta E(X) = D_e(\infty) + \text{BSCE}(X) + \text{BSSE}(X)$$

(the uncorrected bond energy)

$$-\Delta E(\text{CPX}) = D_e(\infty) + \text{BSCE}(X) = -\Delta E(X) - \text{BSSE}(X)$$

(the CP corrected bond energy) (11)

We show in the left panel of Figure 2 the behavior of the uncorrected bonding energy and the counterpoise corrected one as they are sometimes naively thought to be: the uncorrected bonding energy (blue curve) is too high because of the imbalance in BSEs, the BSE for the dimer supposedly being smaller because of the BSSE. After CPC the corrected energies (red curve) should have a much smaller remaining error, BSCE, with respect to $D_e(\infty)$ than the original uncorrected energies. BSCE is pictured as small and positive, but it could also be small and negative. This happens if the CPC “overshoots”. The middle panel shows a different picture, given by Dunning¹¹ as typical behavior and observed by Van Mourik et al.¹⁰ for some dispersion bound systems. The uncorrected energies are too high (larger than D_e), but closer to the $D_e(\infty)$ than the CP corrected values. This is the situation when the (uncorrected) BSE is actually larger for the atoms than for the dimer. This is a state of affairs that is of course possible, as we have seen above with the bond midpoint functions, but it is exceptional. In ref 10 it is only observed for the He and Ar dimers, and only for the doubly and triply augmented basis sets d-aug-cc-pVXZ and t-aug-cc-pvXZ. We will discuss below why the often expressed need for diffuse functions, as added in the double and triple augmentation, for accurate calculation of van der Waals interaction, appears to be mistaken; it complicates rather than helps accurate determination of van der Waals interaction energies.

In Figure 2c we show the situation we have found to prevail in the present study (and in the He₂ case as well for aug-cc-pVXZ basis sets¹³): the uncorrected energies are too small since the BSE is considerably *larger* in the dimer than in the monomer. The CPC for BSSE is relatively small, it is not a large effect, but the correction is in the wrong direction. In He₂ we found in the aug-cc-pVXZ bases larger BSSE effects, the uncorrected values (the blue curve) was closer to the axis, but the qualitative picture was the same as for the panel to the right (cf. the blue curves in the figures of ref 13). We note that the pattern of Figure 2c also prevails in ref 10, notably also in strongly bound systems (“intramolecular BSSE”). This pattern also shows that the larger BSE in the dimer than in the monomers, leading to a too low $D_e(X)$, is a very general phenomenon, ranging from the very weak bonding in (purely or mostly) dispersion bound systems to the normal chemical bonding interaction in molecules like N₂, HF, and HCl.¹⁰ It should be noted that the imbalance in BSEs of monomers and dimer is strongest for the smaller basis sets, and also that the CPC adds a larger error the smaller the basis set. This contradicts the accepted wisdom that applying the CPC is more helpful, or would be even necessary (strongly recommended) with smaller basis sets.

We now turn to the issue of diffuse functions. We wish to stress that the behavior of Figure 2c is typical, while Figure 2b is atypical, having only been observed with very diffuse basis functions, as in the special, doubly and triply augmented, bases d-aug and t-aug in He₂ and Ar₂, not even for aug-cc-pVXZ in He₂^{10,13} (ArHF is the only other case in ref 10 exhibiting similar behavior, which probably has the same origin). The double and triple augmentation with diffuse functions gives a rather special basis set effect: the bond energy is hardly improved compared to the basis set limit value $D_e(\infty)$, very unlike the improvement when increasing the cardinal number X to $X + 1$, cf. the very similar CP corrected bond energies when comparing the aug, d-aug, and t-aug basis sets at a given X in Figure 1 of ref 10. The double and triple augmentation is inadequate for an improved description of van der Waals bonding; its only effect appears to be to assist the basis set on the other atom in the dimer. This is a

real difference with the bond midpoint functions, which are effective because, as we have seen, the MBCP corrected and FCP corrected bond energies (and even often the uncorrected ones) were almost always much improved over the bond energies with the original atom centered basis sets. Since the interaction energies are very small for the purely dispersion bound He₂ and Ar₂, that is, since the total energies of dimer and two monomers are very close, and in particular the BSEs for monomers and dimer are close, the balance can upon augmentation tip in favor of a lower dimer BSE, which actually happens for d-aug and t-aug bases. This can be attributed to the improvement of the basis set on an atom in the dimer by the diffuse functions on its neighbor. This effect, which has nothing to do with the dispersion energy, will make the uncorrected bond energy too high, an exceptional situation. One is actually creating a large BSSE, which naturally increases considerably from d-aug to t-aug. And then of course the CPC works in the right direction, although it typically overshoots, as depicted in Figure 2b. It should be noted that the overshoot of the CPC from uncorrected to CP corrected bond energy in the d-aug and t-aug He₂ and Ar₂ cases depicted in Figure 2b (see Figure 1 of ref 10) is not accidental but means something. It tells us that when the monomer basis has been corrected for the BSSE effect, which is relatively large compared to the (small) bond energy in these cases, we are back at the “normal” situation of a larger BSE in the dimer than in the monomers, which always holds after CPC, and almost always (except for the d-aug and t-aug bases in purely van der Waals bonded systems) for the uncorrected bond energy. A larger BSE in the dimer is a ubiquitous phenomenon.

The often made assumption that (very) diffuse functions are important for a proper description of the dispersion energy is not in agreement with the fact that physically this is a (frequency dependent) polarizability effect. It is not an orbital overlap related phenomenon, such as covalent bonding. In ref 51 the basis set effects for the van der Waals energy have been analyzed, with a differentiation of the convergence with respect to extension of the s basis only, next increasing the p basis, d basis, and so forth. The conclusion is that the $l > 0$ functions are essential, at least p and d functions, but that none of the s , p , or d sets has to be extensive: the dispersion type of correlation energy is not particularly demanding with respect to basis set, in fact much less so than the atomic correlation energy (which is also very much larger). We note that essentially the same argument against the use of diffuse basis sets, based on the physics of the dispersion phenomenon, has been given by Bytautas and Ruedenberg.⁵² Varandas⁹ has given a critical assessment of the counterpoise procedure, arguing against the usual assumption that the extrapolation from the CP corrected energies gives the “true” CBS limit which can serve as benchmark number for the bond energy. He comes to the same conclusion as this paper and ref 52, namely, that it is advisable not to use the CPC at all and use the uncorrected energies in an extrapolation to the basis set limit. It has sometimes been suggested to average over the corrected and uncorrected values.⁵³ From our results it appears that the averaging will not offer an advantage, cf. Figure 2c, while the extrapolation from the uncorrected energies seems to be the best procedure.

VI. CONCLUSIONS

We conclude that the counterpoise procedure is not justified with the use of the standard atom centered basis sets of quantum chemistry, since the basis set error (BSE: difference of the energy with basis set limit value) will be larger for the dimer than for the

atoms. We ascribe the imbalance to the more intricate electronic structure in molecules than in atoms, which puts higher demands on the basis set. This is already the case at the HF level, although the effect is much more striking (much larger BSE in the dimer than in the atoms) at the correlated level. The correlation effects are much more intricate when chemical bonding or dispersion bonding is happening. We have demonstrated this state of affairs for the Be dimer, which appears to be typical for weakly bonded systems, with a considerable dispersion contribution but also chemical bonding effects occurring (total interaction energy 2.5 kcal/mol). The basis set superposition effect is beneficial (and therefore should not be removed by CPC) in that it somewhat reduces the larger basis set error in the dimer, but it is not large enough to cancel the bias of standard atomic basis sets toward the atom. We do not see a reason why the same situation would not occur when a dimer of two molecules rather than two atoms is formed. Again the interactions between the two molecules bring in additional bonding effects that may be more demanding for the monomer basis sets to describe. It would require extremely accurate calculations to establish this with the same confidence as has been possible for the Be dimer. In our opinion such calculations would be necessary to make a convincing case for the necessity or usefulness of the CPC procedure, in particular since we have seen that it normally has an adverse effect. We have noted that the practice of using special, very diffuse, basis sets for van der Waals bonding has no rationalization in the physics of the dispersion phenomenon, and proves in practice not to improve the van der Waals bonding but rather to lead to complications.

We may comment that we have been able for a VO correlation treatment to compare the bonding energy at the FCI level and CCSD(T) level. In spite of the fact that CCSD(T) is generally considered the “gold standard” for intermolecular interaction energy calculations, we have here found that the CCSD(T) calculations differ by about 1000 μE_H from the FCI result, which is 25% of the Be–Be interaction energy of about 4000 μE_H . This repeats the same observation made by Patkowski et al. in ref 54. This “failure” of CCSD(T) might be related to the close proximity of the Be 2p orbitals to the occupied 2s, making a single reference method like CCSD(T) inadequate. One should on the other hand realize that the binding energy is still quite small, not betraying any stronger interaction than in other cases of noncovalent bonding like π – π stacking. One would therefore wonder if this finding does not also jeopardize the application of CCSD(T) in other cases of similar interaction strength; a firmer validation of the CCSD(T) approach seems to be called for.

■ ASSOCIATED CONTENT

Supporting Information

Tables are provided for the augmented basis sets: aug-cc-pVXZ for HF basis set errors for Be dimer and two Be atoms, aug-cc-pVXZ for VO full-CI basis set errors, and aug-cc-pCVXZ for all-electron CCSD(T) basis set errors. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Jansen, H. B.; Ros, P. *Chem. Phys. Lett.* **1969**, *3*, 140–143.
- (2) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553–566.
- (3) Liu, B.; McLean, A. D. *J. Chem. Phys.* **1980**, *72*, 3418.
- (4) Liu, B.; McLean, A. D. *J. Chem. Phys.* **1989**, *91*, 2348.
- (5) van Duijneveldt, F. B.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Lenthe, J. H. *Chem. Rev.* **1994**, *94*, 1873–1885.
- (6) Schwenke, D. W.; Truhlar, D. G. *Chem. Phys.* **1985**, *82*, 2418–2426.
- (7) Frisch, M. J.; Del Bene, J. E.; Binkley, S. J.; Schaefer, H. F., III *Chem. Phys.* **1986**, *84*, 2279–2289.
- (8) Alvarez-Idaboy, J.; Galano, A. *Theor. Chem. Acc.* **2010**, *126*, 75–85.
- (9) Varandas, A. J. *Phys. Chem. A* **2010**, *114*, 8505–8516.
- (10) van Mourik, T.; Wilson, A. K.; Peterson, K. A.; Woon, D. E.; Dunning Jr., T. H. In *Advances in Quantum Chemistry*; Lowdin, P.-O., Ed.; Academic Press: New York, 1998; Vol. 31; pp 105–135.
- (11) Dunning, T., Jr. *J. Phys. Chem. A* **2000**, *104*, 9062–9080.
- (12) Kobus, J. *Comput. Phys. Commun.* **2013**, *184*, 799–811.
- (13) Sheng, X. W.; Mentel, L. M.; Gritsenko, O. V.; Baerends, E. J. *J. Comput. Chem.* **2011**, *32*, 2896–901.
- (14) Blomberg, M. R. A.; Siegbahn, P. E. M.; Roos, B. O. *Int. J. Quantum Chem.* **1980**, *18*, 229–247.
- (15) Diercks, G. H. F.; Kellö, V.; Sadlej, A. J. *Chem. Phys.* **1985**, *96*, 59–79.
- (16) Bruna, P. J.; Di Labio, G. A.; Wright, J. S. *J. Phys. Chem.* **1992**, *96*, 6269–6278.
- (17) Bruna, P. J.; Labio, G. A. D.; Wright, J. S. *J. Phys. Chem.* **1992**, *96*, 6278–6287.
- (18) Evangelisti, S.; Luigi, G.; Ansaloni, R.; Dur, F.; Rossi, E. *Chem. Phys. Lett.* **1996**, *252*, 437–446.
- (19) Stärck, J.; Meyer, W. *Chem. Phys. Lett.* **1996**, *258*, 421–426.
- (20) Gdanitz, R. *Chem. Phys. Lett.* **1999**, *312*, 578–584.
- (21) Kaledin, L. A.; Kaledin, A. L.; Heaven, M. C.; Bondybey, V. E. *J. Mol. Struct. (THEOCHEM)* **1999**, *461–462*, 177–186.
- (22) Martin, J. M. L. *Chem. Phys. Lett.* **1999**, *303*, 399–407.
- (23) Harkless, J. A. W.; Irikura, K. K. *Int. J. Quantum Chem.* **2006**, *106*, 2373–2378.
- (24) Špirko, V. *J. Mol. Spectrosc.* **2006**, *235*, 268–270.
- (25) Patkowski, K.; Podeszwa, R.; Szalewicz, K. *J. Phys. Chem. A* **2007**, *111*, 12822–12838.
- (26) Patkowski, K.; Špirko, V.; Szalewicz, K. *Science* **2009**, *326*, 1382–1384.
- (27) Vetere, V.; Monari, A.; Scemama, A.; Bendazzoli, G. L.; Evangelisti, S. *J. Chem. Phys.* **2009**, *130*, 024301.
- (28) Schmidt, M. W.; Ivanic, J.; Ruedenberg, K. *J. Phys. Chem.* **2010**, *114*, 8687–8696.
- (29) Heaven, M.; Merritt, J.; Bondybey, V. *Annu. Rev. Phys. Chem.* **2011**, *62*, 375–393.
- (30) Mitin, A. *Int. J. Quantum Chem.* **2011**, *111*, 2560–2567.
- (31) Cleland, D.; Booth, G.; Overy, C.; Alavi, A. *J. Chem. Theory Comput.* **2012**, *8*, 4138–4152.
- (32) Šulka, M.; Labanc, D.; Kováč, M.; Pitoňák, M.; Černušák, I.; Neogrady, P. *J. Phys. B: At., Mol., Opt. Phys.* **2012**, *45*, 085102.
- (33) Helal, W.; Evangelisti, S.; Leininger, T.; Monari, A. *Chem. Phys. Lett.* **2013**, *568–569*, 49–54.
- (34) Sheng, X. W.; Kuang, X.; Li, P.; Tang, K. *Phys. Rev. A* **2013**, *88*, 022517.
- (35) Jurecka, P.; Šponer, J.; Cerný, J.; Hobza, P. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985–1993.

- (36) Merritt, J. M.; Bondybey, V. E.; Heaven, M. C. *Science* **2009**, 324, 1548–1551.
- (37) Stanke, M.; Kędziera, D.; Bubin, S.; Adamowicz, L. *Phys. Rev. Lett.* **2007**, 99, 043001.
- (38) Puchalski, M.; Komasa, J.; Pachucki, K. *Phys. Rev. A* **2013**, 87, 030502.
- (39) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, 90, 1007.
- (40) Feller, D. *J. Chem. Phys.* **1992**, 96, 6104.
- (41) Feller, D. *J. Chem. Phys.* **1993**, 98, 7059.
- (42) Feller, D.; Peterson, K. A. *J. Chem. Phys.* **1998**, 108, 154.
- (43) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, 106, 9639.
- (44) Halkier, A.; Helgaker, T.; Klopper, W.; Olsen, J.; Wilson, A. K. *Phys. Lett.* **1998**, 286, 243–252.
- (45) Prascher, B. P.; Woon, D. E.; Peterson, K. A.; Dunning, T. H., Jr.; Wilson, A. K. *Theor. Chem. Acc.* **2011**, 128, 69–82.
- (46) Partridge, H.; Bauschlichter, C. W., Jr. *Mol. Phys.* **1999**, 96, 705–710.
- (47) Gordon, M. S.; Schmidt, M. W. In *Theory and Applications of Computational Chemistry: the first forty years*; Dykstra, C. E., Frenking, G., Kim, K. S., Scuseria, G. E., Eds.; Elsevier: Amsterdam, The Netherlands, 2005; pp 1167–1189.
- (48) Ivanic, J. *J. Chem. Phys.* **2003**, 119, 9364.
- (49) Jones, E.; Oliphant, T.; Peterson, P. *SciPy: Open source scientific tools for Python*; 2001; <http://www.scipy.org/>.
- (50) Gutowski, M.; Verbeek, J.; van Lenthe, J. H.; Chalaśniński, G. *Chem. Phys.* **1987**, 111, 271–283.
- (51) Mentel, Ł. M.; Sheng, X. W.; Gritsenko, O. V.; Baerends, E. J. *J. Chem. Phys.* **2012**, 137, 204117.
- (52) Bytautas, L.; Ruedenberg, K. *J. Chem. Phys.* **2008**, 128, 214308.
- (53) Mackie, I. D.; DiLabio, G. a. *J. Chem. Phys.* **2011**, 135, 134318.
- (54) Patkowski, K.; Cencek, W.; Jeziorska, M.; Jeziorski, B.; Szalewicz, K. *J. Phys. Chem.* **2007**, 111, 7611–7623.