Møller–Plesset perturbation theory calculation of alkaline earth–rare gas complexes: Ground states of Mg–He and Mg–Ar

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We have used Møller–Plesset perturbation theory as carried out through the fourth order for a determination of the potential parameters for the ground states of the alkaline–earth metal magnesium with argon and helium. Mg–He was found to have a potential minimum of ≈ 0.021 mhartree at an internuclear distance of 9.75 a_0 and was determined to be capable of supporting a single vibrational level. Mg–Ar was found to have a potential minimum of ≈ 0.254 at an internuclear distance of 9 a_0, which is slightly shallower and at a larger internuclear distance than a recent experimental determination. A comparison of the homonuclear and heteronuclear bonding is presented and differences in the bonding are attributed to exchange–repulsion effects.

I. INTRODUCTION

The alkaline earth–rare gas van der Waals systems provide a serious challenge to the *ab initio* quantum chemist. They belong to the weakest complexes, which are bound exclusively by intermolecular electron correlation effects, and an accurate description of these potentials using *ab initio* methods would help confirm the predictive powers of quantum chemistry. Few theoretical papers exist on the subject, and most involve either estimates of van der Waals constants $(C_6, C_8, \text{etc.},...)$[1–4] for these molecules or semiempirical model calculation of potential energy curves.[5–8]

Recently, laser excitation studies of the supersonic expansions of metal atoms seeded in the rare gases have allowed characterization of the potential curves for both the ground and excited states for a large number of Group-IIA and IIB metal–rare gas pairs.[9–16] These same studies have demonstrated that no simple combining rules[17–19] might be possible for the ground state molecules. Any theoretical method for a determination of ground state potentials should reflect this and illustrate the underlying nature of these interactions.

In a recent study,[20] we have used Møller–Plesset perturbation theory (MPPT) for the determination of the ground state interatomic potentials of Mg_2 and Ar_2. It was shown that MPPT carried out through the fourth order was effective provided that:

(a) The basis sets used yielded accurate SCF interaction energies.

(b) The basis sets included higher polarization functions with exponents that adequately reproduce intersystem correlation effects.

(c) The Counter–Poise (CP) method of Boys and Bernardi[21] was used to correct for the basis set superposition error (BSSE).

We found that these homonuclear diatomics are bound

by electron correlation effects but that the two species exhibit somewhat different binding characteristics. The Mg_2 bonding can be characterized as part "chemical" (due to SCF deformation effects) and part physical (London dispersion) while the Ar_2 bond is purely physical. We present here, using the same methodology, calculations on the ground states of the correlation bound Mg–He and Mg–Ar systems, which exhibit dispersive binding. To the best of our knowledge, our Mg–He potential energy curve is the most accurate reported and our Mg–Ar curve is the first correlated potential curve reported in the literature for this system.

II. METHOD

We have used the supermolecular approach for determination of the interaction energies as expressed in Møller–Plesset perturbation theory as carried out through the fourth order including single (S), double (D), triple (T), and quadruple (Q) excitation of the valence electrons out of the restricted Hartree–Fock [RHF] reference determinant. Calculations were performed using either GAUSSIAN 82,[22] GAUSSIAN 86,[22] or the GRNFNC/UMBPT[23] codes. Calculations involving correlation of all electrons were also performed near the determined potential minima.

We define the nth order of MPPT as $E^{(n)}$ and the interaction energy *through* the ith order of MPPT as

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

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

$$\Delta E^{\text{SCF}} = \Delta E^{(0)} + \Delta E^{(1)}. \qquad (2)$$

Also of interest is the so-called "zeroth-order" iteration result of the SCF procedure (starting with converged monomer orbitals), referred to as ΔE^{HL}, the Heitler–London interaction energy. The difference between ΔE^{HL} and ΔE^{SCF} reflect mutual deformation of A in the field of B and B in the

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field of A as allowed for through the SCF iterations. It is also convenient to define the total correlation energy through the fourth order as

$$\Delta E^{corr}(4) = \sum_{k=2}^{4} E^{(i)}.$$ (3)

When the energies of A, B, and AB are calculated with finite basis sets (χ_A, χ_B, and χ_{AB}, respectively) the use of Eqs. (1) and (2) involves basis set superposition error (BSSE) problems. As is becoming apparent in an increasing number of theoretical studies, only the full counterpoise correction as first introduced by Boys and Bernardi[21] seems capable of addressing BSSE in a consistent manner,[20,24–28] though many workers in the field are still divided on this matter.[29]

Therefore, we have used the CP method, which consists in the calculation of the energies of AB, A, and B in the same $\chi_A \oplus \chi_B$ basis. The BSSE in the ith order of MPPT is then defined as:

$$\delta_A^{(i)} = E_A^{(i)}(\chi_A \oplus \chi_B) - E_A^{(i)}(\chi_A)$$ (4)

and similarly for B. The total BSSE is

$$\delta = \delta_A + \delta_B = \sum_i (\delta_A^{(i)} + \delta_B^{(i)})$$ (5)

and we will also use the symbols δ^{SCF} and $\delta^{corr}(4)$ to denote the SCF δ and its correlation counterpart, respectively.

III. BASIS SETS

A. Magnesium

We have used a [$16s11p2d$ $1f/7s4p2d$ $1f$] Gaussian basis comprised of the [$16s9p$] well-tempered basis of Huzinaga *et al.*,[50] augmented with two additional p orbitals roughly 2.2 and $(2.2)^2$ times smaller than Huzinaga's most diffuse, and with the $2d$ and $1f$ orbitals of Diercksen *et al.*[30] Details of the exponents and contraction coefficients were given previously (Table II of Ref. 20). Hereafter we denote this basis by its contracted form Mg[$7s4p2d$ $1f$] and to its slightly modified form containing two ten-function contractions in place of two eight-function contractions as Mg [$7s4p2d$ $1f$]$'$. This basis proved to be very good in our previous study of Mg_2, with which we obtained a fairly accurate value of the interaction energy.[20]

B. Argon

We have used a [$14s10p2d$ $1f/7s4p2d$ $1f$] Gaussian basis comprised of the energy-optimized [$14s10p$] set of Rozendaal,[31] the dispersion-optimized $2d$ orbitals of Andzelm *et al.*,[32] and the $1f$ orbital of Chalasinski *et al.*[20] Details of the exponents and contraction coefficients were given previously (Table I of Ref. 20).[33] Hereafter we denote this basis by its contracted form Ar[$7s4p2d$ $1f$]. We note that in our previous study, this basis proved to be effective in describing the Ar_2 interaction, recovering 75% of the interaction energy.

C. Helium

We have used a [$10s3p2d$ $1f/5s3p2d$ $1f$] Gaussian basis comprised of the $10s$ set of van Duijneveldt and[34] the $3p$

orbitals taken from CR1 $\oplus$ DS2 set of Gutowski *et al.*,[35] which were shown to reproduce the He_2 interaction adequately.[24] Finally, the $2d$ and $1f$ orbitals were used of Gutowski *et al.*,[36] who optimized the partial wave component of the variational dispersion energy corresponding to E^{MP} ($1,l;l = 2$ or 3), the leading term in such a decomposition. The exponents and contraction coefficients are listed in Table I. Hereafter we denote the basis as He[$5s3p2d$ $1f$].

IV. THE Mg(^1S) AND He(^1S) INTERACTION

The values of the interaction energy and its components through the fourth order of MPPT, as calculated with the Mg[$7s4p2d$ $1f$]$'$ and the He[$5s3p2d$ $1f$] basis sets, for internuclear distances of 6 to 12 atomic units are listed in Table II.

The potential minimum at the MP4 level occurs near 9.75 a_0 with a D_e of ≈ 0.021 mhartree (4.6 cm^{-1}). This determination of the position and depth of the potential minimum for Mg–He may be fairly accurate, since for Mg_2 and He_2, at the same level of theory and with the same basis sets, we reproduced 110% and 84% of the exact values of D_e, respectively. It is reasonable to expect that the accuracy will lie somewhere in between that for Mg_2 or He_2, as supported by the comparison of the C_6 parameter for Mg_2, He_2, and Mg–He, and by the fact that the MPPT series seems to converge rapidly (see below).

A. Interaction energy in the region of the potential minimum

Decomposition of the MP4 interaction energy into its individual MPPT contributions is listed in Table III, for $r = 9.75$ a_0. The series of the $\Delta E^{(i)}$ appears to converge rapidly. Interestingly, at all levels of the theory, the BSSE is relatively small and does not exceed 4% of the total MP(4) interaction energy. On the other hand, the BSSE obtained with the same bases for Mg_2[20] and He_2 was much more

TABLE I. Helium basis set.

	Symmetry orbital exponent	Expansion coefficients
s^a	4840.888 547	0.000 059
	723.108 918	0.000 463
	164.299 706	0.002 422
	46.636 262	0.009 995
	15.277 787	0.034 249
	5.526 897	0.096 302
	2.132 879	1.0
	0.849 674	1.0
	0.343 643	1.0
	0.138 709	1.0
p^b	3.047 2	1.0
	0.759 10	1.0
	0.194 30	1.0
d^c	0.498 71	1.0
	0.152 93	1.0
f^c	0.183 60	1.0

[a] $10s$ from van Duijneveldt, Ref 34.
[b] $3p$ from Gutowski *et al.* CR1 $\oplus$ DS2, Ref. 35.
[c] $2d + 1f$ from Gutowski, *et al.*, Ref. 37.

TABLE II. The interaction energy and its components for the ground state $^1\Sigma^+$ of Mg–He obtained with basis Mg[$7s4p2d\,1f$]' and He[$5s3p2d\,1f$] (frozen-core approximation). Energies are in mhartree, distance in a_0.

R	ΔE^{HL}	ΔE^{SCF}	δ^{SCF}	$\Delta E^{(2)}$	$\Delta E^{(3)}$	$\Delta E^{(4)}$	$\Delta E^{corr}(4)$	$\delta^{corr}(4)$	$\Delta E(4)$	a
6.0	4.00	2.9513	− 0.0032	− 0.7102	− 0.1359	− 0.027	− 0.8731	− 0.0135	2.0782	3.226
7.0	1.198	0.9053	− 0.0022	− 0.346	− 0.0659	− 0.0116	− 0.4235	− 0.0081	0.4818	0.866
8.0	0.3444	0.2652	− 0.0013	− 0.1606	− 0.0301	− 0.0044	− 0.1951	− 0.0044	0.0701	0.19
9.0	0.0950	0.0751	− 0.0009	− 0.0736	− 0.0132	− 0.0016	− 0.0884	− 0.0020	− 0.0133	0.02
9.5		0.0396	− 0.0007	− 0.0501	− 0.0087	− 0.0008	− 0.0596	− 0.0013	− 0.0200	· · ·
9.7		0.0306	− 0.0006	− 0.0431	− 0.0074	− 0.0007	− 0.0512	− 0.0010	− 0.0206	· · ·
9.75		0.0286	− 0.0006	− 0.0415	− 0.0071	− 0.0007	− 0.0493	− 0.0010	− 0.0207	· · ·
9.8		0.0269	− 0.0006	− 0.0399	− 0.0068	− 0.0006	− 0.0473	− 0.0009	− 0.0204	· · ·
10.0	0.0249	0.0207	− 0.0006	− 0.0345	− 0.0058	− 0.0005	− 0.0408	− 0.0007	− 0.0201	− 0.009
11.0	0.0062	0.0056	− 0.0005	− 0.0171	− 0.0027	− 0.0004	− 0.0202	− 0.0001	− 0.0146	− 0.010
12.0	0.0001	0.0014	− 0.0004	− 0.0091	− 0.0014	− 0.0001	− 0.0106	− 0.0000	− 0.0092	− 0.009

^{a} Semiempirical pseudopotential CI calculations (Ref. 8).

significant with respect to their interaction energies. It seems that the Mg and He valence electrons do not benefit greatly from one another's basis functions.

To check the validity of the frozen-core approximation, we performed all electron correlation calculations for R equal to 9.75 a_0. Although the BSSE then became as large as $\Delta E^{(i)}$, the counter-poise corrected values of $\Delta E^{(i)}$ agreed to within a few percent.

B. The region of large R

To analyze our potential for Mg–He at large distances we have estimated the C_6 coefficients at different levels of the theory through the formula

$$- \Delta E^{(i)} \times R^6 = C_6^{(i)} \quad (i = 2,3,4) \tag{6}$$

at R equal to 15 a_0. For $E^{(i)}$ ($i = 2,3$) the estimates were determined using a subset of our original basis that excluded d- and f-symmetry orbitals to avoid contamination from R^{-8} and lower order terms.[37] We obtained the following estimates:

$$C_6^{(2)} = 20.1 \quad C_6^{(3)} = 2.4 \quad C_6^{(4)} = 0.0 \quad [Ha_0^6]$$

TABLE III. Components of the interaction energy in the ground state $^1\Sigma$ of Mg–He at $R = 9.75\ a_0$ obtained with the [$7s4p2d\,1f$]' basis of Mg and the [$5s3p2d\,1f$] basis of He. Interaction energies and δ in mhartree, atomic energies in hartree.

E^{int} component		δ_{Mg}	δ_{He}
ΔE^{SCF}	0.0286	− 0.0005	− 0.0001
$\Delta E^{(2)}$	− 0.0415	− 0.0014	− 0.0009
$\Delta E^{(3)}$	− 0.0071	0.0013	0.0002
$\Delta E^{(4)}$	− 0.0007	− 0.0003	0.0000
DQ	0.0015	− 0.0002	0.0000
SDQ	0.0027	− 0.0003	0.0000
$\Delta E^{corr}(4)$	− 0.0493	− 0.0004	− 0.0006
Atomic energies		He	Mg
E^{SCF}		− 2.861 672 942 45	− 199.611 049 420
$E^{(2)}$		− 0.032 334 729	− 0.023 446 866
$E^{(3)}$		− 0.005 096 289 6	− 0.006 081 413 0
$E^{(4)}$		− 0.000 908 100 03	− 0.002 305 687 3

with the related BSSE as

$$R^6 \cdot \delta^{(2)} = -0.14 \quad R^6 \cdot \delta^{(3)} = 0.1 \quad R^6 \cdot \delta^{(4)} = 0.0 \quad [Ha_0^6].$$

Thus, we see that our estimated value of C_6 at the MP4 level of 22.6 Ha_0^6, compares favorably with the estimate of Victor and Slavsky,[1] who obtained a C_6 coefficient of 20.87 Ha_0^6 using the Casimir–Polder relation and frequency dependent (dynamic) dipole polarizabilities obtained from model potential calculations. Stwalley[3] obtained a similar value of 21.6 Ha_0^6 also using an approximation to the Casimir–Polder relation. The semiempirical lower and upper limits of Certain and Standard,[2] determined by bounding the dynamic polarizability, are 21.1–22.1 Ha_0^6. Thus, we see that our C_6 coefficient is slightly greater than the upper bound, but lies intermediate in accuracy to the same estimates of Mg$_2^{20}$ (too large by $\sim 10\%$) and He$_2$ (too small by $\sim 3\%$) which were determined at the same level of theory, and with the same basis sets.

C. Determination of bound levels

Due to the shallow potential minimum of Mg–He, one is curious as to whether or not it can sustain any bound vibrational levels. He$_2$, having a potential well approximately twice as deep, was shown (theoretically) to support a single vibrational level and only for the ^{4}He–^{4}He isotopic combination.[39] To answer this question for Mg–He, we have fit our *ab initio* points to a cubic spline and numerically integrated the radial Schrödinger equation.[40] Listed in Table IV are the determined levels and their corresponding binding energies. As seen in the table, the most strongly bound level is the ^{26}Mg^{4}He isotopic combination bound by 0.745 cm^{-1}, which

TABLE IV. Possible rovibrational levels and their corresponding binding energies for the major isotopes of Mg and He. All energies in mhartree (energies in brackets are cm^{-1}).

$v = 0:J$	^{24}Mg^{4}He	^{25}Mg^{4}He	^{26}Mg^{4}He
$J = 0$	0.003 34 [0.734]	0.003 37 [0.740]	0.003 40 [0.746]
$J = 1$	0.002 29 [0.503]	0.002 32 [0.510]	0.002 35 [0.516]
$J = 2$	0.000 34 [0.074]	0.000 37 [0.081]	0.000 40 [0.088]

corresponds an average thermal energy of 0.7 K. Therefore, with the advances in creating super-cooled environments through the use of supersonic expansions, we believe that this molecule will be observed, though the spectrum should consist of few lines. In the analogous Hg–He complex observed by both Duval *et al.*[41] and Yamanouchi *et al.*,[10] they found only two vibronic transitions from the $v'' = 0$ level to the $v' = 0,1$ levels of the Hg–He $A^3 0^+$ electronic state, and deduced a ground state dissociation energy of 3 ± 2 cm^{-1}.[10]

D. Comparison with previous results

The well depth for Mg–He is shallower than the well depth for He$_2$ and appears to be quite challenging for *ab initio* calculation. To the best of our knowledge only Chiles and Dykstra[42] have reported *ab initio* calculations on Mg–He that have found a potential minimum on the ground state potential surface. They obtained a well depth of 0.0091 mhartree (2.00 cm^{-1}) at 10.64 a_0 using an approximate double-substituted coupled-cluster method (ACCD). We believe that the discrepancies between our calculations is due in part to differences in the level of theory used as well as in the quality of the two basis sets. When we performed CCD calculations with our basis set, the value of D_e was reduced to ≈ 0.016 mhartree (3.5 cm^{-1}). We also note that CCD was found to provide lower interaction energies when compared with the MP4DQ level of MPPT for rare earth metal dimers Be$_2$[43,44] and Mg$_2$.[44,45] Further differences in our results can be attributed to the incompleteness of the basis sets. In the calculations of Ref. 42 a poorer basis set was used that included polarization functions only through d symmetry. In addition, the BSSE was not evaluated, so that in fact, the dissociation energies they determine are likely upper limits for the hypothetical "BSSE free" results of their basis. The only other *ab initio* results reported to date are the results of Demetropoulos and Lawley.[46] These authors used the MRSD-CI technique and found the ground state to be repulsive at the internuclear distances they studied, 2.30–3.85 a_0, which is expected based on both our and Chiles and Dykstra's results. Finally, our results are in contrast to a Thomas–Fermi damped scaled-Hamiltonian study of Mg–He which predicted a potential mimimum at 3.84 a_0.[6]

Three other studies of Mg–He have been performed, all involving the use of some form of pseudo or model potential.

Bottcher *et al.*[5] diagonalized a Hamiltonian with a model potential containing a Hartree–Fock core interaction term, a damped dispersion term, and additional Born–Mayer repulsive terms. Their study determined that all valence states contained minima of less than 0.05 eV, which is quite large in comparison to our result (0.05 eV = 1.8 mhartree), though it is difficult to tell from their paper whether or not their ground state potential contains a well. Malvern,[6,7] using nearly the same formalism, obtained results similar to Bottcher *et al.*, and it appears that he found no potential minima for the ground state. Finally, Czuchaj *et al.*,[8] have performed semiempirical CI calculations that treat the noble gas and magnesium 2 + ion core as a pseudopotential for the motion of the two valence electrons of Magnesium. The values for their interatomic potentials are listed in Table II. The interaction energies obtained are smaller than our results by approximately a factor of two in the minimum region.

V. Mg(^1S) AND AR(^1S) INTERACTION

The values of the interaction energy and its components through the fourth order of MPPT, obtained with our [7s4p2d 1f] basis for Mg and our [7s4p2d 1f] basis for Ar, for R ranging from 5 to 12 a_0 are listed in Table V. The minimum at the MP4 level occurs around 9 a_0 and with a D_e of 0.2537 mhartree (55.7 cm^{-1}). For Mg$_2$ and Ar$_2$, at the same level of the theory and with the same bases, we reproduced 110% and 75% of the accurate values of D_e, respectively.[20] As in the Mg–He case, one may expect that our potential parameters are determined to some intermediate level of accuracy as those of Mg$_2$ and Ar$_2$. In fact, recent experimental evidence indicates that the potential minimum occurs at an R_e of 8.49 $\pm$ 0.19 a_0 and with a well depth of 0.374 $\pm$ 0.027 mhartree (82 $\pm$ 12 cm^{-1}).[12,47] Then, if we assume that we reproduce at worse 75% of D_e, as for Ar$_2$,[20] then our estimate for D_e would be 74 cm^{-1}, within the error limits of the experiment. Such an assumption may be justified by the fact that the covergence of the MPPT series appears to be less uniform than for Ar$_2$ or Mg$_2$ (see below). However, there is no reason to expect that the Mg–Ar curve is less accurate than the Ar$_2$ curve, therefore it is not likely that the Mg–Ar D_e is greater than 74 cm^{-1}.

TABLE V. The interaction energy and its components for the ground state $^1\Sigma$ of MgAr obtained with basis [7s4p2d 1f] of Mg and [7s4p2d 1f] of Ar. Energies in mhartree, distance in a_0.

R	ΔE^{HL}	ΔE^{SCF}	δ^{SCF}	$\Delta E^{(2)}$	$\Delta E^{(3)}$	$\Delta E^{(4)}$	$\Delta E^{corr}(4)$	$\delta^{corr}(4)$	$\Delta E(4)$
5		26.1587	− 1.0838	− 6.3869	0.3126	− 0.4767	− 6.5510	− 2.9381	19.6056
6	11.87	9.7350	− 0.6911	− 3.9934	0.1933	− 0.2526	− 4.0527	− 1.7214	5.6823
7	3.799	3.3039	− 0.3148	− 2.1904	0.0906	− 0.1223	− 2.2221	− 0.8490	1.0818
8	1.161	1.0320	− 0.1059	− 1.1216	0.0434	− 0.0557	− 1.1339	− 0.3712	− 0.1019
8.5		0.5639	− 0.0594	− 0.7922	0.0315	− 0.0367	− 0.7974	− 0.2438	− 0.2334
9	0.3417	0.3047	− 0.0258	− 0.5581	0.0237	− 0.0240	− 0.5584	− 0.1530	− 0.2537
9.5		0.1631	− 0.0180	− 0.3940	0.0182	− 0.0156	− 0.3914	− 0.1045	− 0.2283
10	0.0972	0.0865	− 0.0094	− 0.2833	0.0178	− 0.0102	− 0.2757	− 0.0671	− 0.1892
11	0.0266	0.0238	− 0.0026	− 0.1454	0.0091	− 0.0046	− 0.1409	− 0.0258	− 0.1172
12	0.0070	0.0063	− 0.0011	− 0.0797	0.0058	− 0.0023	− 0.0762	− 0.0089	− 0.0699

A. Interaction energy in the region of the potential minimum

Table VI lists a decomposition of the individual MPPT contributions for $R = 9\,a_0$. As can be seen, the MPPT series appears to be converging, but in an oscillatory manner, as in Ar_2,[20] and with the $\Delta E^{(4)}$ contribution cancelling the $\Delta E^{(3)}$ contribution. If we compare the series expansion for smaller R, we see that the $\Delta E^{(4)}$ term becomes even larger in magnitude than the $\Delta E^{(3)}$ contribution. This indicates incomplete convergence, and as is seen in the table, is primarily due to the contribution of the triple excitations. At larger R, the $\Delta E^{(3)}$ contribution is larger in magnitude than the $\Delta E^{(4)}$ contributions, and the perturbation series appears to converge rather nicely. We observe then, what appears to be a qualitative change of behavior of MPPT in describing this system as a function of R (similar to that for Mg_2[20,30]); MPPT describes the long-range part of the potential (as further evidenced in our estimation of the C_6 parameter) fairly well, and convergence deteriorates in the short and intermediate range of the potential, where exchange effects are important, though this could just reflect a need to carry the perturbation series to higher order. Also listed in Table VI is the all-electron correlation calculation and its decomposition for $R = 9\,a_0$. As is seen in the table, the components of the MPPT expansion remain nearly constant when corrected for BSSE using the counterpoise method, while the BSSE itself has increased by a factor of 2. The change in the total correlation contributions is only 2%, indicating that the role of the core electrons is minimal. This also indicates that the larger weakly bound species may be suitable for study using *ab initio* pseudopotential methods.

B. The region of large R

The C_6 coefficient was estimated using equation (1) at $R = 15\,a_0$. Again, as with Mg–He, for $i = 2$ and 3, we calculated the interaction energy using a subset of our original bases, without d- and f-symmetry orbitals on Mg and without f-symmetry orbitals on Ar, and obtained the following results:

$$C_6(2) = 180.3, \quad C_6(3) = -18.67, \quad C_6(4) = 5.3 \quad [Ha_0^6]$$

and the pertinent BSSE results are

$$R^{6}\cdot\delta(2) = -1.0, \quad R^{6}\cdot\delta(3) = +0.5,$$
$$R^{6}\cdot\delta(4) = -0.1 \quad [Ha_0^6].$$

Stwalley[3] obtained a result of 165 Ha_0^6 which compares favorably with our value of 166.9 Ha_0^6 (one should recall that since Ar has both s and p valence electrons, that it is impossible to extract a pure C_6 from this type of calculation; cf. Refs. 17 and 34). The semiempirical bounds for C_6 of Certain and Standard are 158–166 Ha_0^6, and our value of C_6 is very close to the upper bound, consistent with our observation that the perturbation expression appears to be effective at large R.

VI. THE EFFECTS OF SCF DEFORMATION AND THE CORRELATION OF THE ELECTRON MOTION ON THE MgHe AND MgAr POTENTIAL CURVES: COMPARISON TO Mg₂, Ar₂, AND He₂

In an effort to understand the underlying nature of the binding in the mixed metal–rare gas systems, we have decomposed the interaction energy into the following components.

(1) The first-order Coulomb and exchange effects can be expressed through the following Heitler–London expression:

$$E^{HL} = \frac{\langle \Psi_A \Psi_B | H \cdot A | \Psi_B \Psi_A \rangle}{\langle \Psi_A \Psi_B | A | \Psi_B \Psi_A \rangle}, \tag{7}$$

where H is the total Hamiltonian for systems A and B, and A is the antisymmetrizer. The wave functions for A and B are constructed from minimal basis sets, with the occupied orbitals described by single contractions. These single contractions are the Fock orbitals obtained from an SCF calculation done on the atoms, in which all of the Gaussian orbitals were left uncontracted. The energy is then calculated using a standard SCF routine.[48] The Heitler–London (HL) interaction energy, ΔE^{HL} is then obtained by subtracting the monomer energies (calculated in the dimer basis).

(2) SCF interaction energy. The interaction energy calculated using the relaxed Heitler–London wave function, which is obtained through SCF iterations ΔE^{SCF}. The difference between ΔE^{HL} and ΔE^{SCF} is termed the SCF-deformation energy.

(3) The sum of the correlation corrections $\Delta E^{corr}(4)$.

TABLE VI. Components of the interaction energy for the $^1\Sigma^+$ ground state of Mg–Ar for $R = 6, 9$, and 12 a_0.

E^{int} component	$R = 6\,a_0$			$R = 9\,a_0$		
		δ_{Mg}	δ_{Ar}		δ_{Mg}	δ_{Ar}
ΔE^{SCF}	9.7350	−0.0982	−0.5929	0.3047	−0.0062	−0.0268
$\Delta E^{(2)}$	−3.9934	−0.0545	−0.9534	−0.5581	−0.0044	−0.1236
$\Delta E^{(3)}$	0.1933	0.0712	−0.0571	0.0237	0.0045	−0.0026
$\Delta E^{(4)}$	−0.2526	−0.0077	−0.0028	−0.0240	−0.0005	−0.0006
DQ	0.5381	−0.0061	0.0021	0.0470	−0.0002	0.0030
SDQ	0.3796	−0.0077	0.0030	0.0481	−0.0005	0.0039
$\Delta E^{corr}(4)$	−4.0527	0.0090	−1.0133	−0.5584	−0.0004	−0.1268
ΔE^{int}	5.6823	−0.0892	−1.6062	−0.2537	−0.0066	−0.1536

Atomic energies

	Ar	Mg
E^{SCF}	−526.783 783 931	−199.609 791 826
$E^{(2)}$	−0.165 429 70	−0.023 475 857
$E^{(3)}$	−0.013 944 025	−0.006 151 432 8
$E^{(4)}$	−0.002 626 614 1	−0.002 344 577 3

E^{int} component	$R = 9\,a_0$ all electron			$R = 12\,a_0$		
		δ_{Mg}	δ_{Ar}		δ_{Mg}	δ_{Ar}
ΔE^{SCF}	0.3047	−0.0062	−0.0268	0.0063	−0.0006	−0.0005
$\Delta E^{(2)}$	−0.5721	−0.0972	−0.2415	−0.0797	0.0001	−0.0084
$\Delta E^{(3)}$	0.0287	0.0047	−0.0011	0.0058	0.0003	0.0002
$\Delta E^{(4)}$	−0.0252	−0.0039	−0.0007	−0.0023	−0.0001	−0.0000
DQ	0.0482	0.0002	0.0032	0.0077	0.0000	0.0002
SDQ	0.0499	−0.0016	0.0033	0.0084	−0.0001	0.0002
$\Delta E^{corr}(4)$	−0.5685	−0.0039	−0.2433	−0.0762	0.0003	−0.0082
ΔE^{int}	−0.2638	−0.0101	−0.2701	−0.0699	−0.0003	−0.0087

A. Mg–He

Shown in Table VII is the decomposition of the interaction energy into the above components for Mg_2, He_2, and Mg–He at $R = 9 \ a_0$. From the table it is apparent that He_2 has little interaction at this distance and undergoes no SCF-deformation upon relaxation of the HL wave function. Mg_2, however, undergoes huge SCF-deformation effects, with relaxation of the wave function lowering the interaction energy by more than 50%. Mg–He experiences some SCF-deformation effects, the interaction energy is lowered by $\approx 25\%$, but the absolute magnitude of the lowering is small compared to Mg_2, being only 3% of the energy of deformation of Mg_2. This can be understood in part as a result of the small size and polarizability of He, and the small field it should pose to Mg, causing little relaxation to take place. This is in contrast to what occurs in the Mg_2 system; the field of the mutally interacting Mg atoms is high and results in large changes of the wave function, and a large lowering of the energy in the SCF process.

Also shown in Table VII is the sum of the correlation contributions to the interaction energy. We note that that the correlation contribution for Mg–He lies intermediate to that of Mg_2 (smaller by a factor of 23) and He_2 (larger by a factor of 30), indicating that a combination rule may be found for the dispersion interaction. We also note that it is larger than, but on the same order of magnitude as the deformation energy. The Mg–He "bond" appears to result from a combination of dispersion and deformation effects, in contrast to the Mg–Ar species (see below). In fact, without the deformation effects, the interaction energy at $9 \ a_0$ would become positive, and the well would disappear at this level of the theory.

B. Mg–Ar

Shown in Fig. 1 are plots of the Heitler–London, the SCF, and $\Delta E^{corr}(4)$ energies as a function of internuclear distance, with a decomposition listed for $R = 9 \ a_0$ in Table VII. As can be seen, the Heitler–London interaction and the $\Delta E(4)$ correlation contributions for Mg–Ar lie near the middle of the corresponding Mg_2 and Ar_2 curves. However, as seen in Fig. 1(b), the SCF curve of Mg_2 is very much lower in energy than the corresponding Heitler–London curve (as noted above), whereas the Mg–Ar and Ar_2 curves undergo very little lowering in energy through SCF iterations. Thus, we see that Mg–Ar undergoes little SCF deformation. The effect on the Mg–Ar potential is to cause the potential minimum to occur at larger R and with a smaller well depth than anticipated using combination rules. Physically, it appears that the relaxation expected at the SCF level
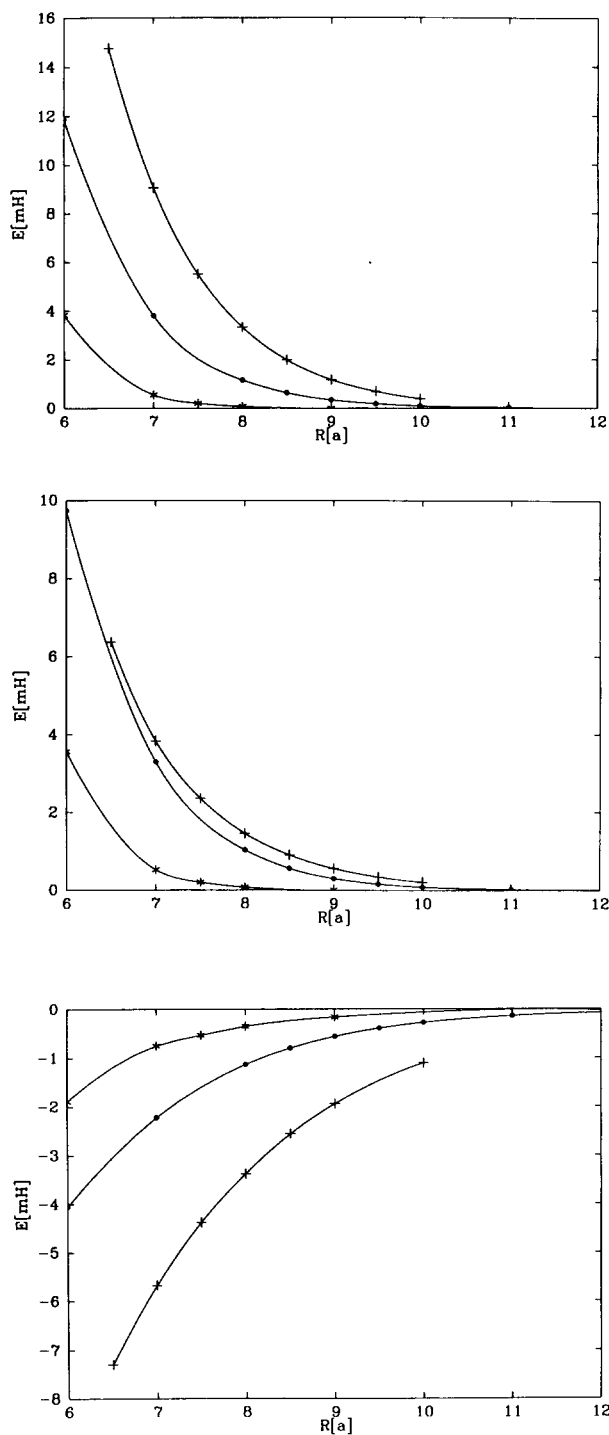

FIG. 1. (a) Plot of the Heitler–London interaction energy, ΔE^{HL}, as a function of R. (+) = Mg_2; ($\bullet$) = Mg–Ar; (*) = Ar_2. (b) Plot of the SCF interaction energy ΔE^{SCF} as a function of R. (+) = Mg_2; ($\bullet$) = Mg–Ar; (*) = Ar_2. (c) Plot of the correlation contribution to the interaction energy $\Delta E^{corr}(4)$, as a function of R. (+) = Mg_2; ($\bullet$) = Mg–Ar; (*) = Ar_2.

TABLE VII. Comparison of ΔE^{HL}, ΔE^{SCF}, and $\Delta E^{corr}(4)$ for He_2, Mg–He, Mg_2, Mg–Ar, and Ar_2 at $R = 9 \ a_0$. All energies in mhartree.

	He_2	Mg–He	Mg_2	Mg–Ar	Ar_2
ΔE^{HL}	0.0000	0.0950	1.1730	0.3420	0.010 28
ΔE^{SCF}	0.0000	0.0751	0.5630	0.3047	0.010 25
$\Delta E^{corr}(4)$	− 0.0030	− 0.0884	− 1.9416	− 0.5584	− 0.162 6

from the interaction of Mg in the field of Ar, and Ar in the field of Mg, though more than 10%, is small compared to the corresponding effect in Mg_2, which is on the order of 50%.

We should note that in other studies of He_2, Ne_2, and Ar_2, the relaxation observed through SCF iterations is minimal, and is typical of the rare gas–dimer interactions. This is in stark contrast to Mg_2, which undergoes large SCF defor-

mation,[20] and this deformation plays an important role in the depth and position of the potential well. We should also note that in a study of the Be dimer[49] and analogous to Mg_2, the SCF deformation was also very large. Furthermore, Chiles and Dykstra[42] study found the Be–Mg well depth and potential minima to occur intermediate to the Be_2 and Mg_2 well depths and potential minima, in contrast to the mixed metal–rare gas complexes studied here. It would appear then, that the van der Waals interactions appear similar amongst families of the elements, possibly giving rise to combination rules for families, but that differences show up between the families, and a failure of combination rules. However, further work is needed in these areas. It would seem that the mixed metal–rare gas dimers are dominated by exchange-repulsion and that only small SCF deformation exists for these pairs, analogous to the rare-gas mixtures which also undergo only very small SCF deformation.

VII. CONCLUSION

We have determined potential curves for the mixed metal–rare gas systems of Mg–He and Mg–Ar. We find that the interaction potentials for these species are governed by the exchange–repulsion in that the mixed pairs undergo little SCF deformation similar to the rare gases, whereas the alkaline earths undergo large SCF deformation. We believe we have the most accurate determination of the Mg–He ground state potential to date, and predict a bound vibrational level to exist. Though the Mg–Ar potential is determined to be shallower than the experimental data indicate at this time, there is no reason to suspect that it is of less quality than our previously determined Ar_2 and Mg_2 potentials, and we look forward to a more accurate determination of the Mg–Ar D_e.

ACKNOWLEDGMENTS

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