Møller–Plesset perturbation theory for van der Waals complexes bound by electron correlation effects: Ground states of the Ar and Mg dimers

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We demonstrate that MPPT through fourth order is suitable for studying van der Waals correlation-bound complexes provided that (a) accurate calculations are carried at the SCF level; (b) efficient basis sets for intersystem correlation effects (i.e., dispersion) are used; and (c) the full counterpoise (CP) method is applied to correct for basis set superposition error (BSSE). Interaction potentials are obtained for Ar_2 and Mg_2 with extended basis sets that contained up through the f-symmetry functions. For Ar_2 the potential is characterized by $R_e \approx 7.3\,a_0$ and $D_e \approx 0.34$ mhartree and for Mg_2 by $R_e \approx 7.4 a_0$ and $D_e \approx 2.1$ mhartree. The discrepancies between our potentials and the most accurate semiempirical and experimental results (Ar_2:$R_e \approx 7.1 a_0$, $D_e \approx 0.45$ mhartree; Mg_2:$R_e \approx 7.35 a_0$, $D_e \approx 1.93$ mhartree, are analyzed in detail and attributed to the lack of higher than f-symmetry functions, as well as, in the Mg_2 case, to the approximate nature of the MP4 approach.

I. INTRODUCTION

van der Waals complexes for which the dominant attractive force is due to intersystem electron correlation effects are particularly interesting to both the theorist and experimentalist. These correlation-bound complexes are not bound (or insignificantly bound) at the self-consistent field (SCF) level and often only weakly bound at the correlated level. Such systems include complexes of closed shell atoms (e.g., Ar_2, $Mg \cdot Ar$, Mg_2), complexes of closed shell atoms with molecules (e.g., $Ar \cdot H_2$, $Ar \cdot Cl_2$, $Hg \cdot H_2$, $Ar \cdot HCl$), and even complexes of molecules that have small higher multipole moments [e.g., $(H_2)_2$, $(Cl_2)_2$]. Over the last few years, a number of spectroscopic and reactive studies have been carried out on such systems yielding challenges to both the electronic structurist (e.g., the determination of accurate interaction potentials) and the chemical dynamicist (e.g., correlation of experimental results with theoretical trajectory studies).

Not surprisingly, the determination of accurate interaction potentials for these correlation-bound species is extremely difficult within the approximate formulations of quantum mechanics that are available today. This is because the determination of electron correlation is still nontrivial and involves both methodological (e.g., the truncation of multiple orbital excitations) and numerical (e.g., the use of an incomplete basis set) approximations. Thus, the percentage errors in the electron correlation energy (with respect to the total electron correlation energy) are rarely small. Moreover, the relative errors in the van der Waals interaction energy are even larger since the interaction energy is composed of the attractive correlation contributions and the repulsive SCF contributions. The matter is further complicated if one chooses the supermolecular approach for determination of the interaction energies because of the following

three points:

(1) The correlation method needs to be size consistent.

(2) The numerical calculations should be "basis set consistent," i.e., one must deal with the basis set superposition error (BSSE).

(3) The basis set should be versatile enough to reproduce efficiently physically different contributions to the interaction energy.

Among the many post-HF theories, Møller–Plesset perturbation theory (MPPT)[1] seems to be particularly attractive since it is straightforward to apply without introducing arbitrary choices or approximations, and it is efficient and often accurate (if applied through the fourth order) as has been demonstrated in many problems of chemical interest. From the perspective of intermolecular interactions it has further importance in that it is size consistent and may be related to the perturbation theory of intermolecular forces.[2]

Recently, extensive calculations using MPPT were carried out for several correlation-bound van der Waals complexes. Preliminary studies of rare gas complexes were published by Wilson et al. (He_2 and He_3,[3] and Ar_2[4]) and alkaline earth metal dimers were treated by Diercksen et al. (Be_2[5] and Mg_2[6]). Effects of basis set superposition errors[7] on the interaction energy in He_2 have recently been examined by Gutowski et al.[8,9]

With the above points in mind, we decided to use the following strategy for supermolecular calculations of correlation-bound complexes within the MPPT method. Rather than focusing on the reduction of BSSE at the correlated level by adding orbitals which saturate the electron correlation of the whole dimer, one should give priority to the orbitals which describe the *intersystem* electron correlation adequately. Such an approach will lead to an inadequate description of the intraatomic electron correlation effects. These effects, although not negligible, are of secondary importance. Their poorer representation will have three consequences:

(a) The supermolecular calculations may suffer from

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nonnegligible values of BSSE at the correlated level. How-
ever, the CP method has been shown to be a satisfactory
remedy for the problem[8–10] and the results of this paper
strongly support this conclusion.

(b) The intrasystem correlation correction to the
Heitler–London interaction energy (to the Coulomb inter-
action and exchange repulsion) may be poorly reproduced.
However, for those correlation-bound systems in which this
effect was studied, it was not large (on the order of 10% of
the interaction energy for the He_2,[11] Ne_2,[12,13] Be_2,[14] $(H_2)_2$,[15]
and HeH_2[16]).

(c) The intra–intersystem electron correlation coupling
may be poorly accounted for. However, studies of the van
der Waals coefficients at the coupled Hartree–Fock (CHF)
level[17] and calculations in the region of the van der Waals
minimum at both the uncoupled Hartree–Fock
(UCHF)[18,19] and the CHF level[20] proved that one can ob-
tain reliable approximate dispersion energies with even com-
plete neglect of this coupling. Since, for large intersystem
separations, the MP2 correlation energy is related to the
UCHF dispersion,[2,21] and since the third-order MPPT cor-
rection contains the most important CHF contributions to
the dispersion,[2] a less refined treatment of intra–intersystem
electron correlation coupling effects appears reasonable.

The purpose of this paper is to demonstrate the useful-
ness of the above strategy using MPPT for two physically
different correlation-bound van der Waals dimers, Ar_2 and
Mg_2. For these systems a plethora of theoretical and experi-
mental data is available and the potential energy curves are
accurately known. Calculations through fourth-order
MPPT, including up through quadruple orbital excitations
relative to the reference HF determinant (using the
GAUSSIAN 82 codes[22]), were carried out with large basis sets
designed along the above lines.

It should be stressed that the above strategy will not
necessarily give highly accurate (i.e., 1%–2% error) inter-
action potentials, but should result in approximate poten-
tials which will be useful for those systems where little or no
experimental data is available, e.g., ground states of very
weakly bound alkaline earth–rare gas and alkaline earth–
hydrogen molecule complexes. Recently, the first reliable
potential energy curves for the ground states of MgHe,[23]
MgAr,[23] and Zn_2[24] were calculated in our laboratory. Such
potentials should be sufficiently accurate for use in Franck–
Condon-type calculations as well as in providing initial start-
ing points and energies for theoretical trajectory studies.

II. METHOD

The method used in the calculations presented in this
paper is the complete fourth-order MPPT, implemented in
the GAUSSIAN 82 code.[22] All contributions to the total energy
through fourth order in the electron correlation perturba-
tion [i.e., those due to single (S), double (D), triple (T),
and quadruple (Q) substitutions in the reference HF deter-
minant] are included.

The interaction energy of the ith order of MPPT is de-
fined as follows:

$$\Delta E^{(i)} = E_{AB}^{(i)} - E_A^{(i)} - E_B^{(i)} \tag{1}$$

where $E_{AB}^{(i)}$, $E_A^{(i)}$, and $E_B^{(i)}$ are the ith-order MPPT energies
of AB, A, and B, respectively. The interaction energy
through the ith order may be defined in like fashion:

$$\Delta E(i) = E_{AB}(i) - E_A(i) - E_B(i), \tag{2}$$

where $E_{AB}(i)$, $E_A(i)$, and $E_B(i)$ are the sums of the MPPT
energies through the ith order of AB, A, and B, respectively.
Note that the HF interaction energy is given in terms of the
zeroth- and first-order energies as

$$\Delta E^{SCF} = \Delta E(0) + \Delta E(1). \tag{3}$$

Also of interest is the so-called "zeroth-order" iteration re-
sult of the SCF procedure, referred to as ΔE^{HL}, the Heitler–
London interaction energy. The difference between ΔE^{HL}
and ΔE^{SCF} reflect mutual deformation of A and B allowed
for in the process of SCF iterations. It is also convenient to
define the total correlation energy through the fourth order
as

$$\Delta E^{corr}(4) = \sum_{k=2}^{4} \Delta E^{(i)}. \tag{4}$$

When the energies of A, B, and AB are calculated with finite
basis sets (χ_A, χ_B, and $\chi_A \cup \chi_B$, respectively) the use of Eqs.
(1) and (2) involves BSSE problems. To circumvent this
apparent basis set inconsistency we use the CP method of
Boys and Bernardi.[7] The CP method consists in the calcula-
tion of the energies of AB, A, and B in the same $\chi_A \cup \chi_B$ basis.
The BSSE in the ith order of MPPT is then defined as

$$\delta_A^{(i)} = E_A^{(i)}(\chi_A \cup \chi_B) - E_A^{(i)}(\chi_A) \tag{5}$$

and similarly for B. The total BSSE is

$$\delta = \delta_A + \delta_B \tag{6}$$

and we will also use the symbols δ^{SCF} and $\delta^{corr}(4)$ to denote δ
at the SCF level and its correlation part through the fourth
order, respectively. Since the pioneering work of Boys and
Bernardi, a large body of evidence has been collected to sup-
port the usefulness of the CP method (cf. the recent review
by van Lenthe et al.[25]). As to whether the CP method over-
corrects the actual BSSE, a number of both theoretical and
numerical arguments have been recently presented by Gu-
towski et al.[8,10] (see also Ref. 26) which support the original
CP approach of Boys and Bernardi over any alternatives yet
put forth. In the present work, this original version of the CP
method is used to handle BSSE difficulties. It is important to
stress that the CP method ensures only the basis set consis-
tent evaluation of Eq. (1) and removes the monomer-ener-
gies contamination of the interaction energy. The interac-
tion energy, however, is still affected by the basis set
extension which is sometimes referred to as the "higher-or-
der BSSE".[27]

III. BASIS SETS

A. General procedure

The calculation of accurate SCF interaction energies
and the reduction of the BSSE to a negligible value proved to
be possible for fairly large correlation-bound systems such as
Ne_2,[28,29] Ar_2,[4,30] Mg_2,[6] and even Zn_2.[24] Such calculations
were carried out using large fully optimized (often even-[31]
or well-tempered[32]) basis sets for the monomers. At the

TABLE I. Basis sets used in this study.

(A) The [7s4p2d 1f] basis set for the Ar atom. Exponents in a_0^{-2}.

Symmetry	orb. exponent	Expansion coefficients						
s^a	118 022.38	0.000 308 0						
	17 683.541	0.002 387 0						
	4 027.765 7	0.012 333 0						
	1 145.397 7		0.049 026 9	− 0.014 344 0				
	377.163 75		0.151 054 8	− 0.046 784 0	0.014 769 0			
	138.159 69		0.331 193 7	− 0.118 758 0	0.037 896 0			
	54.989 117		0.409 223 6	− 0.202 143 9		0.067 261 0		
	23.170 667		0.182 027 8	− 0.134 315 0		0.046 006 0		
	11.059 1		0.010 377 0	0.225 090 9		− 0.083 684 9		
	5.035 36			0.582 561 8		− 0.313 470 8		
	2.368 27			0.349 441 9		− 0.302 828 8		
	0.890 804					0.355 303 7	1.0	
	0.387 814					0.666 001 5		
	0.160 070					0.234 139 8		1.0
p^a	663.620 100	0.003 001 0	− 0.000 843 0					
	157.092 810	0.023 566 0	− 0.006 630 0					
	50.231 100	0.105 540 0	− 0.030 625 0					
	18.635 345	0.285 424 1	− 0.085 157 0					
	7.446 537	0.444 159 1	− 0.143 039 0					
	3.095 698	0.300 217 1	− 0.077 095 0					
	1.269 36	0.041 578 0	0.239 106 0					
	0.544 668	0.001 806 0	0.453 961 0					
	0.235 181			1.0				
	0.099 494				1.0			
d	0.84	1.0						
	0.74		1.0					
f	0.28	1.0						

(B) The [7s4p2d 1f] basis set for the Mg atom. Exponents in a_0^{-2}.

Symmetry	orb. exponent	Expansion coefficients						
s^b	392 037.18	− 0.238 022 04E-04						
	62 898.863	− 0.174 203 77E-03						
	14 238.305	− 0.944 559 91E-03						
	3 965.504 8	− 0.406 023 07E-02		− 0.102 752 05E-02 [c]				
	1 264.041 5	− 0.152 163 30E-01		− 0.389 677 7E-02				
	433.019 31		− 0.521 831 01E-01	− 0.135 834 24E-01	0.262 686 45E-02 [c]			
	155.731 37		− 0.151 989 12	− 0.420 331 42E-01	0.813 275 33E-02			
	58.934 046		− 0.330 171 45	− 0.103 885 02	0.203 737 40E-01			
	23.394 191		− 0.413 215 02	− 0.182 272 73	0.363 684 28E-01			
	9.529 975 0		− 0.176 325 15	− 0.109 481 10	0.232 074 80E-01			
	3.920 859 3			0.268 396 63	− 0.623 001 62E-01			
	1.632 531 6			0.577 182 44	− 0.155 731 80			
	0.692 043 06			0.308 569 02	− 0.210 314 29			
	0.271 010 61				0.569 360 10E-01	1.0		
	0.990 920 06E-01				0.641 600 37		1.0	
	0.372 514 48E-01							1.0
p^b	433.019 31	− 0.952 403 41E-03						
	155.731 37	− 0.376 105 24E-02						
	58.934 046	− 0.179 716 22E-01						
	23.394 191	− 0.639 390 86E-01						
	9.529 975 0	− 0.181 608 42						
	3.920 859 3	− 0.337 859 96						
	1.632 531 6	− 0.384 079 43						
	0.692 043 06	− 0.218 669 28						
	0.271 010 61		1.0					
	0.125 9			1.0				
	0.056 91				1.0			
d	0.26	1.0						
	0.086		1.0					
f	0.14							

[a] Exponents and contraction coefficients from Rozendaal (Ref. 33), see Ref. 30.
[b] Exponents and contraction coefficients from Huzinaga et al. (Ref. 32).
[c] Only the modification of the [7s4p2d 1f] basis, denoted as [7s4p2d 1f][1], contained these GTOs.

post-HF levels it is very desirable to start with the best SCF wave function possible. Fortunately, the correlation-bound complexes are very weakly bound and the mutual deformation of the interacting species is small. One can then start with the occupied orbitals of the individual atoms in the form of single contractions and add orbitals which are necessary to describe the deformation and intersystem correlation effects. This approach reduces considerably the number of basis orbitals without compromising much on the accuracy. It was applied below to form basis sets for both Ar and Mg.

B. Ar atom basis set

The largest basis set used for Ar was [$14s10p2d\ 1f/$ $7s4p2d\ 1f$], which is referred to below as [$7s4p2d\ 1f$]. It was obtained from the energy optimized [$14s10p$] basis of Rosendaal[33] which was used in the calculation of accurate SCF interaction energies and was characterized by small BSSE. The exponents and contraction coefficients were obtained from Ref. 30 and our contractions are listed in Table I(A). Our SCF and consecutive MPPT energies for Ar are listed in Table IV.

In the first stage of this work, we were limited by GAUSSIAN 82 to contractions of eight orbitals or fewer. The larger contractions were used to describe the occupied space of the Ar atom using the fewest orbitals possible without losing much of the accuracy in the SCF monomer energy. The restriction to contraction length of eight orbitals was found to be a tight constraint and our contraction scheme reflects this fact. To allow for deformation of the Ar orbitals in the dimer calculations, we left the two most diffuse s and two most diffuse p orbitals uncontracted.

Our higher polarization functions were chosen to be appropriate for the dispersion interaction. The exponents for the two sets of d orbitals were taken from Andzelm *et al.*,[19] who showed their effectiveness in reproducing both the C_6 van der Waals coefficients and the nonexpanded dispersion energies in the van der Waals minimum region.

Our f exponent was optimized at $R = 7.5\ a_0$ by minimizing $\Delta E^{(2)}$. Since for Ar$_2$, $\Delta E^{(2)}$ is dominated by the dispersion term, one may consider this exponent as dispersion optimized.

C. Mg atom basis set

The largest basis set used for Mg was [$16s11p2d\ 1f/$ $7s4p2d\ 1f$], which is referred to below as [$7s4p2d\ 1f$]. The s- and p-symmetry orbitals were obtained from the well-tempered [$16s9p$] set of Huzinaga *et al.*[32] The exponents and contractions coefficients are listed in Table I(B), along with the details of the diffuse s-, p-, d-, and f-symmetry functions which were added. Our SCF and the consecutive MPPT energies for Mg may be found in Table IX.

Due to the high polarizability of the electron charge cloud of Mg, the diffuse and polarization part of the basis set had to be more flexible than for Ar. To accomplish this we left the three most diffuse s and the most diffuse p function of the Huzinaga *et al.* [$16s9p$] set[32] uncontracted. The p-set was further augmented with two additional diffuse orbitals roughly 2.2 and 2.2^2 times smaller than the most diffuse p

function of Huzinaga. The exponents for the two sets of d orbitals were taken from Diercksen *et al.*,[6] as was the exponent of the f orbital. We used an f exponent of 0.14 which gave the best interaction energy, after correcting the Diercksen *et al.* results for BSSE. Adding their second f function with an exponent of 1.4 did not change the CP-corrected interaction energy (-0.001 mhartree). It is worthwhile to note that, like the Be$_2$ case,[14] and unlike the rare gas dimers, we found the optimal exponents of the polarization functions in the region of the potential minimum to differ appreciably from those obtained at large R.

IV. NUMERICAL RESULTS AND DISCUSSION

A. The Ar$_2$ dimer

1. The SCF level

The SCF interaction energies along with the related values of BSSE we obtained for Ar$_2$ using the [$7s4p2d\ 1f$] basis are listed in Table II. Also listed are the SCF interaction energies of Chałasinski *et al.*[30] Our results, when corrected for the BSSE, agree very well with those of Ref. 30. BSSE is mainly due to our contractions (cf. Table I) which focused on the valence shell and described the core less precisely. This deficiency is reflected by the deterioration of the atomic energy as opposed to the result from Ref. 30 which was obtained without contraction (cf. Table II). Nevertheless, $\Delta E^{\rm SCF}$ is quite good because it is mainly determined by the valence–shell interaction. It should be noted that $\Delta E^{\rm SCF}$ is relatively insensitive to various polarization functions because $\Delta E^{\rm SCF}$ can be approximated quite well by the Heitler–London interaction energy, indicating that mutual deformation effects are small (cf. Table II). At 7.5 a_0, the results of Ref. 30 and our present results agree very well with probably the most accurate value for Ar$_2$, that of Wells and Wilson,[4] 0.197 mhartree. At the same time, the CP-uncorrected results are rather poor.

Recently Hay *et al.*[34] published CP-uncorrected results using an [$8s5p2d$] basis for Ar$_2$ (see Table II). It is seen that their interaction energy vanishes much too quickly and that a spurious minimum appears at $R = 9\ a_0$. Spurious minima on the CP-uncorrected SCF potential curves of rare gas dimers may occur even for large (by common standards) bases as has been shown for Ne$_2$.[35]

2. Interaction energy at the post-HF level. Comparison with semiempirical results.

Interaction energies obtained through the fourth order of MPPT with the [$7s4p2d\ 1f$] basis for Ar$_2$ are listed in Table III. Also listed is the accurate semiempirical potential of Tang and Toennies (TT).[13] One can see that the $\Delta E(4)$ result reproduces $\sim 70\%$–75% of the TT interaction energy in the region of the van der Waals minimum. Our equilibrium distance is 7.3 a_0, compared with 7.1 a_0 for the TT potential. In this and subsequent sections, we show that the accuracy of our results may be fully rationalized by the analysis of our basis and analysis of the MPPT method. It is important to stress that the CP-uncorrected results would give $|\Delta E(4)|$ twice as large as the TT interaction energy in the van der Waals minimum region—a result which is impossible to ra-

TABLE II. SCF interaction energy between two Ar atoms. The SCF atomic energies are also given for the basis sets used in the dimer calculations. The HF limit energy for the Ar atom is -526.8175 hartree (Ref. 47). Interaction energies and δ in mhartree, atomic energies in hartree, distance in a_0.

R	ΔE^{HL} [a]	ΔE^{SCF} [a]	ΔE^{SCF} [b]	δ^{SCF}	ΔE^{SCF} [c]
5.5	...	...	9.000	− 0.716	...
6.0	3.830	3.569	3.529	− 0.407	3.301
7.0	0.554	0.529	0.521	− 0.095	0.427
7.1	...	...	0.429	− 0.080	...
7.3	...	...	0.291	− 0.056	...
7.5	0.207	0.200	0.197	− 0.039	0.116
8.0	0.076 8	0.074 7	0.073 6	− 0.014	0.009
9.0	0.010 3	0.010 3	0.010 1	− 0.001 7	− 0.019
E^{SCF}_{Ar}	526.810 506 31[a]		526.783 783 931[b]		526.744 517[c]
			526.817 5[d]		

[a] The results of Chalasinski et al. (Ref. 30).
[b] Present calculations, basis [$7s4p2d\ 1f$].
[c] Hay et al. (Ref. 34).
[d] Reference 47.

tionalize unless attributed to BSSE. It is worthwhile to mention here that a significant lowering of the interaction energy curve due to BSSE may lead to apparently good interaction energies when using rather limited bases. In our opinion this happened to Hay et al.[34] (cf. Table III), whose results are in fairly good agreement with the TT potential, despite using a far from adequate [$8s5p2d$] basis set.

a. Comparison with ab initio results. In order to analyze our results, Table IV lists the values of $\Delta E(4)$ and its components obtained at 7.5 a_0 with our best basis [$7s4p2d\ 1f$] as well as for our smaller basis, obtained by leaving out the f orbital, [$7s4p2d$]. For the sake of comparison, the almost BSSE-free results of Wells and Wilson ([$12s10p4d\ 1f$]) are also given along with the results obtained with our [$7s4p2d\ 1f$]′ basis (it differs from our [$7s4p2d\ 1f$] by replacing our f exponent by that of Wells and Wilson, 0.928 4116, which was optimized for the monomer electron correlation energy).

One can see that our CP-corrected $\Delta E^{(2)}$ values obtained with the [$7s4p2d\ 1f$]′ basis differ by less than 5% from those obtained by Wells and Wilson although in our case BSSE is half as large as the value of $\Delta E^{(2)}$. At the MP3 level the agreement between our result and that of Wells and Wilson is even better, the difference being ~2%. This confirms the fact

that the full CP method removes BSSE effectively, since the details of our basis and the Wells and Wilson basis were different (with the exception of the f orbital).

If one compares the values of $\Delta E^{(2)}$ and $\Delta E(4)$ obtained with the [$7s4p2d\ 1f$] basis to those obtained with the [$7s4p2d$] basis, one sees that the one f orbital of Wells and Wilson was, as expected, not much of an improvement relative to the basis set without the f orbital. However, if one uses the f orbital with the dispersion-oriented exponent then one obtains a significant improvement over the basis without the f orbital.

It should be noted that all of the results were obtained within the frozen-core approximation. We believe this to be satisfactory since (1) the valence–valence interaction was shown to be dominant for Ar$_2$ at the SCF level by Chałasinski et al.,[30] and (2) the valence–valence dispersion interaction was shown to be the dominant correlation effect for Ne$_2$[36] and Ar$_2$.[19] To further check this assumption, calculations including core-virtual excitations were carried out with the [$7s4p2d$] basis (cf. Table IV). The results at every level of the MPPT method differ insignificantly from those which maintain the frozen core. At the same time, the BSSE increased at the MP2 and MP4 levels by a factor of almost 2. This is not surprising since our basis is not good for the intra-

TABLE III. The total MP4 interaction energies and the contributions from different orders of MPPT for Ar$_2$. Energies in mhartree, distance in a_0.

R	ΔE^{SCF}	$\Delta E^{(2)}$	$\Delta E^{(3)}$	$\Delta E^{(4)}$	$\Delta E^{corr}(4)$	δ^{corr}	$\Delta E(4)$	$\Delta E(4)$ [a]	TT [b]
5.5	9.000	− 3.1141	0.5595	− 0.2741	− 2.829	− 2.0708	6.1713	...	5.005
6.0	3.5293	− 2.0204	0.3270	− 0.1930	− 1.886	− 1.4284	1.6429	1.479	0.978
7.0	0.5210	− 0.8509	0.1286	− 0.0932	− 0.815	− 0.5814	− 0.2942	− 0.377	− 0.4485
7.1	0.4291	− 0.7813	0.1181	− 0.0862	− 0.749	− 0.5274	− 0.3203	...	− 0.4530
7.3	0.2908	− 0.6591	0.1003	− 0.0741	− 0.633	− 0.4369	− 0.3421	...	− 0.4416
7.5	0.1966	− 0.5572	0.0857	− 0.0637	− 0.536	− 0.3547	− 0.3386	− 0.425	− 0.4137
8.0	0.0736	− 0.3697	0.0589	− 0.0435	− 0.354	− 0.2058	− 0.2807	− 0.362	− 0.3209
9.0	0.0101	− 0.1716	0.0297	− 0.0207	− 0.163	− 0.0630	− 0.1526	...	− 0.1683
12.0	0.0000	− 0.0269	0.0053	− 0.0032	− 0.0248	− 0.0004	− 0.0247	...	− 0.0271

[a] Hay et al. (Ref. 34).
[b] Tang and Toennies potential (Ref. 13) ($A = 385.08$, $b = 1.917$, $C_6 = 67.2$, $C_8 = 1610$, $C_{10} = 42\ 700$, $n_{max} = 18$).

TABLE IV. The components of the interaction energy for various basis sets for the Ar dimer in the region of the van der Waals minimum, $R = 7.5\ a_0$. Interaction energies in mhartree, atomic energies in hartree.

	[7s4p2d] frozen core	[7s4p2d] all-electron calculation	[7s4p2d 1f] frozen core	[7s4p2d 1f]' frozen core	[12s10p4d 1f][a]
ΔE^{SCF}	+ 0.196 9	+ 0.196 9	+ 0.196 6	+ 0.196 5	+ 0.197
δ^{SCF}	− 0.032 6	− 0.032 6	− 0.038 8	− 0.032 6	− 0.018
$\Delta E^{(2)}$	− 0.448 0	− 0.450 0	− 0.557 2	− 0.470 9	− 0.482
$\delta^{(2)}$	− 0.222 1	− 0.392 6	− 0.336 8	− 0.228 6	− 0.015
$\Delta E^{(3)}$	+ 0.085 4	+ 0.087 6	+ 0.085 7	+ 0.086 4	+ 0.108
$\delta^{(3)}$	− 0.004 4	− 0.001 2	− 0.014 8	− 0.004 4	− 0.001
$\Delta E^{(4)}$	− 0.039 4	− 0.042 4	− 0.063 7	− 0.042 2	⋯
$\delta^{(4)}$	− 0.002 4	− 0.000 9	− 0.003 1	− 0.002 4	⋯
DQ	+ 0.012 6	+ 0.011 8	+ 0.018 2	+ 0.018 6	⋯
δ^{DQ}	+ 0.006 3	+ 0.006 2	+ 0.008 0	+ 0.006 5	⋯
SDQ	+ 0.003 4	+ 0.001 4	+ 0.003 1	+ 0.013 6	⋯
δ^{SDQ}	+ 0.008 3	+ 0.007 3	+ 0.011 3	+ 0.008 3	⋯
$\Delta E^{corr}(4)$	− 0.402 0	− 0.404 7	− 0.535 2	− 0.426 7	⋯
$\delta^{corr}(4)$	− 0.228 9	− 0.394 8	− 0.354 7	− 0.235 4	⋯
E^{SCF}	− 526.783 783 931	− 526.783 783 931	− 526.783 783 931	− 526.783 783 931	− 526.816 266
$E^{(2)}$	− 0.159 450 92	− 0.182 235 82	− 0.165 429 70	− 0.191 377 20	− 0.211 385
$E^{(3)}$	− 0.012 946 208	− 0.011 987 296	− 0.013 944 025	− 0.017 644 265	− 0.018 752
$E^{(4)}$	− 0.001 818 7622	− 0.002 098 829 6	− 0.002 626 614 1	− 0.004 586 337 3	⋯

[a] Wells and Wilson (Ref. 4).

atomic electron correlation effects [our basis is similar to the "dispersion-oriented" (DS) bases for He$_2$ studied in Ref. 8 and shown there to yield large values of BSSE, but reliable results after CP correction].

3. Analysis of individual $\Delta E^{(i)}$ components at large separations

Table V allows us to analyze the role of the individual $\Delta E^{(i)}$ terms for large R (12 a_0 and 15 a_0). At large R, the interaction between two Ar atoms is governed by the dipole–dipole dispersion which is expected to be determined, analogously to Ne$_2$,[36] by the dispersion interaction of the valence orbitals of the Ar atoms, primarily by the $3p$–$3p$ interaction.

To reproduce the UCHF or CHF dipole–dipole dispersion contribution arising from the $3s$ occupied orbitals requires excitations to p-symmetry orbitals; contribution from $3p$ occupied orbitals requires excitations to s- and d-symmetry orbitals.[36] Since $\Delta E^{(2)}$ asymptotically converges to the UCHF dispersion[2,21] and $\Delta E^{(3)}$ provides the terms which can be related to the CHF dispersion,[2] our [7s4p2d] basis is adequate for reproduction of the dipole–dipole dispersion. To extract the related $C_6^{(i)}$ van der Waals coefficients, the values of $\Delta E^{(i)}$ multiplied by R^6 are listed in Table V. It should be noted that comparison cannot be exact. A small contamination from R^{-8} and higher terms is expected because the $3s$ electrons excited to d-symmetry orbitals yield a quadrupole polarizability as does a $3p$ electron excited to p-symmetry

TABLE V. The total correlation-interaction energy $\Delta E^{corr}(4)$ and its components for different basis sets for the Ar dimer for large R. Energies in hartree a_0^6.

i	[7s4p2d] $\quad R = 12a_0$ $\Delta E^{(i)} \times R^6$	$\delta^{(i)} \times R^6$	[7s4p2d] $\quad R = 15a_0$ $\Delta E^{(i)} \times R^6$	$\delta^{(i)} \times R^6$	[7s4p2d 1f] $\quad R = 12a_0$ $\Delta E^{(i)} \times R^6$	$\delta^{(i)} \times R^6$
2	− 73.5	− 1.7	− 72	0	− 79.8	− 1.7
3	+ 15.9	+ 0.2	+ 16	0	+ 16.1	+ 0.2
DQ	+ 1.6	0.0	+ 2	0	+ 2.0	+ 0.1
SDQ	+ 0.2	0.0	0	0	+ 0.1	0.0
SDTQ	− 6.6	− 0.1	− 6	0	− 9.7	− 0.1
Total	− 64.2	− 1.6	− 60	0	− 71.3	− 1.5
C_6^{UCHF}	73.6[b]					
C_6^{CHF}	61.5[c]					
C_6^a	64.20[d] 64.3[e] 63.6 − 70.8[f]					

[a] Correlated values from the literature.
[b] Reference 19.
[c] Reference 20.
[d] Reference 37.
[e] Reference 38.
[f] Reference 40.

orbitals. One can also see that nonnegligible basis set extension (BSE) effect is still present at 12 a_0 judging from the size of δ. As a result, in the dimer calculation, excitations to charge transfer and exchange configurations will have the effect of simulating the presence of higher than d-symmetry orbitals. Increasing the distance to 15 a_0 makes δ disappear, but the $\Delta E^{(i)}$ values are already close to the numerical accuracy with which the monomer and dimer energies were computed (due to the accuracy in the evaluation of the integrals as well as the optimization procedure at the SCF level). Perusal of the results in Table V leads to the following conclusions:

(1) The accurate C_6 value according to two different sources is 64.2 [37] or 64.3 hartree a_0^6.[38] The C_6 coefficient at the MP2 level overestimates this result by $\sim 10\%$. Note that our value of C_6 at the MP2 level, which was obtained by the supermolecular method, is in excellent agreement with the value obtained by Andzelm *et al.*[19] by means of the variation perturbation method combined with a pseudopotential representation of the core.

(2) The value of C_6 at the MP3 level is 57.6 hartree a_0^6, i.e., it is too small by $\sim 10\%$. One can also see that, at the MP3 level, the full CHF result, 61.5 hartree a_0^6, is not yet fully reproduced.

(3) The fourth-order terms are difficult to interpret. They allow for both "apparent" and "true" intraatomic electron correlation effects[51] in the dispersion contribution. To account for intra–interatomic electron correlation coupling in the C_6 coefficients, one should allow for higher than d-symmetry polarization functions. But higher polarization functions introduce higher multipole polarizabilities which cause the appearance of R^{-8} and higher terms, and make it difficult to extract the R^{-6} term. This effect is seen in Table V: the [7s4p2d 1f] results at the MP2 and MP3 levels are

systematically larger than for the [7s4p2d] basis.

Being aware of this (and the fact that our polarization functions are not necessarily good for intraatomic correlation effects) we can nevertheless try to estimate the role of the fourth-order correction and its components to C_6. One can see that the DQ component of $\Delta E^{(4)} \times R^6$ (basis [7s4p2d 1f]) yields a small positive contribution of 2 hartree a_0^6. This result is significantly modified in the full fourth-order correction, primarily by the inclusion of triple excitations and the final value of $\Delta E^4 \times R^6$ is negative and amounts to -9.7 hartree a_0^6. Taking this as a reliable estimate of the fourth-order contribution to C_6, C_6 at the MP4 level will be ~ 67 hartree a_0^6. This result is within the semiempirical bounds of Certain and Standard,[40] from 63.6 to 70.8 hartree a_0^6.

4. The contributions to the interaction energy in the minimum region

Consideration of the results listed in Table IV leads us to the conclusion that the roles of the individual $\Delta E^{(i)}$ corrections resemble very closely their respective roles at large R. This is due to two well-known facts characteristic for the rare gas dimers: (1) In the region of the van der Waals minimum the dispersion contribution is the dominant contribution to ΔE^{corr} (4); (2) the dispersion contribution may be well approximated by means of its asymptotic multipole expansion corrected only for overlap effects (i.e., correctly damped). The damped multipole expansion of the dispersion energy may be used to explain the role of consecutively higher angular polarization functions in the supermolecular calculation of the interaction energies. This approach (in the form of the well defined partial wave expansion) was very successful for other rare gas dimers He_2 and Ne_2.[18] Toward

TABLE VI. SCF interaction energy for the Mg_2 dimer. Interaction energies in mhartree, atomic energies in hartree distances in a_0.

R	ΔE^{HLc}	d ΔE^{SCF}	δ^{SCF}	[7s4p2d 1f] ΔE^{SCF}	δ^{SCF}	a ΔE^{SCF}	δ^{SCF}	b ΔE^{SCF}
6.5	14.764	6.375	-0.010	6.180	-0.378	6.898	$\cdots$	6.399
7.0	9.071	3.838	-0.005	3.693	-0.209	4.144	-0.010	3.875
7.3	6.744	2.859	-0.004	2.744	-0.134	$\cdots$	$\cdots$	$\cdots$
7.5	5.525	2.357	-0.004	2.259	-0.099	2.529	-0.008	2.390
8.0	3.331	1.462	-0.004	1.397	-0.053	1.559	-0.007	$\cdots$
8.5	1.988	0.909	-0.003	0.866	-0.044	0.964	-0.006	$\cdots$
9.0	1.173	0.563	-0.003	0.535	-0.046	0.596	-0.006	$\cdots$
9.5	0.685	0.346	-0.002	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$
10.0	0.397	0.211	-0.002	0.201	-0.043	0.222	-0.005	$\cdots$

The SCF energies of the Mg atom:
$-199.611\ 049\ 420^d$ $-199.609\ 791\ 826^e$ $-199.603\ 382^a$ $-199.614\ 34^b$
The near-HF value^f: 199.614 636

^{a} Diercksen *et al.* (Ref. 6), basis D, ΔE^{SCF} has been corrected for the BSSE.
^{b} Stevens and Krauss (Ref. 4).
^{c} The Heitler–London interaction energy, with the [16s9p] basis of Ref. 32.
^{d} Obtained with the [16s9p] of Ref. 32 contracted to [3s1p] and augmented with our diffuse three s, three p, two d, and one f.
^{e} Obtained with [7s4p2d 1f] basis.
^{f} Clementi and Roetti (Ref. 48).

TABLE VII. The total MP4 interaction energies and the contributions from different orders of MPPT for Mg_2. Energies in mhartree, distance in a_0.

R	$\Delta E^{\mathrm{SCF}a}$	$\Delta E^{(2)}$	$\Delta E^{(3)}$	$\Delta E^{(4)}$	$\Delta E^{\mathrm{corr}}(4)$	δ^{corr}	$\Delta E(4)$	BD^b
6.5	6.1799	− 6.097	− 0.884	− 0.316	− 7.297	+ 0.0290	− 1.117	− 1.218
7.0	3.6933	− 4.807	− 0.673	− 0.196	− 5.676	+ 0.0164	− 1.983	− 1.841
7.3	2.7442	− 4.148	− 0.571	− 0.144	− 4.863	+ 0.0122	− 2.119	⋯
7.5	2.2588	− 3.752	− 0.512	− 0.115	− 4.379	+ 0.0096	− 2.120	− 1.919
8.0	1.3973	− 2.904	− 0.391	− 0.064	− 3.359	+ 0.0088	− 1.962	− 1.753
8.5	0.8662	− 2.229	− 0.298	− 0.032	− 2.559	+ 0.0086	− 1.693	− 1.499
9.0	0.5354	− 1.700	− 0.229	− 0.013	− 1.942	+ 0.0092	− 1.406	− 1.233
10.0	0.2008	− 0.974	− 0.135	+ 0.003	− 1.112	+ 0.0100	− 0.911	− 0.780
15.0	0.0010	− 0.071	− 0.011	+ 0.002	− 0.084	+ 0.0008	− 0.083	− 0.054

[a] Obtained with the [$7s4p2d\ 1f$] basis.
[b] Morse potential, $\beta = 1.0543$, $D_e = 424\ \mathrm{cm}^{-1}$, $R_e = 3.890$ Å obtained as a fit to accurate spectroscopic data, Balfour and Douglas (Ref. 43).

this end we will use the dispersion terms obtained from the semiquantal TT potential. The partial sums through R^{-6}, R^{-8}, and R^{-10} order terms and the total value, through the R^{-18} order term are at 7.0 a:

$$\mathrm{TT}(6) = -0.3733\ \text{mhartree},$$
$$\mathrm{TT}(8) = -0.5259\ \text{mhartree},$$
$$\mathrm{TT}(10) = -0.5902\ \text{mhartree},$$
$$\mathrm{TT}(18) = -0.6332\ \text{mhartree},$$

respectively.

One can see (cf. Table IV) that the value of the correlation contribution to $\Delta E(4)$ obtained with the [$7s4p2d$] basis, − 0.4020 mhartree, is quite close to the dipole–dipole dispersion term, TT(6). Our value is slightly smaller than TT(6) but the comparison between $\Delta E(4)$ and the TT terms cannot be carried out precisely. First, the dipole–dipole term reproduced by $\Delta E(4)$ is not exactly equivalent to TT(6) (our C_6 differs). Second, $\Delta E(4)$ includes more than just the dipole–dipole term, since (a) the $3s$ electrons in the Ar atom contribute to the quadrupole polarizability when excited to d-symmetry orbitals as does a $3p$ electron when excited to p symmetry; (b) the BSE effect, which is fairly significant in the minimum region, may allow for ionic and charge transfer excitations or occupied orbitals in the supermolecular dimer calculations in this way making up for higher angular polarization orbitals [the (a) and (b) effects will cause the R^{-8} and lower order terms to appear in $\Delta E(4)$]; (c) the intraatomic correlation correction to the Heitler–London interaction energy, which has short-range character, is also included in the $\Delta E(4)$ result but not in the damped multipole expansion of Tang and Toennies.[13]

Reasoning along the same lines, one can conclude that with the [$7s4p2d\ 1f$] basis, one should obtain the value of $\Delta E^{\mathrm{corr}}(4)$ determined approximately by the dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole terms, i.e., should approximately reproduce TT(10). Indeed, our result is between TT(8) and TT(10).

Two more general conclusions arise from the above discussion. First, the MP4 level, provided one includes triple excitation relative to the HF reference state, seems to recover enough of the electron correlation effects to provide accurate interaction energies between two Ar atoms. Second, higher

than f-symmetry orbitals are necessary to achieve high accuracy (1%–2% error).

B. The Mg_2 dimer

1. The SCF level

The SCF interaction energies that we obtained for Mg_2 using our [$7s4p2d\ 1f$] basis are listed in Table VI. Our contracted basis gave a small but nonnegligible BSSE, therefore as a comparison, we repeated the calculations using an alternate atomic integral and SCF package which could handle contractions of 16 GTO's (cf. Ref. d of Table VI).[50] This reduced our BSSE to less than 0.5% of the interaction energy. The values of ΔE^{SCF} obtained with this basis are in excellent agreement with those of an extended STO basis[41] which are probably the best SCF calculations for Mg_2 to date. The values of ΔE^{SCF} obtained with the [$7s4p2d\ 1f$] basis are in close but not complete agreement as are the values of ΔE^{SCF} of Diercksen et al.,[6] despite a very small value of δ^{SCF}.

In fact, we have found the values of ΔE^{SCF} for Mg_2 to be quite sensitive to basis set effects. This can be partly attributed to the fact that, unlike Ar atoms, Mg atoms deform quite significantly upon interaction. The Heitler–London interaction energy ΔE^{HL} (cf. the first column of Table VI) is twice as large as ΔE^{SCF} in the entire region under consideration. Although this fact may be attributed to the high polarizability of the Mg atom, one should remember that the mutual deformation effects for closed shell atoms are accounted for, first of all, by exchange effect.[42]

2. The interaction energy at the post-HF level

The interaction energies between two Mg atoms obtained with the [$7s4p2d\ 1f$] basis (within the frozen-core approximation) through the fourth order of MPPT are listed in Table VII. Our results are compared with the Morse potential fit to the RKR potential reported by Balfour and Douglas.[43] One can see that our values of $\Delta E(4)$ for R smaller than the equilibrium distance $R_e = 7.5$ are not attractive enough, in the region of R_e they are in good agreement, and for $R > R_e$ they become too attractive. We would like to stress that the total value of BSSE at the correlated level (under the frozen-core approximation) is very small, much smaller than the discrepancy between our results and the accurate potential.

TABLE VIII. The total correlation-interaction energy $\Delta E^{corr}(4)$ and its components for different basis sets for the Mg dimer for $R = 15\,a_0$. Energies in hartree $\times a_0^6$.

i	[7s4p]$R = 15a_0$		[7s4p2d 1f] $R = 15a_0$		[7s6p]^a $R = 15a_0$	
	$\Delta E^{(i)} \times R^6$	$\delta^{(i)} \times R^6$	$\Delta E^{(i)} \times R^6$	$\delta^{(i)} \times R^6$	$\Delta E^{(i)} \times R^6$	$\delta^{(i)} \times R^6$
2	− 659.4	+ 8.4	− 813.3	+ 14.5	− 687.8	+ 16.1
3	− 97.6	+ 8.8	− 127.0	+ 9.0	− 111.8	+ 25.2
DQ	+ 106.6	+ 5.0	+ 115.7	+ 2.4	+ 103.7	+ 13.4
SDQ	+ 126.4	+ 3.3	+ 148.1	− 1.0		
SDTQ	+ 107.8	⋯	+ 17.2	⋯		
Total	− 649.2	+ 25.5	− 923.1	+ 24.9		
C_6^b: 630 − 638 [40], 686 [44]						

^{a} The [7s6p] basis was obtained from our [7s4p] basis by adding two more p orbitals of the exponents 0.026 471 7 and 0.012 312 4.
^{b} Correlated values from the literature.

To rationalize the above results, let us investigate the decomposition of $\Delta E(4)$ into individual $\Delta E^{(i)}$ and analyze basis set effects.

3. The role of individual $\Delta E^{(i)}$ components

The decomposition of $\Delta E(4)$ into its components is shown in Table VIII, for $R = 15\,a_0$ and in Table IX, for $R = 7\,a_0$.

a. The region of large R. We begin our analysis at large R since at this distance the interaction energy is determined by the individual dipole–dipole dispersion term. In the case of the Mg_2 dimer, in the frozen-core approximation, only the $3s$ electrons give rise to dipole–dipole dispersion interaction

contributions through excitations to p-symmetry orbitals. The value of $\Delta E^{(i)} \times R^6$ were tabulated to make a comparison with C_6 van der Waals coefficients. The results in the first column of Table VIII were obtained with the [7s4p] basis, derived from the [7s4p2d 1f] basis by leaving out the d and f sets of orbitals. It should be noted that the all-electron calculations did not differ significantly from the frozen-core results. One can see that our C_6, at the MP2 level, equals 659.4 hartree a_0^6 and is larger than the upper bound of the accurate estimate by Certain and Standard[40] which equals 638 hartree a_0^6. In fact, our value of $\Delta E^{(i)} \times R^6$ is not basis set saturated since the exponents of the p orbitals we used were, in fact, not optimal at large distances.[52] Adding two diffuse p orbitals yielded 688 hartree a_0^6 (the fifth column of

TABLE IX. The total interaction energy $\Delta E(4)$ and its components for various basis sets for the Mg_2 dimer in the region of the van der Waals minimum $R = 7\,a_0$. Interaction energies in mhartree, atomic energies in hartree.

	[7s4p2d 1f] frozen core	[7s4p2d 1f]′ frozen core	[7s4p2d 1f]′ full electron calculation	Basis set D from Ref. 6^a	
				Frozen core	Frozen K shell
ΔE^{SCF}	3.693	3.838	3.838	4.144	4.144
δ^{SCF}	− 0.378	− 0.005	− 0.005	− 0.010	− 0.010
$\Delta E^{(2)}$	− 4.807	− 4.762	− 4.813	− 3.999	− 4.144
$\delta^{(2)}$	− 0.088	− 0.096	− 1.219	− 0.859	− 3.420
$\Delta E^{(3)}$	− 0.673	− 0.681	− 0.604	− 0.624	− 0.455
$\delta^{(3)}$	+ 0.111	+ 0.097	+ 0.094	+ 0.174	+ 0.104
$\Delta E^{(4)}$	− 0.196	− 0.197	− 0.176	− 0.119	− 0.080
$\delta^{(4)}$	− 0.007	− 0.010	− 0.052	+ 0.124	+ 0.034
DQ	+ 0.646	+ 0.622	+ 0.676	⋯	⋯
δ^{DQ}	− 0.001	− 0.008	− 0.002	⋯	⋯
SDQ	+ 0.665	+ 0.642	+ 0.712	⋯	⋯
δ^{SDQ}	− 0.007	− 0.010	− 0.012	⋯	⋯
$\Delta E^{corr}(4)$	− 5.676	− 5.640	− 5.593	− 4.742	− 4.679
$\delta^{corr}(4)$	+ 0.016	− 0.010	− 1.177	− 0.561	− 3.282
E^{SCF}	− 199.609 792	− 199.611 049	− 199.611 049	− 199.603 382	− 199.603 382	− 199.614 636^c
$E^{(2)}$	− 0.023 476	− 0.023 447	− 0.059 919	− 0.019 026	− 0.175 189	0.355 43^d
$E^{(3)}$	− 0.006 151	− 0.006 081	− 0.006 495	− 0.006 616	− 0.006 688
$E^{(4)}$	− 0.002 344	− 0.002 306	− 0.004 004	− 0.002 458	− 0.004 981

^{a} Corrected for BSSE.
^{b} Obtained with basis set D of Diercksen *et al.* (Ref. 6).
^{c} Near-HF (Ref. 48).
^{d} Accurate E^2 (Ref. 49) (full electron calculation).

Table VIII). All of these values are not very accurate as, at this distance, BSSE is still nonnegligible. Going to even larger R does not help since the interaction energy becomes on the order of the size of the error in the calculations of the dimer and monomer again, due to the errors involved in the integral evaluation and SCF optimization procedure.

At the MP3 level, the value of C_6 becomes even larger which is in agreement with the fact that CHF theory yields too large a value for alkaline earth metal dimers.[44] The fourth-order MPPT correction to C_6 is harder to estimate for the same reasons as in the Ar_2 system. In addition, unlike Ar_2, the value of $\Delta E^{(4)} \times R^6$ changes drastically when changing the basis set from [7s5p] to [7s5p2d 1f]. The following conclusions may therefore be cautiously drawn:

(1) The SDQ terms reduce the value of C_6 considerably by approximately cancelling the $\Delta E^{(3)}$ contribution. The value of the SDQ contribution is fairly stable with respect to the basis set.

(2) Allowing for the T terms increases the value of C_6 again. However, the T contributions turn out to be extremely sensitive to basis set effects: for the [7s4p] basis the contribution from the triple excitations is insignificant whereas for the [7s4p2d 1f] basis they cancel almost completely the effect of the SDQ terms.

b. The region of van der Waals minimum. Unlike Ar_2, the relationships between the different contributions to the electron correlation are different at large R from those in the region of the van der Waals minimum (cf. Table IX). In particular, $\Delta E^{(4)}$ is positive at large R and negative near the minimum. (Interestingly, the identical effect was found for Be_2.)[5] Thus, conclusions about the performance of MPPT in the long-range region cannot be straightforwardly transferred to the van der Waals region. Nevertheless, it only seems reasonable to conclude that the MP4 level tends to overestimate the correlation contribution to the interaction energy.

It is then quite possible that overestimation of correlation contributions of the interaction energy due to the method compensates, in our case, for the lack of higher polarization functions and that addition of further polarization functions would lead to too deep an interaction energy curve. Another point which is worth mentioning is that the short-range intraatomic correlation correction to the Heitler–London energy is probably repulsive and more significant for Mg_2 than for rare gas dimers, as suggested by Stevens and Krauss.[41]

It is interesting to compare our results with those of Diercksen et al.[6] First, our best basis set gives better SCF and $E^{(2)}$ energies for the Mg atom in the frozen-core approximation than the bases of Diercksen et al.[6] (cf. Table IX). Second, our BSSE in the frozen-core correlated calculations is small whereas theirs is very large and causes the interaction energy to be substantially too large. However, if one corrects the Diercksen et al. results for BSSE by means of the CP method [the authors fortunately report the values of the BSSE calculated from Eq. (4) at each level of theory], they may be meaningfully compared with ours. First, bases without f functions give smaller and similar D_e, 1.343 and 1.461 mhartree for their bases B_1 and B_2, respectively. Second,

their basis C_2, which has the same d and f exponents as our [7s4p2d 1f] basis, gives D_e 2.141 mhartree—quite close to our lowest value of $\Delta E(4)$, 2.12 mhartree. The basis C_1 with one f orbital of 1.4 exponent gives $D_e = 1.48$ mhartree—apparently one f orbital with this exponent is not much of an improvement over the basis set without f orbitals at all. The above diagnosis was confirmed by our calculations with [7s4p2d 1f] augmented with their second f function with the exponent of 1.4. The values of $\Delta E^{(i)}$ differed by only 0.001 mhartree from those obtained with basis [7s4p2d 1f]. As to their basis D (cf. our Table IX), it probably suffers from the unfortunate contraction of the two f orbitals and yields interaction energies close to those of bases B_1 and B_2, without f orbitals at all.

V. CONCLUSIONS

It has been shown that MPPT through fourth order is an adequate method for studying correlation-bound complexes and provides us with reliable interaction energies. Several conditions, however, have to be fulfilled.

(1) Very accurate SCF calculations should be carried out and an accurate representation of the occupied orbitals must be ensured at the correlated level. At the SCF level BSSE should be made as small as possible. This goal may be achieved with large even-[31] and well-tempered[32] basis sets even for systems are large as Zn_2.[24]

(2) Efficient basis sets for intersystem electron correlation effects should be used. The most rigorous approach is to optimize the exponents by using the variation–perturbation method for dispersion energy calculations.[45] Andzelm et al.[19] recently proposed maximizing the overlap of the polarization radial functions with the valence radial functions of the ground state and the average of excited states. Optimizing the exponents with respect to the interaction energy may also be quite effective although we should keep in mind that the interaction energy is not a variational quantity. Higher polarization functions are of utmost importance and the role of any particular symmetry may be often estimated by looking at the multipole expansion of the dispersion term and finding out what symmetry of polarization functions will yield individual R^{-n} terms. The guidelines for adding consecutive higher polarization functions, recently set forth in Refs. 18 and 46, may also be used.

(3) Despite the fact that criteria 1 and 2 make the basis sets large, BSSE at the correlated level will be significant and the CP method should be used. The errors in such calculations, despite quite substantial numerical effort, may still be 10%–20% with respect to the interaction energy. This will depend above all on two factors: the number and symmetry of higher perturbation functions, and the capability of the MPPT method to account for the pertinent electron correlation effects. The role of these factors will vary from one system to another. For Ar_2 our results suggest that MP4 reproduces the correlation effects accurately and the main difficulty involves inclusion of higher than f polarization functions. For Mg_2 the cancellation of methodological and numerical errors in obtaining relatively good interaction energies without higher than f polarization functions is not

quite clear. Including *g*-symmetry orbitals could shed more light on this problem, as would the use of other than MPPT correlated methods. This important problem is, however, outside the scope of our paper.

(4) To achieve better control of the accuracy and better understanding of the supermolecular MPPT calculations one should relate the results to the data provided by the perturbation theory of the intermolecular forces: van der Waals coefficients, overlap, and exchange effect.

Using the above approach we obtained an interaction potential for Ar_2 characterized by $R_e \approx 7.3\,a_0$ and $D_e \approx 0.34$ mhartree, to be compared with the accurate semiempirical values of $R_e \approx 7.1\,a_0$ and $D_e \approx 0.45$ mhartree,[13] respectively. For Mg_2 we obtained an interaction potential characterized by $R_e \approx 7.4\,a_0$ and $D_e \approx 2.1$ mhartree, to be compared with the accurate experimental values of $R_e \approx 7.35\,a_0$ and $D_e \approx 1.93$ mhartree,[43] respectively. To improve on these results higher than *f*-symmetry functions are needed and in the case of Mg_2 also a more accurate correlation method should be used.

It is interesting to compare the character of the binding in Ar_2 and Mg_2. In Ar_2 the binding originates exclusively from the van der Waals attraction (dispersion). In Mg_2, although the dispersion represents the dominant attractive contribution, the short-range exchange-deformation effects (represented by the difference $\Delta E^{HL} - \Delta E^{SCF}$) are quite significant. It is worthwhile to note that if these effects were neglected and ΔE^{SCF} replaced by ΔE^{HL}, R_e, and D_e for Mg_2 would become $\approx 9a_0$ and ≈ 0.7 mhartree, respectively. This is analogous to the situation found for Be_2.[14] One can then distinguish between a dispersive van der Waal's "bond" in rare gas dimers and a partly dispersive, partly short-range "bond" in alkaline earth metal dimers. Mixed alkaline earth–rare gas pairs have been determined to exhibit predominately dispersive "binding."[23]

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[51]For the discussion of "true" as opposed to "apparent" correlation effects see Sadlej Ref. (39) and Chałasiński Ref. (36).
[52]Unlike for rare gas dimers, for alkaline earth metal dimers the exponents optimized at large *R* are not efficient (too diffuse) in the van der Waals minimum region (cf. Ref. 14).