Interactions in Diatomic Dimers Involving Closed-Shell Metals[†]

Konrad Patkowski,* Rafał Podeszwa, and Krzysztof Szalewicz

Department of Physics and Astronomy, University of Delaware, Newark, Delaware 19716

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Interaction energies of dimers containing alkaline earth (Be, Mg, and Ca) metals have been investigated using symmetry-adapted perturbation theory (SAPT) and supermolecular (SM) methods. Also, to enable broader comparisons, some calculations have been performed on the Zn dimer and on the He−Mg dimer. Although all of the investigated metallic atoms have closed electronic shells, the quasidegeneracy of the ground states of these atoms with the lowest-lying excited states leads to convergence problems in theories based on a single-determinant reference state. The main goal of the present work was to establish how the quality of the interaction energies computed using various electronic-structure methods changes across the range of atoms. We show that although the convergence problems become somewhat less severe with the increase of the atomic number, single-determinant-based methods do not provide reliable interaction energies for any of the investigated metallic dimers even at the level of the coupled-cluster method with single, double, and noniterative triple excitations [CCSD(T)]. However, interaction energies accurate to within a few percent can be obtained if CCSD(T) calculations in large basis sets are extrapolated to the complete basis set limit and followed by full configuration interaction (FCI) calculations with a frozen-core (FC) approximation. Since the systems considered contain only two valence electrons, FCI/FC calculations have been feasible for all of them except for Zn_2, providing the best theoretical estimates of the binding energies to date. We found that a large part of the error of the SAPT results originates from limiting some exchange components to terms proportional to the squares of the intermonomer orbital overlap integrals. When the neglected terms were approximately accounted for, the accuracy improved significantly and became comparable to that of CCSD(T), allowing us to obtain for the first time a physical interpretation of the interaction energies in metallic dimers.

I. Introduction

Whereas most metallic atoms have open electronic shells, alkaline-earth (Ae) metals are closed-shell systems. Thus, the interatomic or atom-molecule interactions involving such metals can be investigated using closed-shell coupled cluster (CC) and perturbation theory (PT) methods based on a single-determinant reference state. Another class of metals which can still be described by a single-determinant reference function are alkali atoms, and closed-shell CC/PT methods have been extended to such cases. Both types of metals can also be investigated by symmetry-adapted perturbation theory (SAPT) of intermolecular interactions.[1−3] However, despite this formal simplicity, all systems containing alkaline-earth or alkali metals are difficult cases for theories based on a single-determinant reference state. The reason is that the ground state determinants of such atoms are nearly degenerate with the lowest-energy excited determinants. For the hydrogen atom, the *ns* and *np* orbitals are exactly degenerate. This degeneracy is removed in all other atoms, but the *ns* and *np* orbital energies are fairly close to each other in alkaline earth and alkaline atoms. The *ns*−*np* energy gaps of the metals considered are about 0.3 hartree, compared to 1.0 hartree for helium. Thus, if *ns* is the highest occupied orbital in the ground-state determinant, the determinant with the *ns* orbital replaced by an *np* orbital is energetically close to the former determinant. The quasidegeneracy results in a slow convergence of PT expansions since small energy denominators are present. The best way to treat such systems would be to use methods with multideterminantal reference states. However, CC/PT methods of this type are not well developed. Variational methods are available, but these are significantly more time-consuming than CC/PT approaches and suffer from size-consistency problems which are particularly notable in investigations of intermolecular interactions (since intermolecular interactions are much weaker than chemical bonds).

As an effect of the slow convergence in the theory level, the interaction potentials for systems involving alkaline-earth or alkali atoms are significantly less accurate than for interactions involving rare gases or closed-shell molecules. This situation exists despite a large computational effort invested in investigations of interactions of the former systems, in particular the dimers of alkaline-earth and alkali atoms. (Note that we are discussing here the alkali dimers in their triplet states, as the singlet coupling leads to strong chemical bonds.) For example, a 1996 paper by Røeggen and Almlöf[4] lists a few dozen calculations for Be_2. However, to our knowledge, no papers have been published that would examine consistently the whole set of systems across the board using high-level methods. In particular, there has been no systematic study of the question whether the severity of the convergence problems decreases with the atomic number. There are some indications that this may be the case, since in a recent paper Bussery-Honvault et al.[5] obtained a very good agreement between the depth at the minimum of the Ca_2 potential computed using SAPT and the experimental one. On the other hand, the *ns*−*np* energy gap actually decreases within the group of investigated alkaline-earth atoms and is smallest for Ca, so that this finding may be counterintuitive. The aim of the present work was to examine

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* To whom correspondence should be addressed.

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the trends in the group of alkaline-earth metals. A similar study for alkali metals is in preparation.[6] We have also included in the present work the zinc dimer, as Zn is another example of a closed-shell metal, with the *ns*−*np* energy gap close to that of Be. To see how the severity of the convergence problems changes if only one metal atom is involved, we have also performed some calculations for the dimer consisting of the magnesium and helium atoms. For all of the investigated metals but Zn, one can in the first approximation restrict the correlation energy calculations to the two *ns* valence electrons. For Zn, the 3*d* shell has to be correlated in order to obtain meaningful results. Thus, the core increases from 2 electrons in Be, through 10 in Mg, to 18 in Ca and Zn. We have not considered still heavier closed-shell metals such as Sr, Ba, Cd, or Hg since for the dimers of these metals large relativistic effects require use of different types of electronic-structure methods than for the lighter dimers.

In order to analyze the convergence properties of various methods, one has to know reliable limit values of interaction energies. Although for most of the investigated dimers a large number of computational studies have been published, in most cases the levels of theory and basis sets applied could not provide quantitative accuracies (errors not larger than a few percent) due to the difficult character of these systems. Even if precise calculations were performed, often the results of such calculations disagree with one another. Also, the experimental binding energies, D_e, are not available for He−Mg and are not trustworthy for Be_2 and possibly Zn_2 (see discussions in sections III.A and III.D). Therefore, we have attempted to obtain the best possible estimates of the interaction energies at the potentials minima using advanced electronic-structure methods, large basis sets, and extrapolation techniques. In particular, we have used the CC method with single, double, and noniterative triple excitations [CCSD(T)].[7,8] At this level of theory, it was possible to perform calculations in the largest basis sets available for the investigated elements. In some cases, we have extended these basis sets by adding diffuse functions. We have also used functions centered at the midbond, which very significantly improve basis set convergence for weakly interacting systems.[9,10] The calculations were followed by extrapolations to the complete basis set (CBS) limits. Such an approach yields interaction energies of rare-gas dimers to the accuracy of a few percent.[11,12] In contrast, for Ae dimers, the errors of the CCSD(T)/CBS calculations can be on the order of 25%. Therefore, one cannot stop at this level of theory. Unfortunately, the CCSDT method, including the complete triple excitations, is significantly more time-consuming and, despite providing improvements, still gives significant errors. Therefore, we have accounted for the effects beyond CCSD(T) by using the full configuration interaction (FCI) method in the frozen-core (FC) approximation. Without the FC approximation, FCI provides the exact solution of the Schrödinger equation in a given single-particle basis set, but this method can be applied only to few-electron systems using very small basis sets. Among the systems studied in this work, only for Be_2 all-electron (AE) FCI calculations have been performed[13] and such calculations have to be restricted to very small basis sets (of the augmented double-zeta size in the present work). If the FC approximation is used, i.e., if the Ae atoms are effectively treated as two-electron systems, the FCI method is still very time and memory consuming, and in fact we were not able to perform FCI/FC calculations for Zn_2, even with only two electrons correlated per atom. Although the FC approximation and the use of smaller basis sets than at the CCSD(T) level make the relative accuracy of the post-CCSD(T) FCI contribution low, the absolute errors are not excessively large since this contribution is only a fraction of the interaction energy. In any case, this approach gives the best estimates of D_e that one can obtain currently. For several systems, our work is the first one that has included FCI-level calculations. Thus, although this was not our initial goal, the present paper provides a set of high-accuracy benchmarks for D_e, consistent across the range of investigated systems. These benchmarks will not only provide the needed reference for our convergence studies of the CC/PT methods but also will allow an evaluation of the contradictory literature results mentioned above. One should note here that the intermonomer distances employed in our calculations, although very close to the van der Waals minima for all dimers considered, were chosen on the basis of literature data so as to enable the broadest possible comparison with previous results. We did not perform any actual geometry optimizations.

With the benchmark interaction energies available, we could evaluate the performance of both the supermolecular PT based on the Møller-Plesset (MP) partition of the Hamiltonian in the *n*th order (MP*n*), of SAPT, and of CCSD. One does not expect that any of these methods will give quantitatively correct interaction energies since even CCSD(T) is not very accurate for the investigated systems. However, an understanding of the patterns of convergence is relevant in view of numerous applications of these methods to the quasidegenerate systems. Furthermore, SAPT interaction energies are naturally split into physically interpretable contributions such as the electrostatic, induction, dispersion, and exchange energies. Thus, SAPT will give some information about the physical mechanisms of the interactions. However, the splitting of the interaction energy into components will not be as complete as in the case of interactions of typical closed-shell monomers where the total interaction energy is usually reproduced to within a few percent by the sum of the SAPT components.

II. Methods

We have applied the standard MP2, MP3, MP4, CCSD, and CCSD(T) methods using the MOLPRO program.[14] The CCSDT and CCSDTQ calculations used the ACESII code[15] and the MRCC program developed by Kállay.[16] The FCI calculations were performed using the LUCIA program.[17] SAPT calculations utilized the SAPT2006 set of codes.[18] All of the SM interaction energies were computed using the counterpoise (CP) method.[19−22] The SM interaction energies are defined, e.g., as

$$E_{\rm int}^{\rm CCSD(T)} = E_{\rm AB}^{\rm CCSD(T)} - E_{\rm A}^{\rm CCSD(T)} - E_{\rm B}^{\rm CCSD(T)} \tag{1}$$

where $E_{\rm X}^{\rm CCSD(T)}$ is the total energy of system X at the CCSD(T) level. We will also consider the FCI contribution beyond CCSD(T) level of theory defined as

$$\delta E_{\rm int}^{\rm FCI} = E_{\rm int}^{\rm FCI} - E_{\rm int}^{\rm CCSD(T)} \tag{2}$$

The difference between the AE and FC interaction energies will be denoted as

$$\delta E_{\rm int}^{\rm FC} = E_{\rm int}({\rm AE}) - E_{\rm int}({\rm FC}) \tag{3}$$

For definitions of the SAPT corrections, see, e.g., refs 1 and 2. These corrections have two indices denoting the order of perturbation theory in the intermonomer perturbation operator *V* and in the intramonomer correlation operator *W*. If only one index is present, the intramonomer correlation effects are summed up to the order in *W* which is given in parentheses

TABLE 1: Comparison of the Beryllium Dimer Interaction Energies at $R = 2.44$ Å Obtained Using Various Methods and Basis Sets[a]

method	AE/FC	MP2	MP4	CCSD(T)	CCSDT	CCSDTQ	FCI
aDZ	AE	348	−154	93	−104	−181	−181
aDZ	FC	358	−146	110	−90	−166	−166
aDZ+(332)	AE	−184	−718	−542	−721		
aDZ+(332)	FC	−109	−637	−443	−625	−709	−709
aTZ	AE	−150	−696	−519	−693		
aTZ	FC	−63	−597	−399	−576	−662	−662
aTZ+(332)	AE	−246	−768	−610	−771		
aTZ+(332)	FC	−196	−715	−538	−701		−787
aTZ+(33221)	AE	−287	−797	−646	−797		
aTZ+(33221)	FC	−233	−741	−571	−726		−812
aQZ	AE	−268	−798	−642	−798		
aQZ	FC	−201	−724	−548	−707		−793
aQZ+(33221)	AE	−338	−849	−701			
aQZ+(33221)	FC	−262	−766	−601			−837
a5Z	AE	−330	−846	−696			
a5Z	FC	−255	−764	−599			
a5Z+(33221)	AE	−351	−857	−709			
a5Z+(33221)	FC	−276	−776	−614			
aCVTZ+(33221)	AE	−280	−783	−618			
aCVTZ+(33221)	FC	−238	−745	−576			
aCVQZ+(33221)	AE	−326	−829	−667			
aCVQZ+(33221)	FC	−264	−768	−603			

[a] The symbols "AE'' and "FC'' denote all-electron and frozen-core results, respectively.

after the correction symbol or to infinity. The subscripts of these corrections indicate one of the physical components mentioned above. The SAPT interaction energy is usually calculated at the second-order level

$$E^{[2]}_{\mathrm{SAPT}} = E^{(1)}_{\mathrm{elst,resp}}(3) + E^{(1)}_{\mathrm{exch}}(\mathrm{CCSD}) + E^{(20)}_{\mathrm{ind,resp}} + {}^{t}E^{(22)}_{\mathrm{ind}} + E^{(20)}_{\mathrm{exch-ind,resp}} + {}^{t}E^{(22)}_{\mathrm{exch-ind}} + E^{(2)}_{\mathrm{disp}}(2) + E^{(20)}_{\mathrm{exch-disp}} \quad (4)$$

One often uses a hybrid approach

$$E^{[2]}_{\mathrm{SAPT+HF}} = E^{[2]}_{\mathrm{SAPT}} + \delta E^{\mathrm{HF}}_{\mathrm{int,resp}} \quad (5)$$

where the second term, defined as

$$\delta E^{\mathrm{HF}}_{\mathrm{int,resp}} = E^{\mathrm{HF}}_{\mathrm{int}} - E^{(10)}_{\mathrm{elst}} - E^{(10)}_{\mathrm{exch}} - E^{(20)}_{\mathrm{ind,resp}} - E^{(20)}_{\mathrm{exch-ind,resp}} \quad (6)$$

collects the third- and higher-order (in V) induction and exchange-induction effects contained in the supermolecular Hartree−Fock (HF) interaction energy $E^{\mathrm{HF}}_{\mathrm{int}}$. For dimers composed of nonpolar monomers, $\delta E^{\mathrm{HF}}_{\mathrm{int,resp}}$ may not provide an accurate account of the higher-order effects, and omitting this term, i.e., using $E^{[2]}_{\mathrm{SAPT}}$ as the SAPT interaction energy, is recommended.[23] The convergence properties of SAPT have been extensively studied for small systems;[24−28] for a review, see ref 2. The frozen-core approximation has recently been introduced in SAPT, in a variant that neglects excitations from core but takes into account the intermonomer core−valence exchange interactions.[29] The accuracy of the frozen-core approximation in SAPT is about the same as for supermolecular MP2, MP4, CCSD, and CCSD(T) methods.

The SAPT(DFT) method[30−37] is based on the Kohn−Sham (KS) density functional theory (DFT) description of monomers. In this method, the interaction energy (up to the second order in V) is expressed as[35]

$$E^{\mathrm{SDFT}}_{\mathrm{int}} = E^{(1)}_{\mathrm{elst}}(\mathrm{KS}) + E^{(1)}_{\mathrm{exch}}(\mathrm{KS}) + E^{(2)}_{\mathrm{ind}}(\mathrm{CKS}) + \tilde{E}^{(2)}_{\mathrm{exch-ind}}(\mathrm{CKS}) + E^{(2)}_{\mathrm{disp}}(\mathrm{CKS}) + \tilde{E}^{(2)}_{\mathrm{exch-disp}}(\mathrm{CKS}) \quad (7)$$

where CKS stands for the coupled-KS method of computing the response properties. For detailed definitions of the terms, see ref 35. Analogously to the SAPT method based on the HF description of the monomers, approximate effects beyond second order in V can be included by adding $\delta E^{\mathrm{HF}}_{\mathrm{int,resp}}$, $E^{[2]}_{\mathrm{SDFT+HF}} = E^{[2]}_{\mathrm{SDFT}} + \delta E^{\mathrm{HF}}_{\mathrm{int,resp}}$. The DFT calculations for the monomers were performed using the DALTON[38] program. The KS orbitals of the monomers were obtained using the PBE0 functional[39,40] with the Fermi−Amaldi−Tozer−Handy asymptotic correction.[41] The ionization potentials needed for the asymptotic correction, equal to 0.3426, 0.2809, 0.2247, 0.3452, and 0.9036 hartree for Be, Mg, Ca, Zn, and He, respectively, were taken from experimental values given in ref 42. For CKS calculations, the local-density approximation (LDA) kernel was used for obtaining time-dependent DFT (TDDFT) propagators.[35]

Asymptotic properties (the static polarizability and the C_6 dispersion coefficient) were calculated with the help of the programs of the POLCOR codes by Wormer and Hettema.[43,44] The CHF-based properties were calculated at the level consistent with the level of SAPT employed here.[45] The CKS-based properties were calculated at the level consistent with the interaction energy in SAPT(DFT) calculations, i.e., using the asymptotically corrected PBE0 KS density generated in the monomer-centered part of the basis set and with the LDA kernel in the CKS propagators (see ref 35).

III. Results

A. Be$_2$. We have first attempted to establish as accurately as possible the interaction energy of two beryllium atoms near the minimum of the potential. The results are collected in Table 1 (the energy unit is cm^{-1} in the tables and throughout the entire paper, unless stated otherwise). The augmented Dunning-type correlation-consistent basis sets aug-cc-pVXZ, which will be denoted here as aXZ, have been employed. The nonaugmented bases cc-pVXZ, X = D, T, Q, 5, and their augmented versions, except for X = 5, have been developed in ref 46. All of the literature bases for Be and other atoms have been obtained from the depository described in ref 47. We have augmented the basis set cc-pV5Z[46] by adding a (1s1p1d1f1g1h) set of primitive

Gaussian functions with the consecutive exponents equal to 0.01690, 0.01453, 0.06888, 0.13772, 0.17409, and 0.27403. These additional exponents were chosen such that the three most diffuse functions of each symmetry form an even-tempered sequence (for the *h* functions, the exponent ratio was assumed to be the same as for the *g* functions). To establish the contributions due to the correlation of core electrons, we have used the aug-cc-pCV*X*Z basis sets, $X = \mathrm{T}$ and Q, developed in ref 46 and optimized in AE calculations (the $X = 5$ set is not available). We will denote the augmented core-valence bases as aCV*X*Z. The basis sets centered on atoms were extended with functions centered at the midbond position.[9,10] We have used a $(3s3p2d2f1g) \equiv (33221)$ set of midbond functions with exponents equal to (0.9,0.3,0.1) for *sp*, (0.6,0.2) for *df*, and (0.35) for *g* functions, as well as its subset $(3s3p2d) \equiv (332)$. A near-van-der-Waals-minimum interatomic distance of 2.44 Å has been employed in all calculations of Table 1. This distance was found as the minimum in large-scale calculations of refs 48 and 49. Another recent accurate calculation[50] found a very close distance of 2.45 Å.

The largest, a5Z+(33221), basis set used gives the CCSD(T)/AE interaction energy of -709 cm^{-1}, cf. Table 1. We have utilized in this work the so-called X^{-3} extrapolation based on the assumption that the difference between the CBS value of some energy contribution $E(\infty)$ and its approximation $E(X)$ computed using a basis set with the cardinal number X vanishes like AX^{-3}, where A is a constant.[51] For the supermolecular methods, we have extrapolated only the correlation part of the interaction energy and took the nonextrapolated HF part computed in the larger basis set. In a few cases, when we needed SAPT CBS results, the whole interaction energy was extrapolated. The X^{-3} extrapolation using the $X = \mathrm{Q}$ and 5 CCSD(T)/AE interaction energies gives -715 ± 6 cm^{-1} as the CBS limit, if one simply assumes that the error is equal to the value of the CBS increment.

The calculations discussed above included all electrons. The core-valence correlation effects, $\delta E_{\mathrm{int}}^{\mathrm{FC}}$, are quite substantial for Be_2 and amount to -95 cm^{-1} at the CCSD(T) level in the largest basis set. Since bases cc-pV*X*Z were optimized in FC calculations, their use in AE calculations may result in some inaccuracies of $\delta E_{\mathrm{int}}^{\mathrm{FC}}$. For interactions of typical closed-shell systems, $\delta E_{\mathrm{int}}^{\mathrm{FC}}$ is very small and its accuracy is never critical. However, the very large value of $\delta E_{\mathrm{int}}^{\mathrm{FC}}$ found for Be_2 requires care. Therefore, we have calculated CCSD(T) energies also using aug-cc-pCV*X*Z bases. The results listed in Table 1 show that indeed the values of $\delta E_{\mathrm{int}}^{\mathrm{FC}}$ are significantly different: -64 cm^{-1} in the basis aug-cc-pCVQZ+(33221), whereas aug-cc-pVQZ+(33221) gives -100 cm^{-1}. However, if these increments are extrapolated, core-valence bases give -80 cm^{-1} and valence bases -90 cm^{-1}. Thus, at the CBS limit the differences, as expected, nearly disappear. Although the pCV*X*Z-basis result should be more reliable than the pV*X*Z-basis result with the same *X*, the latter is obtained with *X* larger by one. Therefore, we have decided to adopt the average of the two results, i.e., -85 cm^{-1}, as the limit value of $\delta E_{\mathrm{int}}^{\mathrm{FC}}$. Thus, our CCSD(T)/AE value at the CBS limit becomes -710 ± 11 cm^{-1}, where we have increased the error bars by 5 cm^{-1} to accommodate the additional uncertainty coming from $\delta E_{\mathrm{int}}^{\mathrm{FC}}$.

Unfortunately, the errors due to the neglected levels of theory are found to be much larger than 11 cm^{-1}. The triples contribution beyond CCSD(T) is as large as -156 cm^{-1} (AE) and -159 cm^{-1} (FC) in the largest basis set used, aQZ. The contribution of the complete quadruples, as estimated in the aDZ basis, is -77 cm^{-1} (AE) or -76 cm^{-1} (FC). Clearly, the cluster expansion for Be_2 is extremely slowly convergent. The small difference between the AE and FC results constitutes an important observation for our work, showing that, although the FC effects are very large in the interaction energy at the CCSD(T) level, the post-CCSD(T) contributions are only weakly dependent on this approximation. This observation is also supported by the fact that the FC contributions are almost the same at different levels of theory: MP2, MP4, and CCSD(T), cf. Table 1. When the FC approximation is used for Be_2, CCSDTQ is equivalent to FCI, and therefore the corresponding numbers are equal. As indicated by the results for the smallest, aDZ basis set presented in Table 1, the FCI and CCSDTQ results with all electrons correlated are also very close to each other.

With the implementations available to us, we were able to obtain FCI/FC results for much larger basis sets than CCSDTQ/FC ones, and we will base our estimate of the post-CCSD(T) effects for Be_2 on the FCI/FC calculations alone. The largest basis set we could use at this level was aQZ+(33221). In this basis, the frozen-core post-CCSD(T) contribution is - 236 cm^{-1}. The CBS extrapolation using this result and the result in the aTZ+(33221) basis gives the limit of -232 cm^{-1} and an error estimate of 4 cm^{-1}. We could compute FCI/AE only in the aDZ basis set. The error in $\delta E_{\mathrm{int}}^{\mathrm{FCI}}$ due to the use of the frozen-core approximation is only 2 cm^{-1} in this basis. As discussed above, the FC errors in the post-CCSD(T) triples contribution are very small also in larger basis sets, up to aQZ. Thus, one may expect that the FC effects in $\delta E_{\mathrm{int}}^{\mathrm{FCI}}$ do not exceed a few cm^{-1}. On the other hand, the FC error in CCSD(T) interaction energies amounts to -85 cm^{-1}, and if the relative error were similar in $\delta E_{\mathrm{int}}^{\mathrm{FCI}}$, this term would have 30 cm^{-1} uncertainty due to the FC approximation. Although small basis set results suggest that this proportionality does not hold, to be on the safe side, we have assumed the error of $\delta E_{\mathrm{int}}^{\mathrm{FCI}}$ due to the FC approximation to be 10 cm^{-1}.

Summing up the estimates of $E_{\mathrm{int}}^{\mathrm{CCSD(T)}}$ and $\delta E_{\mathrm{int}}^{\mathrm{FCI}}$, one obtains a value of -942 cm^{-1} for the total interaction energy. If one calculates the square root of the sum of squares of the errors estimated above (11, 4 and 10 cm^{-1}), the resulting uncertainty is 15 cm^{-1} or 1.6%. The relativistic correction from CCSD(T)/AE calculations with the Douglas-Kroll (DK)[52,53] relativistic Hamiltonian and a5Z+(33221) basis set amounts to 4.1 cm^{-1}. We compare our result with recent literature values in Table 2. (An extensive comparison of the beryllium dimer calculations published prior to 1995 can be found in ref 4.) Our result is in near perfect agreement with recent high-level ab initio calculations of Martin[48] and Røeggen and Veseth[50] which gave $D_{\mathrm{e}} = 948 \pm 20$ cm^{-1} [$D_{\mathrm{e}} = 944 \pm 25$ cm^{-1} with inclusion of relativistic effects] and 945 ± 15 cm^{-1}, respectively. The agreement between the results of refs 48 and 50 and our value is in fact even better than the error bars of individual results would suggest, and it confirms that these three studies have achieved high and consistent accuracy. A somewhat worse agreement is obtained with the r_{12}-MR-ACPF (multireference approximate coupled-pair functional in explicitly correlated linear-r_{12} basis) value of $D_{\mathrm{e}} = 903 \pm 8$ cm^{-1} computed by Gdanitz,[49] indicating that the error bars of ref 49 might have been too narrow. For completeness, several other recent results are listed in Table 2, but due to the limited levels of theory and/or basis sets, these results are substantially less accurate than the ones discussed above.

The result of Martin[48] was obtained using a similar approach to that applied by us. The differences in the two approaches provide in fact an additional measure of the reliability of the ab initio values of D_{e} and therefore are worth a further

TABLE 2: Results of Selected Literature Calculations for the Beryllium Dimer since 1995[a]

year	type	results D_e [cm^{-1}]	results R_e [Å]	ref
	Ab Initio			
1996	EXRHF/(9*s*7*p*4*d*2*f*1*g*) + bond (4*s*4*p*4*d*4*f*2*g*)	841 ± 18	2.45	4
1996	MR-CI/FC/(16*s*10*p*5*d*3*f*1*g*) + bond (3*s*2*p*1*d*) +ECP	893	2.45	54
1996	MR-AQCC/AE/(6*s*7*p*4*d*3*f*1*g*)	864	2.45	55
1999	MR-CISD/AE/(5*s*4*p*3*d*2*f*1*g*)	1050	2.41	56
1999	CCSD(T)/FC+FCI/FC+CAS-ACPF/AE + CBS extr.	944 ± 25	2.44	48
1999	CAS r_{12}-MR-ACPF/(19*s*11*p*6*d*4*f*3*g*2*h*)	898 ± 8	2.44	49
2000	CC3/d-aug-cc-pVQZ+FCI	885	2.45	57
2005	EXRHF/(23*s*10*p*8*d*6*f*3*g*2*h*)	945 ± 15	2.45	50
present	CCSD(T)+FCI/CBS	938 ± 15	2.44[b]	
	Experiment and Empirical			
1984		790 ± 30		58
1989		839 ± 10		59
2006		923		60

[a] See text for explanations of most acronyms. The remaining ones are: AQCC, averaged quadratic coupled clusters and CC3, approximate coupled clusters. Relativistic corrections included if calculated. [b] Fixed value.

discussion. The main difference is due to our use of diffuse and bond functions in the basis set, whereas Martin used in the main calculations only bases cc-pV*X*Z with *X* up to 5. Not only the use of diffuse and midbond functions is essential in calculations of intermolecular interactions, but also each aug-cc-pV*X*Z+(33221) basis set is significantly larger than the corresponding cc-pV*X*Z one. As a consequence, Martin's FCI/FC interaction energy in the largest basis used at this level, with $X = $ Q, is −765 cm^{-1} (at $R = 2.45$ Å and without the CP correction), whereas our result is −837 cm^{-1}, much closer to the best estimate of the interaction energy at the FC level amounting to −857 cm^{-1} (obtained by extrapolating our FC results in the same way as done for the AE ones). Martin's best estimate of this quantity is −872 cm^{-1}. This comparison also shows that the agreement to within 6 cm^{-1} at the AE level is partly coincidental since the two FC calculations after extrapolations to the CBS limits differ by 15 cm^{-1} (still consistent with the error estimates). Apart from the type of basis sets, there are several other, but probably less relevant, differences between our work and that of Martin at the FC level. The differences are more substantial at the AE level. Martin computed the FC correction using the complete active space averaged coupled-pair functional (CAS-ACPF) method and a 4/16 active space. This approach, due to its multireference character, takes in an approximate way account of all types of excitations. This may be an advantage compared to our approach where we computed the FC correction only at the CCSD(T) level (but demonstrated that it is negligible at the $\delta E_{\mathrm{int}}^{\mathrm{FCI}}$ level in small bases). The final effect of the FC approximation was calculated by Martin to amount to −76 cm^{-1}, smaller in magnitude than our value of −85 cm^{-1}. One should take into account, however, that the CAS-ACPF method with a 4/8 active space gives an FC correction of +12 cm^{-1}, showing a poor convergence in the size of the reference space. Therefore, it is difficult to say which value of $\delta E_{\mathrm{int}}^{\mathrm{FC}}$, ours or Martin's, is more reliable. Nevertheless, the differences are still consistent with the estimated uncertainties.

It is more difficult to compare our work with the work of Røeggen and Veseth.[50] These authors used a somewhat larger basis set than ours: an uncontracted (23*s*10*p*8*d*6*f*3*g*2*h*) set developed by them, whereas the aug-cc-pV5Z set used by us has an uncontracted composition of (15*s*9*p*5*d*4*f*3*g*2*h*) and is contracted to [7*s*6*p*5*d*4*f*3*g*2*h*]. They have not used, however, CBS extrapolations, except to estimate the uncertainties. They have also used bond functions, but only for the estimates. Since the basis set incompleteness error in our largest basis is only of the order of 10 cm^{-1}, we can expect similar differences with the work of Røeggen and Veseth due to the basis set effects. More substantial differences may result from the levels of theory applied. Røeggen and Veseth used an extended geminal model which they also call the extended restricted Hartree−Fock (EXRHF) model. In the first approximation, this method expands the wave function into sets of determinants resulting from replacements of some occupied pairs of spinorbitals by virtual orbitals. In the next approximation, applied in ref 50, similar replacements are generated for pairs of spinorbital pairs. Thus, at this level, EXRHF would not give an exact result even in the CBS limit, as the method used by us does. Røeggen and Veseth estimated that the theory-level truncation error is smaller than the basis set incompleteness error, and the good agreement with our result may indicate that this is indeed the case. On the other hand, the previous application[4] of the extended geminal model gave $D_e = 841 \pm 18$ cm^{-1}, i.e., significantly underestimated error bars.

The most often cited "experimental" depth of the Be_2 potential obtained by Bondybey,[58] $D_e = 790 \pm 30$ cm^{-1}, dramatically disagrees with all recent ab initio results, including ours. The reason for the large discrepancy originates probably not from experimental procedures but from theoretical assumptions used in the analysis of experimental data. The use of these assumptions is critical enough that the result of Bondybey[58] should really be considered to be a semiempirical one. There also exist other semiempirical estimates of D_e, obtained by tuning ab initio potentials to reproduce experimental spectra. The older semiempirical work listed in Table 2, by Petersson and Shirley,[59] gives a value of D_e close to that of Bondybey,[58] but the very recent one by Špirko,[60] $D_e = 923$ cm^{-1}, is very close to our result. Moreover, the latter work has chosen Gdanitz's potential[49] as the starting point, so it could be reflecting the relative smallness of the theoretical D_e of ref 49.

Having established the limit value of the interaction energy at the minimum, we can now examine the convergence of the perturbation series, shown in Table 3. A more detailed table showing this convergence, as well as analogous tables for the other dimers, can be found in the Supporting Information.[61] This convergence is extremely slow. MP2 recovers only 37% of the interaction energy at the minimum and such an advanced theory as CCSD predicts the wrong sign of this energy. Only MP4 gives a rather good approximation, however, the large difference between MP4 and CCSD(T) still points out to a very poor convergence. SAPT, at the $E_{\mathrm{SAPT}}^{[2]}$ level, gives the interaction energy which is twice too large in magnitude. The hybrid SAPT

TABLE 3: Components of the SAPT and SAPT(DFT) (Denoted "SDFT") Be$_2$ and Mg$_2$ Interaction Energies as Well as Supermolecular Interaction Energies for Different Basis Sets[a,b]

	Be$_2$			Mg$_2$			
	a5ZM		SDFT	a5ZM	aCVQZM		SDFT
method	AE	FC	AE	FC	AE	FC	AE
$E^{(1)}_{\text{elst,resp}}(3)/E^{(1)}_{\text{elst}}$ (KS)	−6174	−6220	−6242	−1098	−1002	−1096	−1034
$E^{(1)}_{\text{exch}}(2)$	15768	15808		2715	2641	2720	
$E^{(1)}_{\text{exch}}$ (CCSD)/$E^{(1)}_{\text{exch}}$ (KS)	13936	13972	13853	2415	2295	2415	2007
$E^{(10)}_{\text{exch}}(S^{k>2})/E^{(1)}_{\text{exch}}(S^{k>2})$ (KS)	1780	1780	1464	77	77	77	49
$E^{(20)}_{\text{ind,resp}}/E^{(2)}_{\text{ind}}$ (CKS)	−13497	−13483	−12667	−2608	−2628	−2626	−2092
$E^{(20)}_{\text{exch-ind,resp}}/\tilde{E}^{(2)}_{\text{exch-ind}}$ (CKS)	8187	8173	7980	2105	2125	2123	1716
${}^{t}E^{(22)}_{\text{ind}}$	583	477		229	371	230	
${}^{t}E^{(22)}_{\text{exch-ind}}$	−353	−289		−185	−300	−186	
$E^{(2)}_{\text{disp}}(2)/E^{(2)}_{\text{disp}}$ (CKS)	−5178	−5129	−4944	−1735	−1697	−1730	−1623
$E^{(20)}_{\text{exch-disp}}/\tilde{E}^{(2)}_{\text{exch-disp}}$ (CKS)	393	382	285	255	273	254	254
$\delta E^{\text{HF}}_{\text{int,resp}}$	−848	−847	−848	−216	−216	−215	−216
$E^{[2]}_{\text{SAPT}}/E^{[2]}_{\text{SDFT}}$	−2102	−2117	−1735	−621	−563	−618	−772
$E^{[2]}_{\text{SAPT+HF}}/E^{[2]}_{\text{SDFT+HF}}$	−2950	−2964	−2583	−837	−779	−833	−988
scaled $E^{[2]}_{\text{SAPT}}/E^{[2]}_{\text{SDFT}}$	−1163	−1161	−759	−506	−474	−499	−723
MP2	−351	−276		−374	−406	−371	
MP3	−607	−538		−463	−463	−463	
MP4	−857	−776		−503	−483	−502	
CCSD	268	349		−99	−101	−98	
CCSD(T)	−709	−614		−390	−363	−388	

[a] The intermonomer distances were $R = 2.44$ Å for Be$_2$ and $R = 3.9$ Å for Mg$_2$. SAPT(DFT) results were obtained with the a5ZM basis set for Be$_2$ and the aCVQZM basis set for Mg$_2$. [b] The columns marked "AE'' and "FC'' list all-electron and frozen-core results, respectively. For the description of scaled $E^{[2]}_{\text{SAPT}}/E^{[2]}_{\text{SDFT}}$, see text. The letter "M" in a basis set symbol denotes the (33221) set of midbond functions. In the first column, the first symbol refers to SAPT and the second one to SAPT(DFT).

result, $E^{[2]}_{\text{SAPT+HF}}$, is even less accurate. Adding the leading SAPT corrections of the third order in V (ref 23) does not help either; in fact, the third-order contribution is far more negative than the benchmark interaction energy. The reason for the poor performance of SAPT is not only the degeneracy issue discussed above but also the sheer size of the interaction. The minimum distance of the Be$_2$ potential amounting to 4.6 bohr is much smaller than that for rare gas dimers (5.6 bohr for He$_2$ and 5.9 bohr for Ne$_2$). Consequently, the intermonomer perturbation operator is not small at such a distance and the condition for developing a perturbation expansion in powers of V is not fulfilled. This is also seen in the size of the interaction energy at the minimum which is several times larger for Be$_2$ than for He$_2$, −7.6 cm^{-1} (ref 12), and Ne$_2$, −29 cm^{-1} (ref 62). Due to the close-approach minimum distance, the largest SAPT component is the first-order exchange term, amounting to 17 times the magnitude of the total interaction energy. The second-order induction energy is of similar size but of opposite sign. It is not surprising that with such cancellations between components the sum of them is unlikely to reproduce the interaction energy well. This is also because several typically small terms not included in the current SAPT codes are for Be$_2$ comparable in magnitude to the total interaction energy. For example, all exchange corrections except $E^{(10)}_{\text{exch}}$ have been so far derived only in the so-called S^2 approximation,[63] i.e., retaining only terms proportional to the squares of the intermonomer orbital overlap integrals S. Table 3 shows that in the case of the $E^{(10)}_{\text{exch}}$ correction, where the contribution beyond the S^2 approximation is available,[64] and is computed by default in SAPT2006,[18] it is almost twice as large as the total interaction energy. The second-order exchange energies without the S^2 approximation were computed for the lowest quintet state of He$_2$ by Przybytek et al.[65] They have found that the percentage contribution of the terms beyond S^2 is very similar in the first and in the second order. This allows one to scale the corrections $E^{(20)}_{\text{exch-ind,resp}}$, ${}^{t}E^{(22)}_{\text{exch-ind}}$, and $E^{(20)}_{\text{exch-disp}}$, as well as the term $\epsilon^{(1)}_{\text{exch}}(\text{CCSD}) = E^{(1)}_{\text{exch}}(\text{CCSD}) - E^{(10)}_{\text{exch}}$, by the proper ratio, i.e.

$$\tilde{E}^{(20)}_{\text{exch-ind,resp}} = E^{(20)}_{\text{exch-ind,resp}} \frac{E^{(10)}_{\text{exch}}}{E^{(10)}_{\text{exch}}(S^2)} \tag{8}$$

and similarly for other components. In eq 8, the tilde denotes the approximate character of this term and $E^{(10)}_{\text{exch}}(S^2)$ represents the first-order exchange energy in the S^2 approximation. Furthermore, the correction $E^{(20)}_{\text{exch-disp}}$ does not fully quench the dispersion energy since it does not include any intramonomer correlation effects. For typical closed-shell systems, this quenching is very small, but for the systems investigated here, it cannot be neglected. Thus, we have additionally scaled the exchange-dispersion energy as

$$\tilde{E}^{(2)}_{\text{exch-disp}} = \tilde{E}^{(20)}_{\text{exch-disp}} \frac{E^{(2)}_{\text{disp}}(2)}{E^{(20)}_{\text{disp}}} \tag{9}$$

The interaction energies $E^{[2]}_{\text{SAPT}}$ with the above components replaced by their scaled counterparts (denoted as "scaled $E^{[2]}_{\text{SAPT}}$'' in the tables) are indeed much closer to the benchmark values. The final scaled SAPT interaction energy in the basis a5Z+(33221) is −1163 cm^{-1}, a 23% error compared to our best estimate of D_e (the CBS-extrapolated SAPT value is −1165 cm^{-1}), whereas CCSD(T) gives 25% error.

Although the error of the SAPT approximation to the interaction energy is fairly large, the components of SAPT may still be used to get a rough interpretation of the physical origins of the Be−Be interactions. Figure 1 illustrates the contributions from the main physical components (in second order, the sum of the induction plus the exchange-induction energy is shown, and similarly for the dispersion components). As one can see, the three attractive contributions are of similar size at the minimum. However, only the dispersion energy is the real

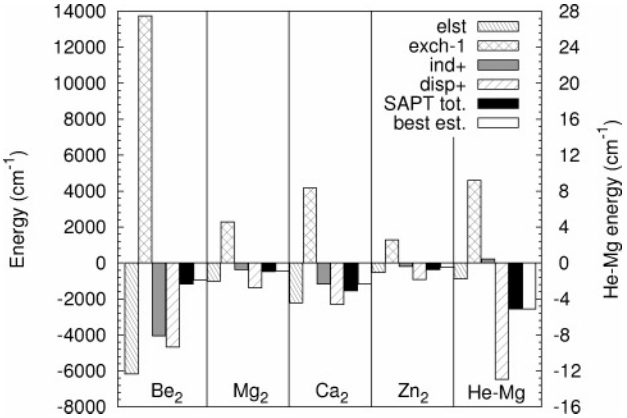

Figure 1. Comparison of SAPT contributions. The bars represent the electrostatic energy (elst), the first-order exchange energy (exch-1), the sum of the induction and exchange-induction energies (ind+), the sum of the dispersion and exchange-dispersion energies (disp+), the total SAPT interaction energy (sum of these components), and our best estimate of the interaction energy. The exchange components are scaled, as described in the text. Left axis for all systems except He−Mg which is plotted according to the right axis. The results plotted were calculated with all electrons in bases a5ZM, aCVQZM, a5ZM, aQZM, and aCVQZM for the consecutive systems.

driving force pulling the atoms together at larger distances since both the electrostatic and the induction energy decay exponentially for Be$_2$. Clearly, the attractive forces are strong and bring the beryllium atoms very close together, as shown by the very large value of the first-order exchange repulsion energy.

The SAPT(DFT) results are similar to the regular SAPT ones. As observed for other systems,[35] SAPT(DFT) reproduces accurately the effects of the intramonomer correlation and SAPT(DFT) terms should be compared to the corresponding SAPT terms with the intramonomer correlation effects included. For the beryllium dimer, $E^{(1)}_{\rm elst}$(KS) agrees well with $E^{(1)}_{\rm elst,resp}(3)$ and $E^{(1)}_{\rm exch}$(KS) with $E^{(1)}_{\rm exch}$(CCSD). Similarly, $E^{(2)}_{\rm ind}$(CKS) is close to $E^{(20)}_{\rm ind,resp} + {}^{t}E^{(22)}_{\rm ind}$ and $E^{(2)}_{\rm disp}$(CKS) to $E^{(2)}_{\rm disp}(2)$. Since the SAPT(DFT) approach uses the same methodology as SAPT for the exchange corrections, similar S-expansion deficiencies are present in the results from both methods; that is, the S^2 results have too large magnitudes in SAPT(DFT) (however, less than those of the regular SAPT). Analogously to eq 8, scaling of the exchange-induction and exchange-dispersion contributions to estimate the effects beyond the S^2 approximation can be performed

$$\tilde{\tilde{E}}^{(2)}_{\rm exch-ind}(\mathrm{CKS}) = \tilde{E}^{(2)}_{\rm exch-ind}(\mathrm{CKS})\,\frac{E^{(1)}_{\rm exch}(\mathrm{KS})}{E^{(1)}_{\rm exch}(S^2)(\mathrm{KS})} \qquad (10)$$

and similarly for $\tilde{E}^{(2)}_{\rm exch-disp}$(CKS). We have used the double tilde here since the CKS exchange energies in SAPT(DFT) already include scaling.[35] This scaling of the SAPT(DFT) corrections improves dramatically the results for the beryllium dimer, and the final energy of −759 cm^{-1} is closer to our best estimate than the CCSD(T) value. However, based on the results of regular SAPT for the beryllium dimer and the accuracy of SAPT(DFT) for other Ae dimers, such a performance of the scaled result is partially accidental for Be$_2$. On the other hand, as discussed below, the CKS asymptotic constants are fairly accurate. Similarly to regular SAPT, the third-order KS induction contribution is large and does not provide an improvement in the accuracy of the total interaction energy.

The rationalizations of the observed performance of SAPT given above can be checked by performing calculations for larger intermolecular separations. The ratio of (unscaled) SAPT and CCSD(T) interaction energies changes from 3 at 2.44 Å to 1.5 at 4 Å (cf. Table 3 in the Supporting Information[61]). This improvement is likely due to the fact that the exchange effects become a smaller part of the total energy. The ratio remains equal to about 1.5 for larger R, where the total interaction is dominated by the dispersion forces. This ratio is showing the difference in the dispersion van der Waals constants for the two levels of theory. The CCSD(T) van der Waals dispersion constants are somewhat more accurate than those of SAPT, as seen by a better agreement of the CCSD(T) interaction energies with the asymptotic expansion[66] (using the $-C_6/R^6 - C_8/R^8 - C_{10}/R^{10}$ terms) than it is the case for SAPT. The asymptotic behavior of SAPT is expected to be very similar to that of MP4 and indeed this is the case. The long-range analysis shows that one of the sources of error of the SAPT approach is an insufficient accuracy of $E^{(2)}_{\rm disp}(2)$ resulting from the omission of terms of the third and higher orders in W. These terms can be partly accounted for by computing $E^{(2)}_{\rm disp}$ via a coupled-cluster approach.[67−70] This observation is further supported by a better performance of SAPT(DFT) than SAPT at large distances since in the SAPT(DFT) method intramonomer correlation effects are effectively accounted for to infinite order by DFT. The asymptotic behavior of SAPT(DFT) is almost as good as that of CCSD(T). The asymptotic C_6 constants (Table 4) are closer to the benchmark for the CKS approach than for SAPT.

B. Mg$_2$. The results of our calculations for Mg$_2$ showing the dependence on the basis set size and type are shown in Table 5. The basis sets aTZ, aQZ, and a5Z, with and without the (33221) set of midbond functions defined in section III.A, have been employed. The bases aTZ and aQZ are from ref 84 (see ref 47), whereas the a5Z basis has been constructed, similarly as for Be$_2$, from the cc-pV5Z set available in the literature[46,47] (denoted by 5Z in Table 5) by adding one diffuse function of each symmetry according to the even-tempered formula. Specifically, the additional exponents were 0.01301, 0.00959, 0.05000, 0.09100, 0.12973, and 0.20270 for the *spdfgh* functions, respectively. The results obtained using the polarized core and valence basis sets aug-cc-pCVTZ and aug-cc-pCVQZ[84] are also given in Table 5. We have performed our calculations at R = 3.9 Å, the rounded equilibrium value obtained in refs 85 or 86.

The results in Table 5 seem to converge quite smoothly to the CBS values except for the energies from the largest, a5Z+(33221), basis set with all electrons correlated. The latter results are significantly below all of the other ones for all of the methods considered including SAPT. No such problems are apparent in the FC calculations. The reasons for this behavior of the AE results are not clear to us. One would naturally suspect linear dependencies in the basis set, in particular since the effect disappears when the midbond functions are removed. On the other hand, although the overlap matrix is more singular for the a5Z+(33221) basis than for the other basis sets used by us, it does not seem to be overly singular and no CCSD convergence problems show up. Nevertheless, the effect is certainly a numerical artifact and we have excluded the all-electron a5Z+(33221) results from further considerations.

The frozen-core CCSD(T) interaction energy in our largest basis set is −390 cm^{-1}, and the CBS extrapolations from the (aQZ+(33221),a5Z+(33221)) and (aCVTZ+(33221),aCVQZ+(33221)) pairs give −393 and −392 cm^{-1}, respectively. Thus,

TABLE 4: Properties of the Investigated Atoms and Asymptotic C_6 Constants for the Dimers[a]

method	Be	Mg	Ca	Zn	He
ns−*np* gap	0.33	0.27	0.21	0.32	1.01
c_0[b]	0.953	0.965	0.958		0.996
atomic radius (Å)	1.99	2.31	2.79	2.10	0.95
			Static Polarizability		
CHF	45.62	81.59	185.40	54.03	1.321
SAPT	44.35	78.47	171.86	49.01	1.347
CKS	41.91	73.27	158.15	42.31	1.399
CKS (ref 72)[c]	43.2	71.8	152		1.28
other theoretical	37.76 ± 0.22 [73][d]	71.3 ± 0.7 [73][d]	157.1 ± 1.3 [73][d]	40.11 [74][e] 37.69 [74][f]	1.384 [75]
experiment		71.5 ± 3.1 [76]	168.7 ± 13.5 [77]	38.8 ± 0.8 [78]	

method	Be_2	Mg_2	Ca_2	Zn_2	Mg−He
			C_6 Dispersion Coefficient		
CHF	279	742	2356	432	21.96
SAPT	279	721	2318	373	22.62
CKS	246	635	1937	313	21.77
CKS (ref 72)[c]	260	631	2055		
other theoretical	214 ± 3 [73][d]	627 ± 12 [73][d]	2121 ± 35 [73][d,g]	282 [74][f]	21.10−22.10 [79]
experiment		683 ± 35 [80]	2081 ± 68 [81][h]	270−296 [78][i]	

[a] The density-based atomic radii are taken from the calculations of Boyd.[71] The basis sets used were: a5Z for He, Be, and Ca, aCVQZ for Mg, and aQZ for Zn. The CKS results are consistent with the SAPT(DFT) approach, i.e., the Fermi-Amaldi asymptotic correction was used and the LDA kernel was applied in the TDDFT propagator. SAPT results are consistent with the SAPT level of theory used in main calculations. For polarizabilities, it corresponds to CHF + true second-order, for C_6, see ref 45. Results are in atomic units, unless stated otherwise. Numbers in square brackets are literature references. [b] Ground-state FCI coefficient in our largest basis sets. [c] Optimized effective potential method with a self-interaction correction. [d] Relativistic semiempirical results. [e] Nonrelativistic. [f] Relativistic. [g] The (non)relativistic values from ref 5 are (2279) 2232 and from ref 82 (2196) 2151. [h] A more recent analysis of experimental data gives 2141 ± 41 (ref 83). [i] Estimated from static polarizability.

TABLE 5: Comparison of the Magnesium Dimer Interaction Energies at $R = 3.9$ Å Obtained Using Various Methods and Basis Sets[a]

method	AE/FC	MP2	MP4	CCSD(T)	FCI
aTZ	AE	−309	−438	−315	
aTZ	FC	−293	−442	−321	−412
aTZ+(33221)	AE	−383	−496	−375	
aTZ+(33221)	FC	−362	−496	−380	−463
aQZ	AE	−360	−475	−355	
aQZ	FC	−342	−484	−368	−453
aQZ+(33221)	AE	−401	−504	−384	
aQZ+(33221)	FC	−369	−500	−386	−467
5Z	AE	−371	−460	−344	
5Z	FC	−344	−479	−365	
5Z+(33221)	AE	−428	−511	−392	
5Z+(33221)	FC	−367	−495	−383	
a5Z	AE	−395	−483	−366	
a5Z	FC	−361	−496	−383	
a5Z+(33221)	AE	−535	−619	−498[b]	
a5Z+(33221)	FC	−374	−503	−390	
aCVTZ+(33221)	AE	−395	−482	−361	
aCVTZ+(33221)	FC	−364	−498	−382	
aCVQZ+(33221)	AE	−406	−483	−363	
aCVQZ+(33221)	FC	−371	−502	−388	

[a] The symbols "AE" and "FC" denote all-electron and frozen-core results, respectively. [b] Result excluded from considerations, see text.

we may assume the CBS limit of −393 ± 3 cm^{-1} at this level. The FCI/FC contribution beyond the CCSD(T) level of theory, $\delta E_{\text{int}}^{\text{FCI}}$, amounts to −81 cm^{-1} in the largest basis employed in our FCI calculations, aQZ+(33221), and the values from smaller basis sets indicate that this contribution is already converged to within a couple cm^{-1}. The (aTZ+(33221),aQZ+(33221))-extrapolated value of the contribution beyond CCSD(T) is −80 cm^{-1}, and we take −80 ± 2 cm^{-1} as our final approximation to this term. Thus, our FCI/FC-level interaction energy at the CBS limit is −473 ± 5 cm^{-1}. The core-valence correlation contribution to the interaction energy is the hardest to estimate, especially in view of the problems of the a5Z+(33221) basis set in AE calculations. In fact, the values of $\delta E_{\text{int}}^{\text{FC}}$ computed at the CCSD(T) level are quite erratic also in other valence-only basis sets. Therefore, we have based our estimate of the core effects exclusively on CCSD(T) calculations in the polarized-core-valence aCVTZ+(33221) and aCVQZ+(33221) basis sets. The aCVQZ+(33221) result [at the CCSD(T) level] is 25 cm^{-1}, and the extrapolation from (aCVTZ+(33221),aCVQZ+(33221)) gives 28 ± 3 cm^{-1}. No method is currently available to estimate the frozen-core effects in $\delta E_{\text{int}}^{\text{FCI}}$. Although we have seen that these effects are negligible for Be_2, this does not need to hold for larger systems. One indication is that for Mg_2 the $\delta E_{\text{int}}^{\text{FC}}$ contribution changes dramatically with the level of theory: in the basis aCVQZ+(33221) it amounts to −35, 19, and 25 cm^{-1} at the MP2, MP4, and CCSD(T) levels. In contrast, this contribution is almost constant for Be_2. To partly account for this effect, we have assumed an additional uncertainty of 6 cm^{-1}, the difference between MP4 and CCSD(T) contributions, in our recommended values. Thus, our final estimate of the complete Mg_2 interaction energy at $R = 3.9$ Å is −445 cm^{-1}, and this estimate should be accurate to about 8 cm^{-1} (with the 3, 2, 3, and 6 cm^{-1} errors added quadratically).

To compare with experiment, one has to know the relativistic correction, but apparently, it has not been computed for Mg_2. We have performed CCSD(T)/AE calculations using the DK relativistic Hamiltonian and the aQZ+(33221) basis. The obtained relativistic contribution was 4.3 cm^{-1}. With this contribution added, the theoretical interaction energy at the minimum of the Mg_2 potential amounts to −441 cm^{-1}. Our result is in good agreement with the most recent experimental estimate of −431.0 ± 1.0 cm^{-1}. This estimate was extracted by Tiesinga et al.[87] from the reanalysis of the measurements of Balfour and Douglas[88] performed by Vidal and Scheingraber.[89] The original experimental value[88] was −424 ± 5 cm^{-1}. Thus, our result supports the reanalyzed experimental value.

There have been numerous calculations published for the magnesium dimer, although not as many as for Be_2. More recent

TABLE 6: Results of Recent Literature Magnesium Dimer Calculations

year	type	results D_e [cm^{-1}]	results R_e [Å]	ref
	Ab Initio			
1990	ICF, SOCI/FC/CBS extr.+ECP	429 ± 10		85
1992	ICF/FC/(9*s*7*p*4*d*3*f*2*g*1*h*) Slater	459	3.88	86
1993	MP2-R12/(19*s*13*p*8*d*4*f*)	461	3.89[a]	90
1994	MP4	475		91
2001	all-electron CCSD(T)	404	3.97	92
2002	small-core MVB-SD/(5*s*4*p*1*d*)	410		87
present	CCSD(T)/AE + FCI/FC	441 ± 8	3.9[a]	
	Experiment			
1970		424 ± 5	3.89	88
1977		431.0 ± 1.0		87,89

[a] Fixed value.

(since about 1990) ab initio obtained values of D_e, listed in Table 6, range between 314 and 475 cm^{-1}. The 1990 work of Partridge et al.[85] found the all-electron nonrelativistic value of $D_e = 429 \pm 10$ cm^{-1}, in good agreement with our result and consistent to within the combined error bars. If our estimate of the relativistic effects is added to this value, the resulting $D_e = 425$ cm^{-1} is in a somewhat better agreement with experiment than our prediction. At the FC level, Partridge et al. estimated the CBS limit value of D_e using the interacting-correlated-fragment (ICF) method, a variant of the CI approach. They also estimated the contribution from the terms neglected in the CI expansion. In addition, they performed calculations using the second-order-CI (SOCI) method and extrapolated the results in a similar manner. The obtained frozen-core limit value of 464 cm^{-1} agrees very well with our result of 473 ± 5 cm^{-1}. However, the core-valence correlation contribution could not be calculated within such an approach and was obtained only using a core polarization potential. Nevertheless, this contribution came out reasonably accurate, amounting to -35 cm^{-1}, close to our value of -28 cm^{-1}. The partial compensation of errors between the FC and AE−FC contributions resulted in the final accuracy of D_e obtained by Partridge et al. higher than that of the components. However, even without this compensation, the calculations of Partridge et al.[85] were quite accurate compared to other applications of the ICF method.[93] It is not possible to determine which of the two ab initio calculations for Mg_2, ours or that of Partridge et al., is more accurate. All of the other calculations for Mg_2 listed in Table 6 used lower levels of theory and smaller basis sets. In particular, none of these papers (except for ref 86 which extended the equilibrium work of ref 85 to other separations) considered post-CCSD(T) excitations which contribute 18% to the interaction energy. Consequently, these results are far from the current best estimates.

The convergence of the CC/PT expansions for Mg_2 is analyzed in Table 3. The expansions appear to converge slightly better than for Be_2, consistent with the finding that $\delta E_{\mathrm{int}}^{\mathrm{FCI}}$ is a smaller fraction of the total interaction energy in the former case (18%) than in the latter case (25%). The MP2 (MP4) method, which after the CBS extrapolation gives the interaction energy of -415 (-483) cm^{-1}, constitutes 93% (109%) of the total interaction energy and (scaled) SAPT gives -488 cm^{-1} or 110%. The 10% SAPT error can be compared to the 18% error of the CCSD(T) approach. The MP3 level of theory accidentally gives a very good approximation to the interaction energy. As for Be_2, CCSD gives a very poor approximation, but at least it is negative. Thus, it looks like an increase of the atomic number within the Ae group indeed leads to a better convergence of the CC/PT expansions.

TABLE 7: Comparison of the Calcium Dimer Interaction Energies at $R = 8.2$ bohr Obtained Using Various Methods and Basis Sets[a]

method	AE/FC	MP2	MP4	CCSD(T)	FCI
aTZ	AE	−775	−925	−784	
aTZ	FC	−667	−996	−876	−1089
aTZ+(33221)	AE	−986	−1114	−972	
aTZ+(33221)	FC	−836	−1138	−1036	−1239
aQZ	AE	−930	−1076	−921	
aQZ	FC	−783	−1117	−1011	−1220
aQZ+(33221)	AE	−1010	−1128	−973	
aQZ+(33221)	FC	−850	−1153	−1054	−1253
a5Z+(33221)	AE	−1028	−1141	−983	
a5Z+(33221)	FC	−858	−1160	−1064	
aCVTZ+(33221)	AE	−1005	−1121	−964	
aCVTZ+(33221)	FC	−839	−1142	−1039	
aCVQZ+(33221)	AE	−1028	−1138	−976	
aCVQZ+(33221)	FC	−851	−1154	−1055	

[a] The symbols "AE" and "FC" denote all-electron and frozen-core results, respectively.

The decomposition of the interaction energy for Mg_2 shown in Figure 1 is quite different than for Be_2. First, although the total interaction energies are smaller in magnitude only by a factor of 2, the components are several times smaller. The main reason is simply the larger size of Mg than of Be, which leads to a significantly larger equilibrium separation. As a result, the electrostatic and induction contributions are now smaller in magnitude than the dispersion contribution. One may say that the response of the system to the pull of the dispersion force is smaller. Similarly, the first-order valence repulsion is only a factor of 2 larger in magnitude than the dispersion energy since the charge penetration is much smaller than for Be_2.

SAPT(DFT) results are similar to the SAPT ones, but in contrast to the beryllium dimer, the total interaction energy for Mg_2 is more negative in SAPT(DFT) than in SAPT and significantly less accurate. Generally, the individual SAPT(DFT) components are similar to the SAPT equivalents but smaller in magnitude. In particular, the smaller value of the first-order exchange contribution seems to be mainly responsible for the more negative total interaction energy given by SAPT(DFT). The poor performance of SAPT(DFT) takes place despite the asymptotic constants at the SAPT(DFT) level (Table 4) being in an excellent agreement with the benchmark calculations (slightly less good with experiment, but the experimental value has a significant uncertainty) showing that the intramonomer correlation effects in the dispersion component are well modeled. The accuracy of the SAPT-level constants is lower than that of the SAPT(DFT) ones.

C. Ca_2. Our calculations for the Ca_2 dimer are presented in Tables 7 and 8. For this system, we will make broad comparisons with the recent SAPT calculations from ref 5, the most extensive literature work. Correlation-consistent basis sets cc-pV*X*Z, X =D, T, Q, and 5, have become available for Ca only recently.[94] Therefore, the authors of ref 5 employed their own basis set (denoted "Bussery" in Table 8), constructed by extending Sadlej's triple-zeta quality basis set[95,96] optimized on atomic polarizabilities. A (3*s*3*p*2*d*) midbond set was added only in calculations of the $E_{\mathrm{disp}}^{(20)}$ correction. We have used this basis without any midbond functions and with our (33221) midbond set defined in section III A. The basis sets aTZ, aQZ, and a5Z have again been obtained by an augmentation of the cc-pVTZ, cc-pVQZ, and cc-pV5Z sets[94] with one diffuse function of each symmetry, with an exponent chosen according to the even-tempered relation. Specifically, these additional exponents are equal to 0.010242, 0.009589, 0.012253, and 0.044403 for the *spdf* functions in the basis aTZ, 0.009577, 0.009248, 0.011035,

TABLE 8: SAPT/SAPT(DFT) Interaction Energy Components and Supermolecular Interaction Energies for the Calcium Dimer at $R = 8.2$ bohr[a]

	Bussery		BusseryM		a5ZM		SDFT
method	AE	FC	AE	FC	AE	FC	AE
$E^{(1)}_{\mathrm{elst,resp}}(3)/E^{(1)}_{\mathrm{elst}}(\mathrm{KS})$	−2286	−2686	−2307	−2704	−2216	−2633	−2313
$E^{(1)}_{\mathrm{exch}}(2)$	5061	5262	5029	5259	4826	5156	
$E^{(1)}_{\mathrm{exch}}(\mathrm{CCSD})/E^{(1)}_{\mathrm{exch}}(\mathrm{KS})$	4354	4689	4354	4709	4223	4666	3741
$E^{(10)}_{\mathrm{exch}}(S^{k>2})/E^{(1)}_{\mathrm{exch}}(S^{k>2})(\mathrm{KS})$	329	329	329	329	328	328	196
$E^{(20)}_{\mathrm{ind,resp}}/E^{(2)}_{\mathrm{ind}}(\mathrm{CKS})$	−12619	−12583	−12694	−12657	−12593	−12553	−9328
$E^{(20)}_{\mathrm{exch-ind,resp}}/\tilde{E}^{(2)}_{\mathrm{exch-ind}}(\mathrm{CKS})$	10453	10419	10497	10463	10414	10377	7847
${}^{t}E^{(22)}_{\mathrm{ind}}$	1740	573	1896	616	2389	843	
${}^{t}E^{(22)}_{\mathrm{exch-ind}}$	−1441	−475	−1568	−509	−1976	−697	
$E^{(2)}_{\mathrm{disp}}(2)/E^{(2)}_{\mathrm{disp}}(\mathrm{CKS})$	−2334	−2318	−2854	−2818	−2913	−2922	−2866
$E^{(20)}_{\mathrm{exch-disp}}/\tilde{E}^{(2)}_{\mathrm{exch-disp}}(\mathrm{CKS})$	434	332	514	409	546	426	484
$\delta E^{\mathrm{HF}}_{\mathrm{int,resp}}$	851	849	806	803	724	721	724
$E^{[2]}_{\mathrm{SAPT}}/E^{[2]}_{\mathrm{SDFT}}$	−1700	−2048	−2162	−2492	−2126	−2493	−2437
$E^{[2]}_{\mathrm{SAPT+HF}}/E^{[2]}_{\mathrm{SDFT+HF}}$	−848	−1199	−1357	−1689	−1401	−1772	−1712
scaled $E^{[2]}_{\mathrm{SAPT}}$ /$E^{[2]}_{\mathrm{SDFT}}$	−1095	−1277	−1519	−1668	−1535	−1683	−1977
MP2	−427	−335	−907	−739	−1028	−858	
MP3	−441	−506	−906	−910	−992	−1016	
MP4	−495	−562	−1033	−1033	−1141	−1160	
CCSD	−17	−33	−429	−409	−508	−510	
CCSD(T)	−350	−413	−866	−913	−983	−1064	

[a] The basis sets employed are described in the text. SAPT(DFT) results were obtained with the a5ZM basis set. For the remaining notation, see footnote *b* of Table 3.

0.027795, and 0.034976 for the *spdfg* functions in the basis aQZ, and 0.008890, 0.008968, 0.010094, 0.028667, 0.033878, and 0.084830 for the *spdfgh* functions in the basis a5Z. The augmented polarized-core-valence sets aug-cc-pCVTZ and aug-cc-pCVQZ were formed from the nonaugmented sets cc-pCVTZ and cc-pCVQZ[94,97] by adding the same diffuse functions as for the bases aTZ and aQZ, respectively. The same (33221) midbond set was used as for the other systems. All our calculations have been performed for 8.2 bohr, the minimum distance found in ref 5.

For the Ca_2 dimer, our CCSD(T)/AE-level result with the largest basis set, a5Z+(33221), is −983 cm^{-1}. This result agrees also reasonably well with those computed in other large basis sets presented in Table 7. The CBS extrapolation from bases aQZ+(33221) and a5Z+(33221) gives −993 ± 10 cm^{-1}. The FCI correction ranges between −199 and −213 cm^{-1}, suggesting also a fairly good basis set convergence. The value of this correction in the largest, aQZ+(33221), basis set used at this level is −199 cm^{-1}, and the extrapolation from this basis and the aTZ+(33221) set gives −196 ± 3 cm^{-1}, where the error bars reflect the difference between the calculated and extrapolated values. Thus, our initial estimate of the interaction energy at the minimum is −1189 ± 13 cm^{-1}, where the error bar reflects only the observed basis set convergence. The uncertainties not included in this error bar are the ones arising from the core-valence correlation effects. At the CCSD(T) level, these effects amount to 81 cm^{-1} in the basis a5Z+(33221) and to 79 cm^{-1} in the basis aCVQZ+(33221), whereas the values of these effects extrapolated from the sequences (aQZ+(33221),a5Z+(33221)) and (aCVTZ+(33221),aCVQZ+(33221)) are 81 and 82 cm^{-1}, respectively. This suggests an uncertainty of the order of 3 cm^{-1} from this source. An even more significant source of error is probably the FC effects in $\delta E^{\mathrm{FCI}}_{\mathrm{int}}$. Similarly as for Mg_2, the FC effects change significantly with the level of theory and amount to −170, 19, and 81 cm^{-1} at the MP2, MP4, and CCSD(T) levels, respectively, in the basis a5Z+(33221). Thus, an FC effect of the order of 50 cm^{-1} in the $\delta E^{\mathrm{FCI}}_{\mathrm{int}}$ contribution cannot be excluded. We have therefore increased appropriately the error bars by summing the squared errors (10, 3, 3, and 50 cm^{-1}) to obtain $D_e = 1189 \pm 51$ cm^{-1} as our final estimate. The relativistic effects, as estimated in ref 5, decrease D_e by about 21 cm^{-1}. Our calculations with the DK Hamiltonian at the CCSD(T)/AE level in the completely decontracted aQZ basis (see the discussion in the next subsection) gave 36.7 cm^{-1} for these effects. This brings our best estimate to $D_e = 1152 \pm 51$ cm^{-1}. This value agrees reasonably with the experimental result: $D_e = 1102.08 \pm 0.09$ cm^{-1} (refs 98 and 81). The agreement with experiment to within 4.5% is better than for any previously published results, except for ref 5, see the discussion below.

The $\delta E^{\mathrm{FCI}}_{\mathrm{int}}$ contribution constitutes for Ca_2 16% of the interaction energy, a slight further decrease in the series Be, Mg, and Ca. The improvement of the convergence of the perturbation expansion observed for Mg_2 compared to Be_2 is much more pronounced for Ca_2. The MP2 (MP4) value computed in the a5Z+(33221) basis set reproduces 86% (96%) of our limit value of the interaction energy. In fact, the MP*n* series performs better than the CCSD(T) method. This is obviously fortuitous and results from the fact that the MP*n* values of D_e lie below the CCSD(T) value. The performance of the low-order MP*n* series can also be measured relative to the CCSD(T) result as such terms constitute the PT expansion of the CCSD(T) energy. In this case, the convergence is not so good and in fact the consecutive terms are farther and farther from the CCSD(T) value. Nevertheless, the overall convergence behavior is still better than in the case of Be_2 or Mg_2. Thus, it does appear that the severity of the CC/PT convergence problems diminishes as the atomic number increases.

SAPT does not reproduce the limit interaction energy as well as MP*n*. The scaled SAPT value in the a5Z+(33221) basis, −1535 cm^{-1}, constitutes 129% of the interaction energy (the CBS-extrapolated value is −1552 cm^{-1}). This 29% error is significantly larger than the 16% error of the CCSD(T) approach. For Ca_2, in contrast to other investigated systems, the correction $\delta E^{\mathrm{HF}}_{\mathrm{int,resp}}$ is positive. This leads to a reasonably accurate value of the unscaled hybrid approach, but this good performance is

TABLE 9: SAPT/SAPT(DFT) Interaction Energy Components and Supermolecular Interaction Energies for the Zn_2 and He−Mg Dimers[a]

	Zn_2			He−Mg			
	aQZM		SDFT	a5ZM	aCVQZM		SDFT
method	AE	FC	AE	FC	AE	FC	AE
$E^{(1)}_{\mathrm{elst,resp}}(3)/E^{(1)}_{\mathrm{elst}}(\mathrm{KS})$	−535	−521	−569	−2.05	−1.77	−2.05	−2.07
$E^{(1)}_{\mathrm{exch}}(2)$	1626	1593		12.75	11.84	12.79	
$E^{(1)}_{\mathrm{exch}}(\mathrm{CCSD})/E^{(1)}_{\mathrm{exch}}(\mathrm{KS})$	1295	1271	1100	10.35	9.21	10.35	10.98
$E^{(10)}_{\mathrm{exch}}(S^{k>2})/E^{(1)}_{\mathrm{exch}}(S^{k>2})(\mathrm{KS})$	29	29	12	0.00	0.00	0.00	0.00
$E^{(20)}_{\mathrm{ind,resp}}/E^{(2)}_{\mathrm{ind}}(\mathrm{CKS})$	−3208	−3208	−2003	−1.46	−1.46	−1.46	−1.03
$E^{(20)}_{\mathrm{exch-ind,resp}}/\tilde{E}^{(2)}_{\mathrm{exch-ind}}$ (CKS)	2907	2906	1841	2.00	2.00	2.00	1.34
${}^{t}E^{(22)}_{\mathrm{ind}}$	783	831		0.24	0.34	0.24	
${}^{t}E^{(22)}_{\mathrm{exch-ind}}$	−710	−753		−0.33	−0.46	−0.33	
$E^{(2)}_{\mathrm{disp}}(2)/E^{(2)}_{\mathrm{ind}}(\mathrm{CKS})$	−1107	−1083	−950	−13.95	−13.63	−13.89	−13.45
$E^{(20)}_{\mathrm{exch-disp}}/\tilde{E}^{(2)}_{\mathrm{exch-disp}}(\mathrm{CKS})$	189	184	124	0.63	0.61	0.61	0.53
$\delta E^{\mathrm{HF}}_{\mathrm{int,resp}}$	−85	−85	−85	−3.09	−3.09	−3.09	−3.09
$E^{[2]}_{\mathrm{SAPT}}/E^{[2]}_{\mathrm{SDFT}}$	−386	−371	−458	−4.57	−5.17	−4.54	−3.70
$E^{[2]}_{\mathrm{SAPT+HF}}/E^{[2]}_{\mathrm{SDFT+HF}}$	−471	−456	−543	−7.66	−8.26	−7.63	−6.79
scaled $E^{[2]}_{\mathrm{SAPT}}/E^{[2]}_{\mathrm{SDFT}}$	−363	−353	−436	−4.47	−5.09	−4.44	
MP2	−450	−438		−3.02	−4.16	−2.95	
MP3	−308	−319		−5.05	−5.98	−5.04	
MP4	−420	−382		−5.18	−5.68	−5.17	
CCSD	−86	−85		−2.71	−3.12	−2.70	
CCSD(T)	−228	−230		−4.39	−4.69	−4.37	

[a] The intermonomer distances are $R = 3.847$ Å for Zn_2 and $R = 5.0$ Å for He−Mg. SAPT(DFT) results are obtained with the aQZM basis set for Zn_2 and with a basis composed of the aCVQZ set on Mg, a5Z on He, and the (33221) midbond set for He−Mg. For the remaining notation, see footnote *b* of Table 3.

almost certainly fortuitous, as the $\delta E^{\mathrm{HF}}_{\mathrm{int,resp}}$ correction is not recommended to be applied for nonpolar systems.[23]

In contrast to Be_2 and Mg_2, there were very few ab initio calculations performed for Ca_2. Dyall and McLean[86] applied the ICF method in the FC approximation and obtained a D_e of 1236 cm^{-1}. This agrees well with our FCI/FC value in the aQZ+(33221) basis equal to 1253 cm^{-1} but worse with the CBS-extrapolated benchmark FC-level value of 1270 cm^{-1}. However, these authors have not computed any correction for the FC approximation. Czuchaj et al.[99] have performed CCSD(T) calculations with a [Ne]-core relativistic pseudopotential, obtaining $D_e = 1015$ cm^{-1}. The calcium dimer has also been employed as a test case for several DFT-based methods. However, the values of D_e obtained in this way (from 1004 to 2760 cm^{-1} for various DFT functionals[100,101] and 926 cm^{-1} for the RSH+MP2 DFT-plus-dispersion method[102]) are not very accurate.

As mentioned earlier, extensive investigations of Ca_2 were performed in ref 5 using SAPT. The final nonrelativistic value of $D_e = 1134$ cm^{-1} from ref 5 should be compared with the value computed in the basis "Bussery" at the level $E^{[2]}_{\mathrm{SAPT+HF}}$, $D_e = 848$ cm^{-1}. The 286 cm^{-1} difference results entirely from the use of bond functions in ref 5 in calculations of $E^{(20)}_{\mathrm{disp}}$. In view of the SAPT performance discussed above, the very good agreement of SAPT with experiment obtained in ref 5 was due to a fortuitous cancellation of the theory-level overshot with the basis set incompleteness error. In our largest basis set, a5Z+(33221), the value of D_e at the $E^{[2]}_{\mathrm{SAPT+HF}}$ level is 1401 cm^{-1}. Also, as discussed above, the use of the $\delta E^{\mathrm{HF}}_{\mathrm{int,resp}}$ term is probably not advisable for Ca_2.

The decomposition of the interaction energy into SAPT components, shown in Figure 1, is for Ca_2 similar to that for Mg_2, except that all of the contributions are proportionally larger in magnitude, as are the total interaction energies. In particular, the dispersion plus exchange-dispersion energy of Ca_2 is nearly two times larger in magnitude than that of Mg_2, despite the interatomic separation being 0.4 Å larger (the sixth power of the ratio of the separations is 1.9). This is clearly related to the very large polarizability of Ca, more than twice that of Mg.

The performance of SAPT(DFT) for Ca_2 is very similar to that for Mg_2; that is, the SAPT(DFT) interaction energy is much too large in magnitude. Again, as for Mg_2, the major deficiency seems to come from the first-order exchange energy. This contribution can be shown to be potentially exact in SAPT(DFT) but only asymptotically.[34] However, the very strong interactions in Ae dimers result in the minimum separations which are relatively short, i.e., farther from the asymptotic limit than the minima of typical dimers, which may lead to less accurate SAPT(DFT) exchange energies than in most other cases. The electrostatic, induction, and dispersion corrections agree better between SAPT and SAPT(DFT). Also the asymptotic C_6 constants of SAPT and SAPT(DFT) (Table 4) are in fairly good agreement with each other and with the benchmark calculations: the SAPT constant is 9% too large and the SAPT(DFT) one is 9% too small. Thus, the asymptotic accuracy of SAPT/SAPT(DFT) is very good for Ca_2.

D. Zn_2. Our calculations for Zn_2 were done at $R = 3.847$ Å, the R_e distance found in the CCSD(T) calculations of ref 103. The basis sets aTZ, aQZ, and a5Z employed by us have been taken from ref 104, and the midbond functions were the same as for the previous dimers. The results are collected in Table 9. The FC calculations were performed using small core; that is, both the 3*d* and 4*s* electrons were correlated. Therefore, the FC effects are very small, virtually negligible for Zn_2, amounting to only 2 cm^{-1} in the aQZ+(33221) basis at the CCSD(T) level. The use of the large core, i.e., correlating only the 4s electrons, gives very large errors. Our best basis set, a5Z+(33221), gives the CCSD(T)/FC interaction energy of −234 cm^{-1}, and the (aQZ+(33221),a5Z+(33221)) extrapolation gives −237 ± 3 cm^{-1}. If the FC correction is added to this result, our best estimate of the CCSD(T)/AE interaction energy of Zn_2 is −235 cm^{-1}. The post-CCSD(T) effects are very difficult to compute for Zn_2. The best we could do was to perform small-core CCSDT calculations in the aTZ basis set. The triples contribution beyond CCSD(T) obtained in this way amounts to -3 cm^{-1}. The basis set incompleteness and FC errors of this contribution are difficult to estimate but should not be larger than a couple of cm^{-1}. This leads to our final nonrelativistic estimate of the interaction energy at the CCSDT/AE level equal to -238 ± 8 cm^{-1}, where we have increased the CCSD(T)/FC-level uncertainty by 5 cm^{-1} to account for the effects discussed above.

As for other systems, we have also computed the relativistic correction using the DK Hamiltonian and the CCSD(T)/AE method. Whereas for lighter atoms large basis sets developed at the nonrelativistic level are also adequate for relativistic calculations, this is not true anymore for Zn with its nuclear charge of 30. Apparently, the relativistic and nonrelativistic inner orbitals are significantly different. In turn, bases developed at the relativistic level[104] work poorly in nonrelativistic calculations. Thus, to obtain reliable values of the relativistic correction to the interaction energy of Zn_2, which requires subtraction of relativistic and nonrelativistic values computed in the same basis set, we have decided to use the fully decontracted aTZ basis set which we found to be flexible enough to describe the inner-shell orbitals at both the nonrelativistic and relativistic levels. The resulting value of the relativistic contribution to the Zn_2 interaction energy is 3.5 cm^{-1}, which leads to our best estimate of this energy of -235 ± 8 cm^{-1}.

The zinc dimer has been studied by many other groups during the past several years. The most accurate previous work is probably that of Peterson and Puzzarini.[103] These authors developed relativistic effective-core potential (ECP)-based basis sets up to $X = 5$, both of valence and core-valence type. The results of ref 103 were extrapolated to the complete basis set limit giving a CCSD(T)/AE value of $D_e = 226 \pm 3$ cm^{-1}, in very good agreement with our CCSD(T) value of 232 cm^{-1}, in particular taking into account that two completely different families of basis sets and different ways of accounting for relativistic effects were used. Note that the relativistic correction itself cannot be extracted from the results of ref 103. The spin–orbit coupling correction has been found in ref 103 to be negligible. The FC correction of 3 cm^{-1} computed by Peterson and Puzzarini is in good agreement with the value of 2 cm^{-1} obtained by us.

Ellingsen et al.[105] applied several methods, including CCSD(T) and complete active space second-order perturbation theory (CASPT2), and obtained small-core nonextrapolated values of D_e of 242 and 274 cm^{-1}, respectively. They also computed the interaction energy using a relativistic scalar Hamiltonian and no ECPs and found that the relativistic correction enters beyond the digits listed in their table. The CCSD(T)/FC value of D_e is larger than our estimated CBS limit for this quantity amounting to 237 ± 3 cm^{-1} which is somewhat unexpected as finite basis set values tend to be smaller than the limit. The CASPT2 result of Ellingsen et al. is in an excellent agreement with experiment;[106] however, this agreement may be fortuitous like, for example, the one achieved by MP3 for Mg_2. Very recently, Bera and Das[107] obtained $D_e = 266$ cm^{-1} using CCSD(T) and a $6s5p4d3f$ basis. Clearly, there must have been some numerical problems in these calculations as this result is incompatible with our results and with all literature CCSD(T) calculations. Several other calculations for Zn_2 have been published in recent years,[101,108−112] but these papers have not achieved the accuracy of some of the work discussed above.

Our best estimate of $D_e = 235 \pm 8$ cm^{-1} at the relativistic CCSDT/AE level of theory is in a rather poor agreement with the experimental value of 279.1 cm^{-1} (ref 106). It is possible that the effects of quadruple and higher excitations are responsible for this difference, but it is not very likely in view of the fact that the triple excitations beyond CCSD(T) contribute only 3 cm^{-1}. Typically, these effects are larger than the effects of quadruple and higher excitations. For example, for Be_2 the former effects contribute 20% and the latter ones 11% to the interaction energy. Thus, it is difficult to expect the effects beyond CCSDT to be much larger than 10 cm^{-1}, and the reasons for the discrepancy with experiment remain unclear to us. Unfortunately, CCSDTQ calculations, which scale as N^{10} with the system size, much worse than CCSD(T) (N^7) and CCSDT (N^8), are currently not feasible for Zn_2.

It follows from the discussion given above that the post-CCSDT effects in the Zn_2 interaction energy at the minimum of the potential cannot be determined accurately at the present time. The theoretical estimates may indicate that these are only of the order of 10 cm^{-1} or 4% of the interaction energy, but comparisons with experiment suggest effects as large as nearly 50 cm^{-1} or 17%. If the latter is correct, this contribution is of similar size as for Ca_2. However, the SM PT expansion for Zn_2 converges much worse than for Ca_2. In particular, MP4 gives the interaction energy almost twice as large as that given by CCSDT. The CCSD method gives a nonsensical interaction energy, as for the other systems. On the other hand, the scaled CBS-extrapolated SAPT result is in a 29% error compared to experiment, a similar performance as in the case of Ca_2. The poor convergence of the MPn expansion for Zn_2 is a bit baffling. Even if we take into account that the expansions for Ca_2 somewhat fortuitously agree with the total interaction energy, and compare the convergence patterns relative to the CCSD(T) interaction energies, the convergence is still much worse in the Zn_2 case, despite the much smaller magnitude of the interaction energy. The equilibrium separation is smaller for Zn_2 than for Ca_2, but this is due mainly to the smaller size of Zn and not to strong attractive interactions. The only explanation which comes to mind is that the presence of the 3d electrons in Zn has a strong impact on the convergence properties. The slow convergence of the SM PT expansion may indicate that the post-CCSDT effects are large for Zn_2.

The zinc dimer is similar to Mg_2 and Ca_2, and different from Be_2, in terms of the sizes of the individual SAPT contributions relative to the total interaction energy. The Zn_2 interactions have been previously interpreted in terms of SAPT components by Lukes et al.[112] These authors used the CCSD(T) and SAPT methods with ECPs and relatively small basis sets. The SAPT results were presented only graphically and for a larger R than used by us, so it is difficult to make detailed comparisons. However, most of the components agree reasonably with those computed by us.

The behavior of SAPT(DFT) for Zn_2 is similar as for Mg_2 and Ca_2, and the error of the SAPT(DFT) total interaction energy is also similar as for these systems. The C_6 constants (Table 4) obtained at the SAPT and SAPT(DFT) levels are larger than the best ab initio literature value[74] by 32% and 11%, respectively. Part of the difference is due to the literature result including the relativistic effects which, based on the values of the static polarizabilities listed in Table 4, can be as large as 15%. Compared to the estimated nonrelativistic C_6 of 324 a.u., the SAPT(DFT)-level value is 3% too small whereas the SAPT value is 15% too large. Thus, asymptotically SAPT(DFT) should perform better than SAPT. One should mention, however, that the literature value[74] of C_6 for Zn_2, computed using a multireference CI wave function and a relatively small basis set, is

TABLE 10: Comparison of the He−Mg Interaction Energies at $R = 5.0$ Å Obtained Using Various Methods and Basis Sets[a]

method	AE/FC	MP2	MP4	CCSD(T)	FCI
aTZ	AE	−2.21	−4.25	−3.38	
aTZ	FC	−1.75	−3.92	−3.18	−3.54
aTZ+(332)	AE	−3.32	−5.56	−4.58	
aTZ+(332)	FC	−2.69	−5.06	−4.23	−4.61
aTZ+(33221)	AE	−3.40	−5.63	−4.63	
aTZ+(33221)	FC	−2.80	−5.18	−4.33	−4.71
aQZ	AE	−3.03	−4.94	−4.00	
aQZ	FC	−2.38	−4.53	−3.76	−4.12
aQZ+(332)	AE	−3.56	−5.55	−4.57	
aQZ+(332)	FC	−2.88	−5.11	−4.31	−4.68
aQZ+(33221)	AE	−3.64	−5.62	−4.63	
aQZ+(33221)	FC	−2.95	−5.18	−4.37	−4.74
a5Z	AE	−3.74	−5.33	−4.35	
a5Z	FC	−2.65	−4.77	−4.01	
a5Z+(33221)	AE	−4.20	−5.82	−4.79[b]	
a5Z+(33221)	FC	−3.02	−5.18	−4.39	
aCVTZ+(33221)[c]	AE	−3.85	−5.61	−4.61	
aCVTZ+(33221)[c]	FC	−2.78	−5.15	−4.31	
aCVQZ+(33221)[c]	AE	−4.16	−5.68	−4.69	
aCVQZ+(33221)[c]	FC	−2.95	−5.17	−4.37	

[a] The symbols “AE” and “FC” denote all-electron and frozen-core results, respectively. [b] Result with possible numerical errors, not included in the final estimates. [c] Helium basis set was a*XZ*, with the same *X* as for Mg.

much less accurate than those used in comparisons for the other dimers. In fact, the values of C_6 obtained by us may be closer to the exact result.

E. He−Mg. In the calculations for He−Mg, we have employed for magnesium the same basis sets as in the Mg_2 calculations (section III.B), whereas for helium the standard aug-cc-pV*XZ* sets[113] were used. The midbond functions were the same as for the previous systems. There exists a very accurate ab initio He−Mg potential by Hinde,[114] and we will make extensive comparisons to it. Therefore, we performed all calculations for the intermonomer distance of 5.0 Å, for which comparisons between methods and basis sets were presented in ref 114, rather than for 5.1 Å, the van der Waals minimum distance obtained in this reference.

The He−Mg interaction energies calculated using different methods and basis sets are presented in Table 10. The all-electron CCSD(T) interaction energy in the largest basis listed in Table 10, the a5Z+(33221) set, is −4.79 cm^{-1}. In view of the problems of this basis set in the case of Mg_2, and of the fact that the Mg a5Z and aQZ bases have been constructed in different ways, one should use caution when analyzing the results and in particular when extrapolating to the CBS limit. Indeed, Table 10 shows that the convergence pattern of the AE values is not uniform, as the interaction energies in the a*XZ*+(332) and a*XZ*+(33221) families are almost constant for $X = \text{T}$ and Q at the CCSD(T)/AE level of theory. However, in contrast to the Mg_2 case, the behavior of the FC energies is almost the same as that of AE ones. Another observation is that the CCSD(T)/AE energy in the basis a5Z+(33221) appears to be too large in magnitude compared to the FC result. This is also reflected in the CBS extrapolations of the CCSD(T)/AE interaction energies from the basis set pairs (aQZ+(33221), a5Z+(33221)), (aQZ,a5Z), and (aCVTZ+(33221),aCVQZ+(33221)) which give −4.97, −4.72, and −4.75 cm^{-1}, respectively. The first number stands out and confirms the suspicion that, similarly as for Mg_2, the use of the basis a5Z+(33221) in AE calculations leads to some numerical problems. Therefore, to estimate the CBS limit of the He−Mg interaction energy, we have extrapolated the FC results. The extrapolations from the three pairs of basis sets listed above give −4.41, −4.27, and −4.41 cm^{-1}, respectively. Since the a*XZ* series is converging slowly due to the lack of bond functions, whereas the computed a5Z+(33221) and aCVQZ+(33221) values are only 0.02 and 0.04 cm^{-1}, respectively, from their CBS limits, we have taken −4.41 ± 0.04 cm^{-1} as our best estimate of the CCSD(T)/FC interaction energy, where we have chosen the uncertainty to include both computed values. We have then separately extrapolated $\delta E_{\text{int}}^{\text{FC}}$ from the results in (aCVTZ+(33221), aCVQZ+(33221)) bases, obtaining a contribution of −0.33 cm^{-1}. An extrapolation from (aQZ,a5Z) gives a contribution of −0.44 cm^{-1}, significantly larger in magnitude, but the (aTZ,aQZ) extrapolation gives only −0.27 cm^{-1}. Since the CV bases are more appropriate for investigating the core−valence correlation effects, we will adopt −0.33 ± 0.10 cm^{-1} as our best estimate, where the conservative error bars are chosen to reflect the spread of the results in different types of basis sets. This gives the value of the CCSD(T)/AE interaction energy of −4.74 ± 0.11 cm^{-1}, consistent with two out of the three AE-based extrapolations quoted above, and confirming that the a5Z+(33221) AE calculation has some numerical inaccuracy. Finally, Table 10 shows that $\delta E_{\text{int}}^{\text{FCI}}$ seems to be very well converged, and the (aTZ+(33221),aQZ+(33221)) extrapolation gives −0.36 ± 0.01 cm^{-1}. Thus, our final estimate of the interaction energy at 5.0 Å is −5.10 ± 0.11 cm^{-1} with errors added quadratically. The relativistic effects for He−Mg are small: a DK CCSD(T)/AE estimate of these effects in the aQZ+(33221) basis amounts to −0.012 cm^{-1}.

Due to its very small value, D_e has not been measured for He−Mg. Thus, the only information about this quantity comes from ab initio calculations. It turns out that a precise knowledge of this value is relevant for experiments on atoms, molecules, and clusters solvated in superfluid helium nanodroplets.[115−125] Experiments have determined that some atoms are solvated in the droplets whereas some others only attach to the surface of a droplet.[126−138] Clearly, the trend depends on the ratio of the He−atom potential depth to the He−He depth of 7.6495 cm^{-1} (ref 139). In the case of magnesium, Reho et al.[136] have found that Mg atoms do get solvated.

Hinde[114] computed the He−Mg potential using the CCSDT method with the (large-core) FC approximation and a basis set which was composed of the cc-pVQZ set for Mg, the aug-cc-pVQZ set for He, and a (3*s*3*p*2*d*) set of bond functions. The core-valence correlation contribution was then taken into account at the CCSD(T) level using the aug-cc-pVTZ basis set on He, the (3*s*3*p*2*d*) set of bond functions, and a polarized core and valence MT-TZ set on Mg, obtained by an extension of the cc-pVTZ basis according to the prescription of Martin and Taylor (MT) given in ref 140. Hinde obtained an interaction energy of −4.97 ± 0.06 cm^{-1} at 5.0 Å (the value obtained from data in the Supporting Information, Tables 1 and 3 of ref 114 give −4.95 cm^{-1}). This value is within the combined error bars of our and Hinde’s calculations. Our interaction energy is larger in magnitude mainly due to the use of larger basis sets in our work (the cardinal number larger by one, diffuse functions on Mg, and a larger midbond set) and due to our use of CBS extrapolations. This effect can be precisely determined by comparing our extrapolated CCSD(T)/FC interaction energy of −4.41 ± 0.04 cm^{-1} to the largest basis set result of −4.26 cm^{-1} in Hinde’s work. The difference of 0.15 cm^{-1} is close to the 0.13 cm^{-1} spread between the final estimates. As far as the level of theory is concerned, our calculations are practically equivalent to those of ref 114 since this reference found that the frozen-core FCI and CCSDT results are identical to within 0.03 cm^{-1}.

TABLE 11: Comparisons of the Interaction Energies and Their Components near the van der Waals Minima[a]

	Be_2	Mg_2	Ca_2	Zn_2	He−Mg
R (Å)[b]	2.44	3.9	4.33925	3.847	5.0
E_{int} (NR)[c]	−942 ± 15	−445 ± 8	−1189 ± 51	−238 ± 8[d]	−5.10 ± 0.11
E_{int}[e]	−938	−441	−1152	−235	−5.11
$-D_e$ (exp.)[f]	−790 ± 30 [58]	−431.0 ± 1.0 [87]	−1102.08 ± 0.09 [81]	−279.1 [106]	
$E_{int}^{CCSD(T)}$/FC[g]	−625 (66%)	−393 (88%)	−1075 (90%)	−237 (85%)[h]	−4.41 (86%)
δE_{int}^{FC}[g]	−85 (9%)	28 (6%)	82 (7%)	2 (1%)[h]	−0.33 (6%)
$E_{int}^{CCSD(T)}$/AE[g]	−710 (75%)	−365 (82%)	−993 (84%)	−235 (84%)[h]	−4.74 (93%)
δE_{int}^{FCI}[g]	−232 (25%)	−80 (18%)	−196 (16%)		−0.36 (7%)
scaled SAPT[g]	−1165 (124%)	−488 (110%)	−1552 (131%)	−359 (129%)[h]	−5.15 (101%)

[a] All energies are in cm^{-1}. [b] For Be_2, Mg_2, and Zn_2, the interatomic separations are very close to minimum values, probably to within 0.01 Å. For He−Mg, $R_e = 5.1$ Å, see text. For Ca_2, an accurate value of R_e is unknown but should be within 0.1 Å of the one used in our calculations.[c] Best estimate of the nonrelativistic interaction energy from our calculations. [d] The results obtained at the CCSDT level of theory and the uncertainty is relative to the exact energy at this level. [e] Best estimate with relativistic corrections computed by us. [f] Experimental values, numbers in square brackets are literature references. [g] All values extrapolated to CBS limit. The numbers in parentheses are percentage contributions to the best nonrelativistic estimates of the total interaction energy. [h] Relative to the experimental D_e.

Our core-valence correlation contribution is 0.03 cm^{-1} different from that of ref 114 (0.02 cm^{-1} if the result of ref 114 with X = Q is considered). Thus, one may conclude that the agreement with the work of Hinde is excellent, but our calculations indicate that the true interaction energy in the minimum is slightly below the error bars of ref 114. The slightly deeper potential well reinforces the analysis of Hinde[114] indicating that Mg should indeed dissolve in the helium droplets, as found experimentally.[136]

Another recent study, by Partridge et al.,[141] used somewhat larger basis sets than ref 114 but only the CCSD(T) level of theory. These authors performed small-core (i.e., only the Mg $1s^2$ frozen) CCSD(T) calculations in an aug-cc-pVQZ+ (33211) basis set, partially uncontracted and augmented with compact functions to describe the core-valence correlation (where core means here the $2s^22p^6$ electrons of Mg). They obtained R_e = 5.1 Å and $D_e = 4.76$ cm^{-1}. At 5.0 Å, the interaction energy of ref 141 amounted to −4.65 cm^{-1}. This result, which should be compared to our CCSD(T)/AE value since the $1s^2$ effects should be negligible, is indeed nearly identical to the interaction energy of −4.63 cm^{-1} in the aQZ+(33221) basis. The 0.02 cm^{-1} difference is expected from basis set differences. However, due to the lack of CBS extrapolations and due to the neglect of post-CCSD(T) effects, the potential of Partridge et al.[141] is significantly too shallow.

Convergence of the SAPT and Møller-Plesset expansions for the He−Mg dimer in the aQZ+(33221), a5Z+(33221), and aCVQZ+(33221) basis sets is presented in Table 9. The error of the CCSD(T) approach is 7%, significantly smaller than for all other systems investigated here but still much larger than in the case of interactions of typical closed-shell systems. Thus, the mixed systems, containing only one quasidegenerate monomer, represent an intermediate case of the convergence properties of CC/PT expansions. The MP series also represents an intermediate case. The MP2 (MP4) CBS-extrapolated result of −4.23 (−5.69) cm^{-1} recovers 83% (114%) of the interaction energy. As for Mg_2, the performance of MP3 is excellent, and as for all systems, CCSD gives a very poor approximation to the interaction energy. The scaled and extrapolated SAPT result (note that the scaling here involves only the use of eq 9 as the terms beyond S^2 are completely negligible) amounting to −5.15 cm^{-1} is in an excellent agreement with the best estimate of the interaction energy, the error being only 1%. This is not a fortuitous agreement, as SAPT always performs very well for systems with very small interaction energies. The hybrid SAPT energies $E^{[2]}_{SAPT+HF}$ are by far less accurate, providing a strong support for inappropriateness of the hybrid approach for nonpolar systems.[23]

The components of the He−Mg interaction energy displayed in Figure 1 (note that the energy scale in Figure 1 is different for He−Mg than for all of the remaining dimers) show a system completely dominated by the sum of the dispersion and exchange-dispersion energies. This sum is even larger in magnitude than the first-order exchange energy. The remaining components are nearly negligible. Thus, He−Mg has a qualitatively different physical decomposition of the interaction energy than the other dimers considered here.

The SAPT(DFT) method performs relatively poorly for He−Mg, recovering only 73% of the interaction energy. This results again from the error coming from the first-order exchange energy which is larger by 1.77 cm^{-1} than the SAPT $E^{(1)}_{exch}$ (CCSD) value (note that for all other systems $E^{(1)}_{exch}$ (KS) is smaller than $E^{(1)}_{exch}$ (CCSD)). In contrast, the dispersion energies are very close, in line with the C_6 coefficients which are to within 4% of one another and both agree well with the literature values from ref 79.

IV. Conclusions

We have computed the interaction energies at the minima of the potentials for the Be_2, Mg_2, Ca_2, Zn_2, and He−Mg dimers. Very large basis sets including diffuse and bond functions have been used. In all cases but Zn_2, all possible electron excitations have been accounted for within the frozen-core approximation by using the FCI method. This approach provided what we believe to be the best estimates to date of the depths at the minima for the investigated systems. The summary of our results is given in Table 11. Our values were estimated to be accurate to within 1.6%, 1.8%, 4.3%, and 2.3% for Be_2, Mg_2, Ca_2, and He−Mg, respectively. For Zn_2, we can only reliably estimate the uncertainty with respect to the CBS limit of the CCSDT interaction energy, and this uncertainty amounts to 3.4%, however, unknown post-CCSDT effects can contribute additional several percent. For Be_2, our predictions agree closely with the previous large-scale calculations from refs 48 and 50, and only slightly worse with the work of ref 49. However, all of these results are far from the experimental value of ref 58. This agreement among the theoretical predictions indicates that for Be_2 theory is currently more reliable than experiment. For Mg_2, our predictions agree very well both with the calculations of ref 85 and the experimental value from refs 87 and 89. For Ca_2, our calculations provide the first accurate theoretical value of D_e and agree reasonably well with the experimental value from refs 98 and 81. We show that the previous calculations[5] that very closely agreed with experiment relied on significant cancellations of errors. For Zn_2, our result agrees very well with the calculations of ref 103 but differs by 44 cm^{-1} or 16% from experiment.[106] For He−Mg, our potential depth is somewhat more accurate than that obtained in ref 114, but the two sets of results are consistent. There are no experimental values known for this system.

We have analyzed the performance of the CC/PT methods as a function of the atomic number. The expectations that the CC/PT convergence problems diminish with the increase of the atomic number were confirmed, but the improvements are relatively small and for all dimetallic dimers the problems are severe. In particular, any calculations for such systems aiming at a few percent or better accuracy have to include at least the effects of up to quadruple excitations of valence electrons. In fact, the only reason that accurate ab initio calculations are possible for these systems is that the frozen-core effects are apparently relatively small beyond the CCSD(T) level of theory. We were able to show that these effects are very small for Be_2. For larger systems, no calculations of these effects are possible, but comparisons with accurate experiments indicate no more than a few percent contributions to potential depths. If only the CCSD(T) method is used, the errors of the predicted depths range from 16% to 25% for dimetallic dimers. These are very large errors compared to only a few percent errors given by CCSD(T) for interactions of typical closed-shell molecules. The CCSD method performs extremely poorly for all systems. The MP*n* expansion converges very erratically and sometimes the errors are of the order of 100% even at the MP4 level. The mixed dimer, He−Mg, is an intermediate case, with CCSD(T) predicting the interaction energy with 7% error.

The performance of standard SAPT on Ae_2 dimers is poor. We have traced the problem to the neglected exchange terms proportional to powers of the overlap integrals higher than S^2. For Ae_2 dimers, the dispersion interaction is much larger than for typical closed-shell systems of similar size due to the very large atomic polarizabilities, see the discussion below. The large attractive dispersion force leads to significantly decreased equilibrium distances and therefore to larger than normal values of the overlap integrals. After the effects beyond S^2 are approximately accounted for, SAPT through the second order in V gives reasonable approximations to the interaction energies, with errors of about the same magnitude as the errors of the CCSD(T) method (the scaled-SAPT errors are smaller than those of CCSD(T) for Be_2, Mg_2, and He−Mg and larger for the remaining systems). The inclusion of the third-order level of theory makes the predictions worse, showing the divergence of the perturbation series. Also the inclusion of the $\delta E^{\mathrm{HF}}_{\mathrm{int,resp}}$ term worsens the predictions in most cases.

One might have hoped that the SAPT(DFT) approach will be more successful than SAPT in the description of the Ae dimers. After all, the DFT method with periodic boundary conditions is extensively used to describe metallic solids and DFT cohesion energies for Mg, Ca, and Zn crystals are accurate to within about 10% (see, e.g., refs 142−144). However, this is not the case. Although for Be_2 SAPT(DFT) provides a slightly better approximation to the interaction energy than SAPT does, for other systems SAPT(DFT) performs significantly worse than SAPT. We have checked that this is not related to the exchange-correlation potential used by us. In particular, potentials often used in periodic boundary condition calculations for metals such as BPW91[145,146] give similar results. The problems of SAPT(DFT) appear to originate mainly from the first-order exchange energy. On the other hand, the electrostatic, induction, and dispersion corrections are very similar in SAPT(DFT) and SAPT approaches. The CKS approach consistent with SAPT(DFT) also gives in most cases more accurate values of the polarizabilities and C_6 dispersion constants than those given by wave function calculations at the level consistent with SAPT. The former values compare also well with CKS calculations by Chu and Dalgarno.[72]

The dependence of the observed convergence patterns on the atomic number can be understood in simple terms by considering the competition between the polarizabilities of atoms and atomic size. In all cases, the main force pulling the atoms together comes from the dispersion interaction. Although the negative induction energies are also quite large in magnitude, they are very significantly quenched by their exchange counterparts. The dispersion interaction is very large since the metallic atoms have large polarizabilities. This, in turn, results to a large extent from the quasidegeneracy. The main force opposing the dispersion pull is the valence repulsion of the electrons. This repulsion is related to the extent of the electron density, which increases with the atomic number in the series Be−Mg−Ca. Since the quasidegeneracy also increases in this series (as determined by the *ns*−*np* gaps, the contribution of the leading FCI determinant gives the order Mg−Ca−Be, see Table 4), the two effects act in the opposite direction. The size of the atom slightly prevails, and therefore the convergence of the CC/PT expansions improves with the atomic number. The same arguments also explain the behavior of D_e which increases in the series He−Mg, Zn_2, Mg_2, Be_2, Ca_2.

The Zn_2 dimer shows relations distinctly different from the Ae_2 dimers. Although zinc's atomic radius, *ns*−*np* gap, and polarizability are very close to the corresponding quantities for beryllium, the interaction energy is more than three times smaller in magnitude for Zn_2 than for Be_2. Whereas the CCSD(T) method gives a similar error for Zn_2 (relative to the experimental D_e) as for the Ae_2 dimers, the convergence of the MP*n* series is arguably the worst for Zn_2. On the other hand, the physical contributions to the interaction energy given by SAPT are relatively small in magnitude, in a strong contrast to Be_2 where the final interaction energy results from large cancellations between physical components of opposite sign. Clearly, it is the presence of the 3*d* electrons which makes Zn_2 behave differently from the other systems.

Although for all systems the uncertainties of our predictions are only a few percent (except for Zn_2 if one compares to experiment), more accurate calculations would still be valuable for many purposes. Only for He−Mg is the current accuracy probably sufficient. Since we have used the largest available orbital basis sets in most cases, a further decrease of the error resulting from basis set incompleteness would require optimizations of new basis sets. Alternatively, one could use explicitly correlated basis sets, such as Gaussian-type geminals,[147−150] up to the CCSD level. However, the main current source of uncertainty is not basis set effects but the frozen-core approximation in calculations of post-CCSD(T) contributions, and it will be extremely difficult to avoid this approximation.

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Supporting Information Available: More detailed tables showing the convergence of SAPT components for all studied dimers. This material is available free of charge via the Internet at http://pubs.acs.org.

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