

Nature of binding in the alkaline–earth clusters: Be_3 , Mg_3 , and Ca_3

Ilya G. Kaplan^{a)}

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apdo. Postal 70-360, 04510 México, D.F. México and The Computational Center for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, P.O. Box 17910, J. R. Lynch Street, Jackson, Mississippi 39217

Szczepan Roszak

The Computational Center for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, P.O. Box 17910, J. R. Lynch Street, Jackson, Mississippi 39217 and Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wyb. Wyspińskiego 27, 50-370 Wrocław, Poland

Jerzy Leszczynski

The Computational Center for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, P.O. Box 17910, J. R. Lynch Street, Jackson, Mississippi 39217

(Received 6 March 2000; accepted 9 June 2000)

The study of the interaction energy and its many-body decomposition in a broad distance interval for the Be_n , Mg_n , and Ca_n ($n=2,3$) clusters at the SCF and MP4 levels are performed. A comparative analysis of the obtained results allows one to conclude that the only stabilization factor in the dimers is the dispersion forces. So, the alkaline–earth dimers can be attributed to the van der Waals molecules. The trimers are stabilized by the two-body localized dispersion forces and three-body delocalized exchange forces. The binding in the alkaline–earth trimers has a mixed physical (van der Waals) and chemical (nonadditive exchange) nature. An NBO population analysis reveals a relatively large p -population in all clusters. A surprisingly large p -population at the MP4 level is also obtained for the isolated atoms. © 2000 American Institute of Physics.

[S0021-9606(00)30333-6]

I. INTRODUCTION

It is well known that noble gas atoms are bound by van der Waals forces. This results in a weak bond. The weakest measured bond was found in He_2 : the dissociation energy is $D_0=1.2$ mK or $2.38 \cdot 10^{-6}$ kcal/mol (Ref. 1) (the well depth is larger and equals 0.02 kcal/mol). Even in bulk, the noble gas atoms have such small cohesive energy that they are able to form solids only at low temperatures, and He remains liquid at all temperatures. This is a consequence of the closed-shell electronic structure of the noble gas elements. On the other hand, the alkaline earth elements Be, Mg, Ca, etc. have a closed electronic subshell, (ns^2), but form solids with a quite large cohesive energy, see Table I. The cohesive energy in the solid Be equals 3.32 eV/atom which is larger than that in solids of open one-valence ns shell atoms: Li (1.63 eV/atoms), Na (1.10 eV/atom), and Cu (1.0 eV/atom).

The dimers of Be, Mg, and Ca are very weakly bound by the electron correlation effects [at the self-consistent field (SCF) level they are not stable]. Thus, the alkaline–earth dimers can be attributed to the van der Waals molecules. The situation is changed in many-atom clusters, even in trimers (Table II). This is evidently a manifestation of the many-body effects. The crucial role of the three-body forces in the stabilization of the Be_n clusters was previously revealed at the SCF level.^{2–4} More recently it was established at the

Møller–Plesset perturbation theory level up to the fourth order (MP4).^{5,6} The study of binding in the Be_n clusters^{7–9} revealed that the three-body exchange forces are attractive and give an important contribution to the attractive two-body dispersion forces. The latter at equilibrium distances are almost completely compensated by the repulsive two-body exchange forces. This makes the role of the three-body exchange attraction even more important.

In order to reveal the details of binding in the alkaline–earth clusters, it is important to carry out a comparative study of binding in clusters of Be, Mg, and Ca. There are many publications, in addition to those cited above, devoted to calculations of alkaline–earth clusters, see Refs. 10–21, and references therein. But in most of these studies, different computational approaches were applied to calculate the geometry and binding energy. The nature of binding in these clusters was not studied. The only exception, to the best of our knowledge, are two works by Bauschlicher *et al.*^{10,11} In their study of alkaline–earth clusters, the authors came to the conclusion that the promotion of atomic electrons from ns to np orbitals leading to hybridization is a major mechanism responsible for the binding in the alkaline earth compounds. Later on, we will discuss this concept in the connection with our results.

In the present paper, we present the results of accurate calculations at the Møller–Plesset electron correlation level of the distance dependence of the interaction energy and its many-body decomposition for the Be_n , Mg_n , and Ca_n (n

^{a)} Author to whom correspondence should be addressed. Electronic mail: kaplan@fenix.ifisicacu.unam.mx

TABLE I. Some properties of alkaline earth atoms and solids.

	Atoms			Solids	
	Polarizability $10^{-24} \text{ cm}^3 \text{ a}$	ΔE_{at} , kcal/mol ^b	$\langle r_{nl} \rangle^c$	E_c , kcal/mol ^d	T_m , K ^d
Be	5.6	$2s^2 \rightarrow 2s2p^3 P^0$ 62.84	$\langle r_{2s} \rangle = 2.65$	76.5	1562
Mg	10.6	$3s^2 \rightarrow 3s3p^3 P^0$ 62.47	$\langle r_{3s} \rangle = 3.25$	34.7	922
Ca	22.8–25.0	$4s^2 \rightarrow 4s4p^3 P^0$ 43.34 $4s^2 \rightarrow 4s3d^3 D$ 58.14	$\langle r_{4s} \rangle = 4.22$	42.5	1113

^aReference 22.^bReference 23.^cReference 24.^dReference 25.

=2,3) clusters using a reasonably large basis set [6-311+G(3df)]. The calculations are performed also at the SCF level for study the electron correlation contributions to the total interaction energy and its many-body parts. All clusters are calculated at the same level of approximation which is accurate enough to allow meaningful comparisons among clusters with different atoms.

The plan of this paper is as follows: In Sec. II we describe the computational method and present the basic formulas for the energy decomposition. In Sec. III we analyze the numerical results obtained and give a comparative discussion of the nature of binding in the alkaline-earth clusters. A summary and the conclusions of our study are given in Sec. IV.

II. COMPUTATIONAL METHOD AND BASIC FORMULAS FOR ENERGY DECOMPOSITIONS

The calculations presented here were performed with a standard 6-311+G(3df) basis set.^{29–31} The potential energy surfaces scan was performed by means of the Møller–Plesset perturbation theory up to the fourth order (MP4) in the frozen core approximation.^{32,33} The interaction energies were corrected for the basis set superposition error (BSSE) applying the Boys and Bernardi scheme,³⁴ in which the three-body interactions were determined within the trimer

basis set.³⁵ The electronic density distribution was studied within the population analysis scheme based on the natural bond orbitals.^{36,37} Population analysis was performed for the SCF density and the MP4(SDQ) generalized density determined by applying the Z-vector concept.³⁸ These data and all other results presented in this work were obtained by utilizing the GAUSSIAN-98 code.³⁹

The quality of the calculations were assured by a comparison with the Møller–Plesset calculations with no frozen core, $1s^2$ frozen, and $1s^2 2s^2 2p^6$ frozen core electrons for Be, Mg, and Ca clusters, respectively. The inclusion of more electrons in the correlation energy calculations slightly lowers two- as well as three-body interaction energies. The largest frozen space in the case of Ca clusters leads to total energy changes around 10% and does not affect the qualitative picture of the interactions studied. The test calculations were also performed by the coupled cluster method with single and double substitutions from the Hartree–Fock determinant and with inclusion of triple excitations noniteratively, CCSD(T).^{40,41} The calculated interaction energies are within few percent of those of the Møller–Plesset calculations, indicating that the choice of the MP4(SDTQ) approach is well justified as a basic tool for the presented studies.

In Table II we present the results of our calculations of the equilibrium geometry and binding energy together with published data. A comparison of our results with literature data indicates a quite satisfactory agreement. The values of the binding energy for the Be₃ and Mg₃ trimers are very close to the best estimations in Ref. 18.

In all variational methods, the interaction energy is not calculated directly even if the Møller–Plesset perturbation theory is used. The interaction energy is expressed as the difference,

$$E_{\text{int}}(N) = E(N) - NE_a, \quad (1)$$

where $E(N)$ is the total energy of cluster A_N ; E_a is the atomic energy calculated at the same level of accuracy as $E(N)$. For taking into account the BSSE, the atomic energy in Eq. (1) was calculated using the dimer basis set for $N=2$ and the trimer basis set for $N=3$.

In order to check the convergence of the MP perturbation series, we calculated separately the perturbation contributions $\varepsilon_{\text{MP}}^{(n)}$ to the interaction energy in each order,

TABLE II. Comparison of our calculations with literature data for the equilibrium geometry; distances are in Å, energies are in kcal/mol, $E_b = -E_{\text{int}}$.

Refs.	Method of calculation	Be ₂		Be ₃		Mg ₂		Mg ₃		Ca ₂		Ca ₃	
		r_0	E_b	r_0	E_b	r_0	E_b	r_0	E_b	r_0	E_b	r_0	E_b
12	CASSCF/CI	2.50	1.86	2.23	19.02								
14	MRCI			2.22	22.4			3.37	6.3				
19	MP4(SDTQ)			2.23	21.6								
18	Best estimations based on MP2-R12			2.20	26.9			3.37	8.0				
11	CI											3.97	11.53
17	MRCI											4.16	12.10
26	Experiment	2.45	2.26 ± 0.08										
27, 28	Experiment					3.89	1.157 ± 0.003						
this work	MP4(SDTQ)	2.56	1.83	2.24	25.90	3.92	1.09	3.32	7.12	4.56	2.14	4.12	11.66

TABLE III. Contributions to the interaction energy of dimers at different levels of calculation, $\Delta E^{\text{corr}} = \epsilon_{\text{MP}}^{(2)} + \epsilon_{\text{MP}}^{(3)} + \epsilon_{\text{MP}}^{(4)}$, $\Delta E_{\text{int}}^{\text{MP4}} = E_{\text{int}}^{\text{SCF}} + \Delta E^{\text{corr}}$; energies are in kcal/mol.

$r, \text{\AA}$	$E_{\text{int}}^{\text{SCF}}$	$\epsilon_{\text{MP}}^{(2)}$	$\epsilon_{\text{MP}}^{(3)}$	$\epsilon_{\text{MP}}^{(4)}$	ΔE^{corr}	$E_{\text{int}}^{\text{MP4}}$
(a) Be ₂						
1.5	103.87	-17.38	-4.37	-3.01	-24.762	79.106
2.0	22.54	-12.39	-2.04	-1.39	-15.81	6.73
2.5	6.82	-7.21	-0.89	-0.50	-8.60	-1.78
3.0	3.00	-3.78	-0.43	-0.07	-4.29	-1.29
3.5	1.35	-1.96	-0.24	0.03	-2.18	-0.83
4.0	0.56	-1.05	-0.15	0.03	-1.17	-0.61
4.5	0.21	-0.57	-0.09	0.02	-0.64	-0.43
5.0	0.07	-0.31	-0.06	0.01	-0.36	-0.29
5.5	0.02	-0.18	-0.02	0.00	-0.20	-0.18
6.0	0.00	-0.10	-0.02	0.00	-0.11	-0.11
6.5	0.00	-0.06	-0.01	0.00	-0.06	-0.06
7.0	0.00	-0.04	0.00	0.00	-0.04	-0.04
(b) Mg ₂						
1.5	269.89	-11.65	-2.73	-1.45	-15.83	254.06
2.0	94.39	-9.76	-1.96	-1.00	-12.73	81.66
2.5	30.22	-7.80	-1.38	-0.68	-9.86	20.36
3.0	9.84	-5.52	-0.85	-0.38	-6.75	3.09
3.5	3.55	-3.54	-0.50	-0.16	-4.20	-0.65
4.0	1.40	-2.16	-0.29	-0.04	-2.49	-1.08
4.5	0.58	-1.30	-0.16	-0.02	-1.48	-0.90
5.0	0.23	-0.75	-0.12	0.00	-0.87	-0.65
5.5	0.08	-0.44	-0.07	0.00	-0.51	-0.43
6.0	0.04	-0.29	-0.05	0.00	-0.33	-0.29
6.5	0.00	-0.17	-0.02	0.00	-0.19	-0.18
7.0	0.00	-0.12	-0.01	0.00	-0.12	-0.12
8.0	0.00	-0.04	0.00	0.00	-0.04	-0.04
(c) Ca ₂						
2.5	95.07	-6.91	-2.05	-1.19	-10.15	84.92
3.0	37.68	-5.95	-1.38	-0.84	-8.17	29.51
3.5	13.07	-4.88	-1.00	-0.56	-6.44	6.63
4.0	4.12	-3.73	-0.72	-0.35	-4.80	-0.68
4.5	1.22	-2.68	-0.48	-0.19	-3.35	-2.13
5.0	0.38	-1.85	-0.29	-0.09	-2.23	-1.85
5.5	0.14	-1.23	-0.18	-0.04	-1.45	-1.31
6.0	0.06	-0.80	-0.12	0.00	-0.92	-0.86
6.5	0.02	-0.53	-0.06	0.00	-0.59	-0.57
7.0	0.01	-0.34	-0.05	0.00	-0.39	-0.38
8.0	0.00	-0.15	-0.02	0.00	-0.17	-0.17
9.0	0.00	-0.06	-0.02	0.00	-0.08	-0.08
10.0	0.00	-0.04	0.00	0.00	-0.04	-0.04

$$\begin{aligned}\epsilon_{\text{MP}}^{(2)} &= E_{\text{int}}^{\text{MP2}} - E_{\text{int}}^{\text{SCF}}, \\ \epsilon_{\text{MP}}^{(3)} &= E_{\text{int}}^{\text{MP3}} - E_{\text{int}}^{\text{MP2}}, \\ \epsilon_{\text{MP}}^{(4)} &= E_{\text{int}}^{\text{MP4}} - E_{\text{int}}^{\text{MP3}}.\end{aligned}\quad (2)$$

According to its definition, the correlation energy at the MP4 level is equal to

$$\Delta E^{\text{corr}} = E_{\text{int}}^{\text{MP4}} - E_{\text{int}}^{\text{SCF}} = \sum_{n=2}^4 \epsilon_{\text{MP}}^{(n)}.\quad (3)$$

In Table III we present $\epsilon_{\text{MP}}^{(n)}$ for the three calculated dimers, Be₂, Mg₂, and Ca₂. At all distances the convergence is quite good.

Let us express the MP series as the ratios to the second order contribution

TABLE IV. Interaction energy for dimers at the equilibrium distance at different levels of calculation, in kcal/mol.

Dimers	$E_{\text{int}}^{\text{SCF}}$	$\epsilon_{\text{MP}}^{(2)}$	$\epsilon_{\text{MP}}^{(3)}$	$\epsilon_{\text{MP}}^{(4)}$	ΔE^{corr}	$E_{\text{int}}^{\text{MP4}}$
Be ₂ $r_0 = 2.56 \text{\AA}$	6.12	-6.71	-0.81	-0.43	-7.94	-1.83
Mg ₂ $r_0 = 3.92 \text{\AA}$	1.62	-2.34	-0.32	-0.06	-2.72	-1.09
Ca ₂ $r_0 = 4.56 \text{\AA}$	1.05	-2.56	-0.46	-0.17	-3.19	-2.14

$$\Delta E^{\text{corr}} = \epsilon_{\text{MP}}^{(2)} \left(1 + \frac{\epsilon_{\text{MP}}^{(3)}}{\epsilon_{\text{MP}}^{(2)}} + \frac{\epsilon_{\text{MP}}^{(4)}}{\epsilon_{\text{MP}}^{(2)}} \right).\quad (4)$$

At the equilibrium distance (Table IV), the MP series (4) are the following:

$$\begin{aligned}\text{Be}_2: & \epsilon_{\text{MP}}^{(2)}(1 + 0.12 + 0.06), \\ \text{Mg}_2: & \epsilon_{\text{MP}}^{(2)}(1 + 0.14 + 0.03), \\ \text{Ca}_2: & \epsilon_{\text{MP}}^{(2)}(1 + 0.18 + 0.07).\end{aligned}\quad (5)$$

Thus, the limitation of our calculations to the MP4 level is quite justified.

The many-body decomposition of the interaction energy at different approximations is performed according to the general definitions, see Refs. 42, 5. For trimers we have only the two- and three-body interaction energies. In the homoatomic case they are represented by the following formulas:

$$E_2(A_3) = \sum_{a < b} \epsilon_{ab},\quad (6)$$

$$\epsilon_{ab} = E(ab) - 2E_a,\quad (7)$$

where $E(ab)$ is the total energy of two atoms at the distance they have in the trimer abc . In a general case of a nonsymmetrical triangle, the sum (6) contains three different two-body interaction energies. The three-body interaction energy is defined as the difference

$$E_3(A_3) = E(A_3) - E_2(A_3) - 3E_a,\quad (8)$$

where $E(A_3)$ denotes the total energy of trimer A_3 .

Formulas (6)–(8) were applied to the calculations of the two- and three-body contributions to the interaction energy at the SCF and MP4 levels and for the decomposition of the electron correlation energy.

III. NUMERICAL RESULTS AND DISCUSSION

As follows from Table III, the interaction energy at the SCF level is positive for all three dimers at all distances. It is the electron correlation energy that stabilized the close-subshell-atom dimers. The potential energy curves are very shallow with the depths of the well about several kcal/mol. The equilibrium distance rises from $r_0 = 2.56 \text{\AA}$ for Be₂ to $r_0 = 4.56 \text{\AA}$ for Ca₂. The increase of the equilibrium distance in the row Be₂, Mg₂, and Ca₂ is well correlated with an increase in the average radius of the atomic valence shell (Table I). However, the binding energy does not have such monotonic behavior. The decrease of E_b from 1.83 kcal/mol

for Be₂ to 1.09 kcal/mol for Mg₂ alters on the increase of E_b to 2.14 kcal/mol for Ca₂. The equilibrium distance for Ca₂ is very large (4.56 Å), and it could be expected that the bond will be weaker than in Mg₂. But this is not a case, the increase of the equilibrium distance compared with that in Mg₂ does not lead to a weaker bond. It is explained by the smaller repulsive SCF energy and the larger correlation attraction at the equilibrium distances in the Ca₂ dimers, in respect to the Mg₂ dimer, see Table IV. The same nonmonotonic behavior takes place for the binding energy of the trimers; $E_b = 25.9, 7.12,$ and 11.66 kcal/mol for Be₃, Mg₃, and Ca₃, respectively (Table II). It can be expected that this trend is also preserved in large clusters because in solid alkaline earths the cohesive energy and melting temperature show similar behavior (Table I).

It is well known that physical contributions to the SCF energy can be classified as the electrostatic, exchange, induction, and some additional interactions not having such clear physical meaning.^{42–44} Atoms with closed subshells have no multipole moments and their electrostatic and induction interactions have a pure overlap origin from which follows their short-range character. The exchange interaction between atoms with closed subshells (or almost closed, as we will see later, for the alkaline atoms, this is the case) is repulsive, as in the noble-gas atom systems. All this leads to the instability of the alkaline earth dimers at the SCF approximation. They are stabilized by the attractive electron correlation forces.

At large distances, the electron correlation energy can be interpreted as a dispersion energy. At intermediate distances where the overlap of the atomic valence shells becomes essential, the dispersion forces cannot be defined without allowing for exchange effects. At these distances the multipole expansion is not valid.⁴² It is instructive to compare the magnitudes of the pure dispersion energy and the electron correlation energy at different distances.

The energy of the dispersion interaction between two atoms can be presented with fine precision as a sum of three terms,

$$E_2^{\text{disp}} = - \left(\frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} \right), \quad (9)$$

where the dipole–dipole (r^{-6}), dipole–quadrupole (r^{-8}), and dipole–octupole plus quadrupole–quadrupole (r^{-10}) dispersion interactions are taken into account. The dispersion coefficients C_n for the Be, Mg, and Ca atoms were estimated in Ref. 45 by the Padé approximate method. Using the values of C_n converted to [(kcal/mol)Å^{*n*}] units, we have found the sum (9) at equilibrium and large distances and compare it in Table V with ΔE^{corr} from Tables III and IV. As follows from Table V, at large distances the electron correlation energy coincides with the pure dispersion energy with very good precision; for Be₂ at $r \geq 5$ Å, for Mg₂ at $r \geq 6$ Å, and for Ca₂ at $r \geq 9$ Å.

At equilibrium distances, the absolute value of the pure dispersion energy is much larger (in the case of Be₂ in 10 times!) than ΔE^{corr} . This means that the exchange and overlap contributions to the electron correlation energy are repulsive and cause a decrease in the dispersion attraction. At

TABLE V. Comparison of E_2^{disp} , Eq. (9), with ΔE^{corr} for equilibrium and large distances, in kcal/mol.

<i>r</i> , Å	Be ₂		Mg ₂		Ca ₂	
	E_2^{disp}	ΔE^{corr}	E_2^{disp}	ΔE^{corr}	E_2^{disp}	ΔE^{corr}
2.56	-79.62	-7.94				
3.92			-8.95	-2.27		
4.56					-14.40	-3.19
5.00	-0.35	-0.36	-1.29	-0.87	-6.85	-2.23
6.00	-0.10	-0.11	-0.35	-0.33	-1.68	-0.92
7.00	-0.03	-0.04	-0.11	-0.12	-0.55	-0.39
8.00			-0.04	-0.04	-0.22	-0.17
9.00					-0.10	-0.08
10.0					-0.05	-0.04

large distances, the dispersion energy in Ca₂ is about five times larger than that in Mg₂. This is correlated with the larger value of the polarizability of the Ca atom compared with the Mg atom (Table I).

Let us now turn to the trimers. In Table VI we present the interaction energy and its many-body decomposition for trimers Be₃, Mg₃, and Ca₃ in the equilateral triangle conformation in a wide distance range. The trimers as well as dimers are not stable in the SCF approximation. The SCF energy is positive at all calculated distances. On the other hand, the electron correlation corrections are negative and lead to stabilization of the alkaline–earth trimers. A more detailed analysis of the nature of binding is based on the many-body decomposition of the interaction energy,

$$E_{\text{int}}^{\text{MP4}}(A_3) = E_2^{\text{MP4}}(A_3) + E_3^{\text{MP4}}(A_3), \quad (10)$$

which is presented in Tables VI and VII.

The three-body interaction energy E_3^{MP4} is negative for all distances while E_2^{MP4} at small distances is positive and becomes negative at distances near equilibrium and larger. The ratio $|E_3^{\text{MP4}}/E_2^{\text{MP4}}|$ passes with distance through a maximum. For Be₃ and Mg₃ this maximum is located near the equilibrium distance. The extremely large values of the ratio of the three-body to two-body energy for the equilibrium conformations of Be₃ and Mg₃ (see Table VII) is connected with almost zero values of the two-body interaction energies [the equilibrium distance in the Be₃ and Mg₃ equilateral triangle is located in the vicinity of the intersection of the $E_2(3)$ potential curve and the abscissa axis]. Thus, in the frame of the many-body decomposition of the interaction energy, we have to conclude that for the Be₃ and Mg₃ trimers, the dominant factor of their stability are the three-body forces. For the Ca₃ trimer, the two-body contribution to the interaction energy is non-negligible and amounts to 38% although the three-body interactions are a main contributor to the stability of the cluster.

As discussed above, the equilibrium distances for the dimers are rather large, especially for Mg₂ and Ca₂. The addition of one more atom leads to a decrement in the equilibrium interatomic distance. In an equilateral triangle (the conformation which is the most stable conformation in the case of close-subshell-atom trimers) according to our calculations, the largest reduction, 0.6 Å, is revealed for Mg₃. However, for Be₃ and Ca₃, the reduction is also large

TABLE VI. Many-body energy decomposition for trimers in the equilateral triangle conformation (C_{3v}) at the SCF and MP4 levels; energies are in kcal/mol.

$r, \text{\AA}$	$\Delta E_{\text{int}}^{\text{MP4}}$	$E_{\text{int}}^{\text{SCF}}$	ΔE^{corr}	E_2^{MP4}	E_2^{SCF}	ΔE_2^{corr}	E_3^{MP4}	E_3^{SCF}	ΔE_3^{corr}	$\left \frac{E_3^{\text{MP4}}}{E_2^{\text{MP4}}} \right $
(a) Be ₃										
1.5	121.90	147.02	-25.12	236.57	311.59	-75.02	-114.67	-164.57	49.90	0.48
2.0	-18.41	6.39	-24.80	19.79	67.62	-47.84	-38.19	-61.23	23.04	1.93
2.5	-21.52	2.54	-24.07	-5.52	20.46	-25.98	-16.01	-17.92	1.91	2.90
3.0	-8.52	4.27	-12.79	-3.99	8.98	-12.97	-4.52	-4.71	0.18	1.13
3.5	-3.56	2.81	-6.38	-2.60	4.07	-6.66	-0.97	-1.26	0.29	0.37
4.0	-2.03	1.37	-3.39	-1.84	1.69	-3.54	-0.18	-0.33	0.14	0.10
4.5	-1.32	0.55	-1.87	-1.32	0.62	-1.94	0.00	-0.07	0.07	0.00
5.0	-0.84	0.19	-1.04	-0.85	0.20	-1.05	0.00	0.00	0.00	0.00
5.5	-0.52	0.06	-0.58	-0.53	0.05	-0.58	0.00	0.00	0.00	0.00
6.0	-0.33	0.02	-0.35	-0.36	0.00	-0.36	0.00	0.00	0.00	0.00
6.5	-0.21	0.00	-0.21	-0.21	0.00	-0.21	0.00	0.00	0.00	0.00
7.0	-0.13	0.00	-0.13	-0.13	0.00	-0.13	0.00	0.00	0.00	0.00
(b) Mg ₃										
1.5	654.51	691.49	-39.98	761.43	809.33	-47.89	-106.92	-117.83	10.91	0.14
2.0	178.22	209.51	-31.29	244.55	283.14	-38.59	-66.33	-73.63	7.30	0.27
2.5	28.75	55.61	-26.85	60.81	90.63	-29.82	-32.05	-35.02	2.97	0.53
3.0	-4.42	15.86	-20.28	9.09	29.54	-20.44	-13.52	-13.68	0.16	1.49
3.5	-6.81	5.88	-12.69	-2.10	10.62	-12.73	-4.71	-4.74	0.03	2.24
4.0	-4.73	2.66	-7.39	-3.39	4.20	-7.59	-1.34	-1.54	0.19	0.40
4.5	-3.07	1.24	-4.31	-2.75	1.71	-4.46	-0.33	-0.48	0.15	0.12
5.0	-2.02	0.55	-2.57	-1.98	0.68	-2.65	-0.05	-0.13	0.08	0.03
5.5	-1.35	0.22	-1.57	-1.34	0.24	-1.58	0.00	-0.03	0.03	0.00
6.0	-0.88	0.09	-0.97	-0.87	0.09	-0.96	0.00	0.00	0.00	0.00
6.5	-0.61	0.00	-0.61	-0.58	0.00	-0.58	0.00	0.00	0.00	0.00
7.0	-0.37	0.00	-0.37	-0.36	0.00	-0.36	0.00	0.00	0.00	0.00
(c) Ca ₃										
2.5	195.43	222.02	-26.59	253.26	284.99	-31.72	-57.84	-62.97	5.13	0.23
3.0	51.22	73.30	-22.08	87.37	112.88	-25.51	-36.15	-39.58	3.43	0.41
3.5	0.31	18.94	-18.63	19.03	39.10	-20.07	-18.72	-20.16	1.44	0.98
4.0	-11.38	3.55	-14.94	-2.52	12.31	-14.83	-8.86	-8.76	-0.10	3.52
4.5	-10.18	0.26	-10.43	-6.59	3.65	-10.24	-3.59	-3.39	-0.19	0.54
5.0	-6.91	-0.12	-6.79	-5.70	1.15	-6.85	-1.20	-1.27	0.06	0.21
5.5	-4.36	-0.05	-4.31	-3.99	0.41	-4.41	-0.37	-0.46	0.09	0.09
6.0	-2.74	0.00	-2.74	-2.65	0.13	-2.79	-0.09	-0.14	0.05	0.03
6.5	-1.78	0.00	-1.78	-1.73	0.06	-1.79	0.00	0.00	0.00	0.00
7.0	-1.18	0.00	-1.18	-1.17	0.00	-1.17	0.00	0.00	0.00	0.00

enough; 0.32 Å and 0.44 Å, respectively. The explanation of this decrement is based on the interplay of the two and three-body interactions in the cluster formation;⁵ the attractive three-body forces become larger with a decrease in the atom-atom distances while the two-body forces undergo small changes because of the relative flatness of the two-body potential curves.

In the same manner, as was done for the full interaction energy, the two- and three-body interaction energies can also be decomposed on the SCF and electron correlation parts,

$$E_n^{\text{MP4}} = E_n^{\text{SCF}} + \Delta E_n^{\text{corr}}, \quad n = 2, 3. \quad (11)$$

The two-body SCF energy for an equilateral triangle is equal to

TABLE VII. Interaction energy and the many-body decomposition at the equilibrium geometry for the C_{3v} symmetry, in kcal/mol.

Trimer	$E_{\text{int}}^{\text{MP4}}$	$E_{\text{int}}^{\text{SCF}}$	ΔE^{corr}	E_2^{MP4}	E_2^{SCF}	ΔE_2^{corr}	E_3^{MP4}	E_3^{SCF}	ΔE_3^{corr}	$\frac{E_3^{\text{MP4}}}{E_2^{\text{MP4}}}$
Be ₃ $r_0 = 2.24 \text{\AA}$	-25.90	0.60	-26.50	-0.79	35.45	-36.24	-25.11	-34.80	9.75	31.8
Mg ₃ $r_0 = 3.32 \text{\AA}$	-7.12	8.06	-15.18	-0.15	15.00	-15.15	-6.97	-6.94	-0.03	46.5
Ca ₃ $r_0 = 4.12 \text{\AA}$	-11.66	2.16	-13.82	-4.44	9.15	-13.59	-7.22	-6.98	-0.23	1.6

$$E_2^{\text{SCF}}(A_3) = 3E_{\text{int}}^{\text{SCF}}(A_2). \quad (12)$$

It indicates that the physical sense of the two-body SCF energy in trimers is the same as the SCF interaction energy in dimers; it is predominantly the exchange interactions which are repulsive for two interacting atoms with closed subshells. The attractive contributions from the electrostatic and induction energies which exist only in the overlap region are less than the repulsive exchange contribution. This is the reason that $E_2^{\text{SCF}}(A_3)$ is positive for the alkaline trimers in all calculated distance regions.⁴⁶

The different situation is in the case of the three-body SCF energy. The main contribution to $E_3^{\text{SCF}}(A_3)$ is given by the three-body exchange forces. These forces originate from the three-atomic electron exchange which mixes electrons of all three atoms. In closed-shell-atom systems, contrary to the two-body exchange forces, the three-body exchange forces are attractive and make a contribution to the stabilization of trimers.

The two-body electron correlation energy, $\Delta E_2^{\text{corr}}(A_3)$, as in the case of dimers, is reduced at large distances to the dispersion energy. At intermediate distances, it contains both the exchange and dispersion contributions which cannot be separated. The exchange effects decrease the dispersion attraction; nevertheless, the two-body electron correlation appears as a main factor of stabilization, especially for the Mg_3 and Ca_3 trimers.

The three-body electron correlation energy, $\Delta E_3^{\text{corr}}(A_3)$, at large distances can be represented as the Axilrod–Teller three-body dispersion energy⁴⁷

$$E_3^{\text{dis}}(A_3) = \frac{C_9}{r_{ab}^3 r_{ac}^3 r_{bc}^3} (1 + 3 \cos \theta_a \cos \theta_b \cos \theta_c). \quad (13)$$

For an equilateral triangle, Eq. (13) is transformed to

$$E_3^{\text{disp}}(A_3) = \frac{11}{8} \frac{C_9}{r_{ab}^9}. \quad (14)$$

According to Eq. (14), the three-body dispersion energy is positive and so is ΔE_3^{corr} at large distances. At intermediate distances, the negative contributions from the three-body exchange and overlap effects can lead to negative values for ΔE_3^{corr} . This is what is revealed for Ca_3 and, close to the equilibrium distances, for Mg_3 .

Note that the larger value of binding energy $E_b(\text{Ca}_3) = 11.66$ kcal/mol compared with $E_b(\text{Mg}_3) = 7.12$ kcal/mol in spite of the greater equilibrium distance in the Ca_3 trimer is due to the smaller value of the repulsive SCF energy for the Ca_3 : $E_2^{\text{SCF}}(\text{Ca}_3) = 9.15$ kcal/mol and $E_2^{\text{SCF}}(\text{Mg}_3) = 15$ kcal/mol. This results in a greater stability of Ca_3 although the total attractive contribution for Ca_3 is smaller than for Mg_3 : $\Delta E_2^{\text{corr}} + E_3^{\text{SCF}} + \Delta E_3^{\text{corr}} = -20.8$ and -22.12 kcal/mol for Ca_3 and Mg_3 , respectively (see Table VII).

It is instructive to study the vacant atomic orbital population in the dimers and trimers. As mentioned in the Introduction, in the 1980s Bauschlicher *et al.*^{10,11} came to the conclusion that the promotion of ns -electrons to np -orbitals leading to the sp -hybridization is the main mechanism responsible for binding in the alkaline–earth clusters. This

TABLE VIII. The net valence population, Δn_i^a for the isolated atoms and clusters at the equilibrium geometry, obtained by the Natural Bond Orbital Analysis at the SCF and MP4 levels.

$A_n/1$	SCF				MP4			
	ns	$(n+1)s$	np	nd	ns	$(n+1)s$	np	nd
Be	0.000	0.000	0.000	0.000	-0.135	0.004	0.130	0.001
Be_2	-0.044	0.006	0.037	0.001	-0.199	0.008	0.185	0.006
Be_3	-0.257	0.005	0.246	0.005	-0.315	0.009	0.288	0.016
Mg	0.000	0.000	0.000	0.000	-0.112	0.004	0.105	0.003
Mg_2	-0.007	0.001	0.005	0.000	-0.123	0.004	0.113	0.005
Mg_3	-0.045	0.002	0.040	0.002	-0.173	0.005	0.154	0.012
Ca	0.000	0.000	0.000	0.000	-0.138	0.003	0.124	0.011
Ca_2	-0.016	0.002	0.011	0.003	-0.161	0.005	0.139	0.018
Ca_3	-0.074	0.003	0.057	0.015	-0.229	0.006	0.184	0.039

^aFor atoms $\Delta n_1^{\text{MP4}}(A) = n_1^{\text{MP4}}(A) - n_1^{\text{SCF}}(A)$, for clusters $\Delta n_1^{\text{MP4}}(A_n) = n_1^{\text{MP4}}(A_n) - n_1^{\text{SCF}}(A)$, the similar definition is for Δn_1^{SCF} , therefore $\Delta n_1^{\text{SCF}}(A) = 0$.

conclusion was based on study of the SCF Mulliken population analysis. At the present, we can perform more precise analyses using the natural bond orbital (NBO) analysis and calculate it at the electron correlation level.

In Table VIII we present the net population of valence orbitals in dimers and trimers. We have obtained not only the p -population but partly the d -population (for the Ca clusters to a larger extent). The latter is correlated with experimental atomic excitation energies ΔE_{at} .²³ According to Table I, the energy of the $4s \rightarrow 3d$ excitation in the Ca atom is even smaller than the $ns \rightarrow np$ excitation energies in the Be and Mg atoms. On the other hand, there is no quantitative relation between ΔE_{at} and the net population numbers Δn_l in Table VIII. The magnitude of $\Delta E(ns \rightarrow np)$ in Be is larger than that in Ca, nevertheless, the np -population in the Be clusters is larger than in the Ca clusters.

We have also calculated the NBO valence population at the MP4 level for the isolated atoms. It could be expected that the inclusion of the electron correlation effects leads to some population of the vacant (in the SCF approximation) atomic orbitals. But the values obtained are surprisingly large. The p -population in the Mg and Ca atoms are only slightly smaller than that in their dimers, and in the Be atom the population is 0.7 of the p -population in Be_2 .

The calculation in Ref. 10 was performed at the SCF level. In the frame of the latter, the isolated atoms are not populated at the excited orbitals. The authors¹⁰ found the ratio of p -population in different trimers proportional to the ratio of their dissociation energies. However, at an electron correlation level because of the p -population in the isolated atoms, we cannot expect such proportionality although the amount of the p -population in trimers reflects qualitatively the bond strength in the alkaline–earth clusters.

We also have to take into consideration that some of atom–atom interactions, which enhance the excited orbital population, lead to the antibonding state. The last statement is confirmed by the valence orbital population at the SCF level. According to Table VIII, at the SCF level there is a non-negligible p -population, especially for trimers. But in the SCF approximation, the dimers and trimers are not stable. Thus, the repulsive SCF interactions also lead to the

vacant orbitals population, although this kind of hybridization has an antibonding character. The same is true for the repulsive ΔE_3^{corr} interactions in the Be_3 case.

Note that the calculations at large distances, at which there are mainly the pure dispersion forces, give the same values of the p - and d -population as for the isolated atoms; thus, the pure dispersion forces without exchange contributions do not enhance the excited orbital population, at least at large distances. It is also important to stress that for studies of the influence of the interatomic interactions on the promotion of ns -electrons to the vacant orbitals, we have to consider, as a reference level, the valence orbital population in the isolated atoms calculated at an appropriate electron correlation level.

IV. CONCLUSIONS

The alkaline dimers and trimers studied in this work are unstable at the SCF level. They are stabilized by the electron correlation energy. For a comparative study of the stability of the closed-subshell atom clusters, we have to consider the interplay of the two interactions, exchange and dispersion. In dimers the exchange interactions are repulsive. The main stabilization factor in dimers is the dispersion forces. Thus, the alkaline–earth dimers to a great extent can be attributed to van der Waals bonded molecules.

The situation in trimers is more complicated. In the frame of the many-body decomposition, we have to conclude that the main factor in the trimer stability is the three-body forces; they predominate in Be_3 and Mg_3 and contribute more than 60% to the binding energy in Ca_3 . The reason is that at equilibrium distances the attractive two-body correlation interactions are almost compensated by the repulsive two-body SCF interactions.

In the three-body energy, the attractive contribution comes from E_3^{SCF} which has the exchange nature. This attraction is essentially larger than the three-body electron correlation energy, ΔE_3^{corr} (Table VII), and it provides the crucial role of the three-body forces in the trimer stability. But if we consider only the stabilization factors in the trimer stability selecting them from Table VII, we obtain the two main stabilization energies; ΔE_2^{corr} and E_3^{SCF} . Thus, the alkaline–earth trimers are stabilized by the two-body localized dispersion forces and three-body delocalized exchange forces. As was revealed recently for Be_3 (Refs. 6–9) and has been confirmed in this study, the binding in the alkaline–earth trimers has a mixed physical (van der Waals) and chemical (delocalized exchange) nature. This type of binding, as we expect, will be preserved in larger alkaline–earth clusters.

The NBO population analysis reveals a sufficiently large p -population in clusters. This p -population does not necessarily lead to binding, e.g., we have obtained the p -population also at the SCF level where studied clusters are not stable. More remarkable is the surprisingly large amount of the p -population obtained for the isolated atoms at the MP4 level. From this follows that the alkaline–earth atoms, assumed traditionally as the closed ns -subshell atoms, can to some extent manifest the anisotropic p -symmetry behavior.

It is important to find the experimental evidences of this theoretical finding.

ACKNOWLEDGMENTS

I.G.K. is grateful to John Murrell for the hospitality and numerous valuable discussions during his stay at Sussex University. This work was facilitated in part by an agreement of scientific collaboration between the Mexican Academy of Sciences and the Royal Society (London) and by the projects IN108697 of DGAPA UNAM and 32227-E of CONACYT (Mexico), the NSF Grant No. 9805465, Wroclaw University of Technology Grant No. 341–794, and the U.S. Army High Performance Computing Research Center under the auspices of the Department of Army, Army Research Laboratory cooperative agreement No. DAAH04-95-2-0003/Contract No. DAAH04-95-C-0008. This work does not necessarily reflect the policy of the USA government, and no official endorsement should be inferred. We would like to thank the Mississippi Center for Supercomputing Research, Poznan and Wroclaw Supercomputing and Networking Centers, and the Interdisciplinary Center for Mathematical and Computational Modeling of Warsaw University for a generous allotment of computer time.

¹F. Luo, G. Kim, G. C. McBane, C. F. Giese, and W. R. Gentry, *J. Chem. Phys.* **98**, 9687 (1993); **99**, 10084 (1993).

²W. Kolos, F. Nieves, and O. Novaro, *Chem. Phys. Lett.* **41**, 431 (1976).

³O. Novaro and W. Kolos, *Chem. Phys. Lett.* **67**, 5066 (1977).

⁴J. P. Daudey, O. Novaro, W. Kolos, and M. Berrondo, *J. Chem. Phys.* **71**, 4297 (1979).

⁵I. G. Kaplan, J. Hernández-Cobos, I. Ortega-Blake, and O. Novaro, *Phys. Rev. A* **53**, 2493 (1996).

⁶I. G. Kaplan, *Adv. Quantum Chem.* **31**, 137 (1999).

⁷J. Hernandez-Cobos, I. G. Kaplan, and J. N. Murrell, *Mol. Phys.* **92**, 63 (1997).

⁸I. G. Kaplan, *Pol. J. Chem.* **72**, 1454 (1998).

⁹I. G. Kaplan, *Int. J. Quantum Chem.* **74**, 241 (1999).

¹⁰C. W. Bauschlicher, Jr., P. S. Bagus, and B. N. Cox, *J. Chem. Phys.* **77**, 4032 (1982).

¹¹S. P. Walch and C. W. Bauschlicher, Jr., *J. Chem. Phys.* **83**, 5735 (1985).

¹²R. J. Harrison and N. C. Handy, *Chem. Phys. Lett.* **123**, 321 (1986).

¹³F. Reuse, S. N. Khanna, V. de Coulon, and J. Buttet, *Phys. Rev. B* **39**, 12911 (1989); **41**, 11743 (1990).

¹⁴T. J. Lee, A. P. Rendell, and P. R. Taylor, *J. Chem. Phys.* **92**, 489 (1990); **93**, 6636 (1990).

¹⁵T. J. Lee, A. P. Rendell, and P. R. Taylor, *J. Phys. Chem.* **94**, 5463 (1990).

¹⁶J. D. Watts, I. Cernusak, J. Noga, R. J. Bartlett, C. W. Bauschlicher, Jr., T. J. Lee, A. P. Rendell, and P. R. Taylor, *J. Chem. Phys.* **93**, 8875 (1990).

¹⁷T. J. Lee, A. P. Rendell, and P. R. Taylor, *Theor. Chim. Acta* **83**, 165 (1992).

¹⁸W. Klopper and J. Almlöf, *J. Chem. Phys.* **99**, 5167 (1993).

¹⁹P. V. Sudhakar and K. Lammertsma, *J. Chem. Phys.* **99**, 7929 (1993).

²⁰L. A. Eriksson, *J. Chem. Phys.* **103**, 1050 (1995).

²¹E. R. Davidson and R. F. Frey, *J. Chem. Phys.* **106**, 2331 (1997).

²²*CRC Handbook of Chemistry and Physics*, 74th ed., edited by D. R. Leed (CRC Press, Boca Raton, 1993–1994).

²³C. E. Moore, *Atomic Energy Levels*, Circular of the NBS 467 (U.S. GPO, Washington, D.C., 1949), Vol. I.

²⁴C. F. Bunge, J. A. Barrientos, and A. Vivier-Bunge, *At. Data Nucl. Data Tables* **53**, 113 (1993).

²⁵C. Kittel, *Introduction to Solid State Physics*, 7th ed. (Wiley, New York, 1996), p. 57.

²⁶V. E. Bondybey, *Chem. Phys. Lett.* **109**, 436 (1984).

²⁷W. J. Balfour and A. E. Douglas, *Can. J. Phys.* **48**, 901 (1970).

²⁸C. R. Vidal and H. Scheingraber, *J. Mol. Spectrosc.* **65**, 46 (1977).

²⁹R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.* **72**, 650 (1980).

- ³⁰A. D. McLean and G. S. Chandler, *J. Chem. Phys.* **72**, 5639 (1980).
- ³¹J.-P. Blaudeau, M. P. McGrath, L. A. Curtiss, and L. Radom, *J. Chem. Phys.* **107**, 5016 (1997).
- ³²C. Møller and M. S. Plesset, *Phys. Rev.* **46**, 618 (1934).
- ³³R. Krishnan and J. A. Pople, *Int. J. Quantum Chem.* **14**, 91 (1978).
- ³⁴S. F. Boys and F. Bernardi, *Mol. Phys.* **19**, 553 (1970).
- ³⁵L. Touri and J. J. Dannenberg, *J. Phys. Chem.* **97**, 2488 (1993).
- ³⁶F. W. Biegler-König, R. F. W. Bader, and T. H. Tang, *J. Comput. Chem.* **3**, 317 (1982).
- ³⁷K. B. Wiberg, C. M. Hadad, T. J. LePage, C. M. Breneman, and M. J. Frisch, *J. Phys. Chem.* **96**, 671 (1992).
- ³⁸A. E. Reed, L. A. Curtiss, and F. Wienhold, *Chem. Rev.* **88**, 899 (1988).
- ³⁹GAUSSIAN 98, Revision A.6, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Lui, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople (Gaussian, Inc., Pittsburgh, Pennsylvania, 1998).
- ⁴⁰G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982).
- ⁴¹J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.* **87**, 5968 (1987).
- ⁴²I. G. Kaplan, *Theory of Molecular Interactions* (Elsevier, Amsterdam, 1986).
- ⁴³K. Kitaura and K. Morokuma, *Int. J. Quantum Chem.* **10**, 325 (1976).
- ⁴⁴G. Chalasiniski, M. M. Szczesniak, and S. M. Cybulski, *J. Chem. Phys.* **92**, 2481 (1990).
- ⁴⁵J. M. Standart and P. R. Certain, *J. Chem. Phys.* **83**, 3002 (1985).
- ⁴⁶The analysis based on the more detailed physical decomposition of the SCF energy will be published elsewhere.
- ⁴⁷B. M. Axilrod and E. Teller, *J. Chem. Phys.* **11**, 299 (1943).