Many-body forces and stability of the alkaline-earth tetramers

C.C. Díaz-Torrejón [a,b], Ilya G. Kaplan [c,*]

[a] Centro Nacional de Supercómputo, IPICyT, A.C., Camino a la Presa San José 2055, 78216 San Luis Potosí, SLP, Mexico
[b] Centro de Investigación en Materiales Avanzados, S.C., Av. Miguel de Cervantes 120, 31109 Chihuahua, Chih., Mexico
[c] Instituto de Investigaciones en Materiales, UNAM, Apdo. Postal 70-360, 04510 México D.F., Mexico

ARTICLE INFO

ABSTRACT

The comparative study of the interaction energy and its many-body decomposition for Be_4, Mg_4, and Ca_4 at the all-electron CCSD(T)/aug-cc-pVQZ level is performed. For study of dependence of the binding energy and the orbital population on the cluster size the corresponding dimers and trimers were also calculated at the same level of theory. In comparison with weakly bound dimers, the binding energy in trimers and, especially, in tetramers drastically increases; e.g., E_b/N in Be_3 is 7 times larger and in Be_4 is 18.4 times larger than in Be_2. This sharp increase is explained as a manifestation of many-body forces. As follows from the many-body decomposition, the tetramers, and trimers as well, are stabilized by the three-body forces, whereas the two- and four-body forces are repulsive. The attractive contribution to the three-body forces has a three-atom electron exchange origin. The latter benefits the promotion of ns-electrons to np-orbitals. The natural bond orbital (NBO) population analysis reveals a relatively large np-population in trimers and tetramers (in Be_4 it is equal to $2p^{0.44}$). The population of the valence np-orbitals leads to the sp-hybridization providing the covalent bonding.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

As is well known, the noble-gas atoms interact only by the van der Waals (dispersion) forces. This results in a very weak binding. Even in a bulk, the noble-gas atoms have such small cohesive energy that they can form solids only at low temperature and He remains liquid at all temperatures. This is the 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 closed upper electronic subshell, $(ns)^2$, but form solids with a quite large cohesive energy. 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) and Na (1.10 eV/atom).

The alkaline-earth atoms have no valence electrons and it is important to study the nature of binding in small clusters of these elements. The dimers of Be, Mg and Ca are very weakly bound by the dispersion forces (at the self-consistent field (SCF) level they are not stable), therefore they can be attributed to the van der Waals molecules. The nature of bonding is drastically changed in many-atom clusters. This can be considered as a manifestation of many-body effects. The crucial role of the three-body forces in the stabilization of the Be_n clusters was revealed at the SCF level a long ago. [1,2] Then it was established at the Møller–Plesset perturbation theory level up to the fourth order (MP4(SDTQ)). [3,4] The detailed MP4(SDTQ) studies of the trimers Be_3, Mg_3, and Ca_3

in Ref. [5,6] demonstrated that it is the three-body interactions that stabilized these trimers.

The energy of many-particle classical system is always additive, because charges are considered as point objects and bodies are rigid. The charges in atoms and molecules are distributed and they are not rigid. The electronic structure of atoms and molecules can be modified in different environments. Thus, in quantum mechanics the interaction energy of many-particle system is usually nonadditive. The exchange and induction interactions are nonadditive and the dispersion interactions of the third and higher orders as well, see Chapter 4 in Ref. [7].

The nonadditivity arising from the polarization forces is the most evident. The third atom polarized the electronic charge distribution of two others and their interaction depends on its location. As a result, each pair interaction depends on coordinates of all three atoms:

$$V(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = V_{12}(r_{12}, r_{13}, r_{23}) + V_{13}(r_{13}, r_{12}, r_{23}) + V_{23}(r_{23}, r_{12}, r_{13}). \quad (1)$$

Thus, terms in Eq. (1) cannot be considered as pure two-body interactions. However, Eq. (1) can be always represented as a sum of the two-body interactions of isolated pairs, ε_{ik}, and a remainder, depending upon coordinates of three atoms:

$$V(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \varepsilon_{12}(r_{12}) + \varepsilon_{13}(r_{13}) + \varepsilon_{23}(r_{23}) + V_3(r_{12}, r_{13}, r_{23}). \quad (2)$$

This additional term stems from the three-body interactions and is called the three-body interaction energy.

* Corresponding author.
  E-mail address: kaplan@iim.unam.mx (I.G. Kaplan).

The alkaline-earth atoms have closed electronic shells and do not possess multipole moments. Therefore the induction forces between them have a pure charge overlap origin, from which follows their short-range character. It is the exchange and the dispersion forces of the third and higher orders that give main contributions to the nonadditive energy of alkaline-earth clusters [7]. It is important to study the many-body decomposition for tetramers and reveal the role of three- and four-body forces in their stability.

There are many publications devoted to calculations of alkaline-earth tetramers [1,8–24]. But in most of these studies, different computational approaches were applied to calculate the equilibrium geometry and binding energy. The nature of binding has been discussed only in few studies. We will discuss them in relation with our results in Section 3.

In this paper we calculated the binding energy of the tetramers Be_4, Mg_4, and Ca_4 at the CCSD(T) level with the quite large aug-cc-pVQZ basis set [25] taking into account all electrons, including inner-shell electrons. Using these data we performed the many-body decomposition and analyzed each many-body contribution. For studying the dependence of the binding energy and the orbital population on the cluster size, we also calculated at the same level of theory corresponding dimers and trimers.

2. Computational method and basic formulae for the many-body decomposition

All presented results were performed using MOLPRO 2008.1 suite of program [26] with the basis set aug-cc-pVQZ, taken directly from EMSL Basis Set Exchange web site [25]. The potential energy surfaces (PES) were calculated by means of the Coupled Cluster method at the CCSD(T) level [27,28] with all electrons involved (the frozen-core approximation is not used). The electron density distribution was studied by the Natural Bond Orbital (NBO) analysis [29,30] at the MP4(SDQ) level, using the *Gaussian 03 Revision D.02* suite of programs [31].

In all variational methods only the total energies are calculated. The interaction energy of N-atomic cluster is found as a difference of the total energy of the system $E(N)$ and a sum of the energies of the isolated atoms, $E_1(N)$:

$$E_{int}(N) = E(N) - E_1(N) = E(N) - \sum_{a=1}^{N} E_a. \qquad (3)$$

For clusters composed with the same atoms:

$$E_{int}(N) = E(N) - NE_a. \qquad (4)$$

The interaction energy can be represented as finite many-body decomposition:

$$E_{int}(N) = E_2(N) + E_3(N) + \cdots + E_N(N), \qquad (5)$$

where $E_k(N)$ is the k-body interaction energy in N-atomic cluster. The many-body contributions is convenient to obtain using the recurrent procedure [7,32]:

$$E_2(N) = \sum_{a<b} E(ab) - a_{2N}^1 E_1(N), \qquad (6)$$

$$E_3(N) = \sum_{a<b<c} E(abc) - a_{3N}^1 E_1(N) - a_{3N}^2 E_2(N), \qquad (7)$$

$$E_4(N) = \sum_{a<b<c<d} E(abcd) - a_{4N}^1 E_1(N) - a_{4N}^2 E_2(N) - a_{4N}^3 E_3(N), \qquad (8)$$

$$\vdots$$

where the coefficients in Eqs. (6)–(8) are given by expression:

$$a_{mN}^k = \frac{(N-k)!}{(N-m)!(m-k)!}. \qquad (9)$$

3. Results and discussion

For study of dependence of cluster properties on the cluster size we calculated not only tetramers, but also all smaller clusters. In Table 1 the total energy of clusters at the equilibrium distance of the optimized geometry, calculated at different approximation, is represented. For trimers the optimized geometry corresponds to the symmetry group D_{3h}, for tetramers it corresponds to the T_d symmetry. As follows from Table 1, the negative ground-state energy, E_o, is gradually increases with increasing account of the electron correlation in employed methods. But if for dimers and trimers the ground-state energy is the largest at the CCSD(T) level, for tetramers the MP4(SDTQ) method gives a slightly deeper potential well than the CCSD(T) approach.

The increase of the equilibrium distance in the row Be_n, Mg_n, and Ca_n is correlated with an increase in the average radius of the atomic ns valence shell for $n = 2$, 3, and 4, see Ref. [33]. On the other hand, the increase of the cluster size leads to a decrease in an interatomic distance, R_o, for all elements. This decrement stems from the interplay of many-body interatomic forces and will be discuss later.

In Table 2 the interaction energy of the Be_n, Mg_n, and $Ca_n (n = 2–4)$ clusters and the electron correlation energy at the all-electron SCF and CCSD(T)/aug-cc-pVQZ level are represented. The electron correlation energy was defined by Löwdin [34] as a difference between the precise value of the energy and the Hartree–Fock value. But except for one-electron systems or simplest two-electron systems, as H_2 molecule, the exact energy cannot be calculated. So, the definition of the electron correlation energy is conventional and its value depends upon the approximation used. At the CCSD(T) level, the correlation energy is defined as:

$$\Delta E^{corr}(CCSD(T)) = E^{CCSD(T)} - E^{SCF}. \qquad (10)$$

All dimers and trimers are unstable at the SCF level; they are stabilized by the correlation energy. In the tetramer case only Mg_4 is unstable at the SCF level and stabilized by the correlation energy, although in the stabilization of Ca_4 the correlation energy also plays a dominant role. The Be_4 is stabilized by both the SCF and the correlation energies.

As is well known [7], the SCF energy can be divided on the electrostatic, exchange, and induction energies. Atoms with closed shells (and 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 electronic shells is repulsive, as in the noble-gas atom systems. In this connection a question arises, what kind of energy stabilized Be_4 at the SCF level?

As follows from the analysis of the many-body decomposition, at the SCF level the three-body energy, for which the main contribution stems from the three-body exchange forces, is negative and for Be_4 its absolute value is the largest, see Table 4, below we discuss this in detail.

If in dimers the binding energy, $E_b = -E_{int}^{CCSD(T)}$, is relatively small, in trimers and tetramers its value rapidly increases. What is important, the binding energy per atom also essentially increases in the row: dimers, trimers, and tetramers. In comparison with dimers, E_b/N is 7–3.5–3.5 times larger in trimers and 18–10–7 times larger in tetramers in the consecutive order: Be–Mg–Ca. This increase stems from the many-body forces. A large increase of the binding energy in trimers is evidently the effect of the three-body forces, which are absent in dimers. In tetramers the binding per atom becomes considerably larger. The latter can be attributed to the four-body forces, but this conclusion is not correct. For study the many-body effects, we should obtain the many-body decomposition (5)–(8) for $N = 4$.

Table 1
Total energy of alkaline-earth clusters calculated at different approximations, distances are in Å, energies are in hartree.

ATOMO	R_o(Å)	SCF	MP2	MP4(SDTQ)	CCSD(T)
Be$_2$	2.43	−29.13348051	−29.24642169	−29.27649945	−29.28437963
Mg$_2$	3.79	−399.2252223	−399.3411086	−399.3604327	−399.3632206
Ca$_2$	4.26	−1353.5130010	−1354.0143650	−1354.0643610	−1354.06573
Be$_3$	2.18	−43.71781762	−43.91956078	−43.95830909	−43.96373758
Mg$_3$	3.33	−598.8300097	−599.0222194	−599.0524335	−599.0548734
Ca$_3$	3.87	−2030.2663590	−2031.0417080	−2031.1180880	−2031.118258
Be$_4$	2.03	−58.35858460	−58.67119510	−58.71260068	−58.71214461
Mg$_4$	2.86	−798.4261868	−798.7389344	−798.7746563	−798.7731644
Ca$_4$	3.73	−2707.0329900	−2708.1013920	−2708.2010710	−2708.196098

Table 2
Dependence of the energy of alkaline-earth clusters on the cluster size; $E_b = -E_{int}^{CCSD(T)}$, distances are in Å, energies are in kcal/mol.

Cluster	R_o(Å)	E_{int}^{SCF}	$E_{int}^{CCSD(T)}$	ΔE_{corr}	(E_b/N)
Be$_2$	2.43	7.811134	−2.582690	−10.393824	1.2913
Mg$_2$	3.79	2.035196	−1.653788	−3.688984	0.8269
Ca$_2$	4.26	2.059210	−3.182928	−5.242138	1.5915
Be$_3$	2.18	0.683385	−27.178642	−27.862027	9.0595
Mg$_3$	3.33	7.958324	−8.777380	−16.735704	2.9258
Ca$_3$	3.87	5.059178	−17.103192	−22.162370	5.7011
Be$_4$	2.03	−41.826174	−95.068711	−53.242537	23.7672
Mg$_4$	2.86	19.280153	−32.603257	−51.883410	8.1508
Ca$_4$	3.73	−0.263091	−46.894206	−46.631114	11.7236

In Table 3 the many-body contributions to the interaction energy, calculated at the all-electron CCSD(T)/aug-cc-pVQZ level, are represented. Using these data, the decomposition (5) can be represented as:

$$E_{int}(Be_4) = E_2(Be_4)[1 - 8.92 + 1.18],$$
$$E_{int}(Mg_4) = E_2(Mg_4)[1 - 2.78 + 0.44], \qquad (11)$$
$$E_{int}(Ca_4) = E_2(Ca_4)[1 - 7.13 + 1.65].$$

From these data follows that for all studied tetramers the three-body forces are not only a single factor of stabilization, but the dominant factor of the many-body expansion. The four-body contributions, as the two-body ones, are repulsive. Nevertheless, the binding in tetramers is stronger than in trimers, where the repulsive four-body forces are absent. This can be simply explained, if we take into account that in tetramers we have four attractive three-body contributions, while in trimers there is only one. In the expression for the three-body energy [7]:

$$E_3(N) = \sum_{a<b<c} \varepsilon_{abc}, \qquad (12)$$
$$\varepsilon_{abc} = E(abc) - E_1(abc) - E_2(abc), \qquad (13)$$

the sum (12) contains 4 terms – number of different combinations of 3 objects from 4 objects: 4!/3! = 4.

For the interpretation of the physical sense of many-body forces it is useful to decompose them in the SCF and correlation components. It can be done in the same manner as for the total interaction energy. Many-body energies can be represented as:

$$E_m^{CCSD(T)} = E_m^{SCF}(N) + \Delta E_m^{corr}. \qquad (14)$$

In Table 4 we present the SCF and correlation components for each term in the many-body decomposition of the interaction energy of tetramers. The two-body SCF energy for tetrahedral tetramers can be presented as:

$$E_2^{SCF}(A_4) = 6E_{int}^{SCF}(A_2). \qquad (15)$$

It indicates that the physical sense of the two-body SCF energy in tetramers is the same as for the SCF interaction energy in dimers; it is predominantly the exchange interactions, which are repulsive for two interacting atoms with closed electronic shells. The attractive contributions from the electrostatic and induction energies are less than the repulsive exchange forces. This is the reason that E_2^{SCF} is positive for all alkaline-earth tetramers.

The situation is different in the case of the three-body SCF energy. For a tetrahedral tetramer it is equal to:

$$E_3^{SCF}(A_4) = 4E_3^{SCF}(A_3). \qquad (16)$$

The main contribution to $E_3^{SCF}(A_4)$ stems from the three-body exchange forces. These forces originate from the three-atomic electron exchange, which mixes electrons of three atoms involved in this exchange. In closed-shell atom systems, contrary to the two-body exchange forces, the three-body exchange forces are attractive and make a main contribution to the stability of tetramers.

Similarly to Eq. (15), the two-body correlation energy, $\Delta E_2^{corr}(A_4)$, can be presented as:

$$\Delta E_2^{corr}(A_4) = 6\Delta E_2^{corr}(A_2). \qquad (17)$$

Table 3
Many-body energy decomposition for the alkaline-earth tetramers at the CCSD(T)/aug-cc-pVQZ level; distances are in Å, energies are in kcal/mol.

	R_o(Å)	$E_{int}^{CCSD(T)}$	E_2	E_3	E_4	E_{nonadd}	E_{nonadd}/E_{add}
Be$_4$	2.03	−95.068711	14.099411	−125.797468	16.629345	−109.168123	7.742743
Mg$_4$	2.86	−32.603257	24.362530	−67.751151	10.785364	−56.965787	2.338254
Ca$_4$	3.73	−46.894206	−7.235889	−51.606023	11.947706	−39.658317	5.480781

Table 4
Detailed many-body energy decomposition for the alkaline-earth tetramers; distances are in Å, energies are in kcal/mol.

	R_o(Å)	E_2^{SCF}	ΔE_2^{corr}	E_3^{SCF}	ΔE_3^{corr}	E_4^{SCF}	ΔE_4^{corr}
Be$_4$	2.03	123.822665	−109.723254	−229.491329	103.693861	63.842489	−47.213144
Mg$_4$	2.86	80.062770	−55.700240	−72.038862	4.287711	11.256245	−0.470881
Ca$_4$	3.73	44.652286	−51.888175	−55.609826	4.003803	10.694448	1.253258

Table 5
The NBO valence orbital population in the alkaline-earth atoms and clusters calculated at the MP4(SDQ)/aug-cc-pVQZ level.

	2s	2p	3s	3p	4s	3d	4p	5s	4d	4f	5p
Be	1.87	0.12	–	–	–	–	–	–	–	–	–
Be$_2$	1.79	0.19	0.01	–	–	0.01	–	–	–	–	–
Be$_3$	1.67	0.29	0.01	0.01	–	0.02	–	–	–	0.01	–
Be$_4$	1.50	0.44	–	0.01	–	0.02	–	–	–	0.01	–
Mg	–	–	1.89	0.10	–	–	–	–	–	–	–
Mg$_2$	–	–	1.88	0.11	–	0.01	–	–	–	–	–
Mg$_3$	–	–	1.84	0.14	0.01	0.01	–	–	–	–	–
Mg$_4$	–	–	1.74	0.21	–	0.02	0.01	–	–	0.01	–
Ca	–	–	–	–	1.88	0.09	0.11	–	0.01	–	0.01
Ca$_2$	–	–	–	–	1.85	0.10	0.12	0.01	0.01	–	0.01
Ca$_3$	–	–	–	–	1.78	0.11	0.16	0.01	0.03	–	0.01
Ca$_4$	–	–	–	–	1.72	0.13	0.19	0.01	0.03	0.01	0.01

As in the case of dimers, it is reduced at large distances to the dispersion energy of the second order. At intermediate distances it contains both the dispersion and exchange contributions, the latter decreases the dispersion attraction. For Be$_4$ and Mg$_4$, the two-body $E_2^{SCF}(A_4)$ repulsion is larger than the $\Delta E_2^{corr}(A_4)$ attraction and, upon the whole, for these two tetramers the two-body forces, $E_2(A_4)$, are repulsive. Only for Ca$_4$ they give a small attractive contribution.

For tetrahedral tetramers the three-body correlation energy $\Delta E_3^{corr}(A_4)$ is equal to:

$$\Delta E_3^{corr}(A_4) = 4\Delta E_3^{corr}(A_3). \tag{18}$$

At large distances $\Delta E_3^{corr}(A_3)$ is reduced to the Axilrod–Teller–Mutto (ATM) dispersion energy [35,36]. The tetrahedron consists of four equal equilateral triangles. For each triangle the ATM dispersion energy is transformed to:

$$\varepsilon_{disp}^{(3)} = \frac{11}{8}\frac{C_9(ABC)}{R_{ab}^9}, \tag{19}$$

see discussion in Ref. [7]. Thus, it is positive. At intermediate distances the dispersion energy cannot be separated from the exchange effects; the three-body exchange gives some negative contribution, although, as follows from Table 4, for all three tetramers $\Delta E_3^{corr}(A_4) > 0$.

The analysis above demonstrates that it is the three-body interactions that stabilize the alkaline-earth trimers and tetramers. This fact and the relative small values of the repulsive two- and four-body interactions explain the decrement in the interatomic distances, as the size of the cluster increases, see Table 2. The attractive three-body forces become larger with a decrease of the interatomic distance, while the repulsive two- and four-body forces undergo small changes.

The physical origin of the three-body attraction stems from the three-atomic electron exchange forces. This leads to a rearrangement of the atomic orbital structure. It is instructive to study the atomic orbital population in clusters of different size. In Table 5 we present the valence orbital population obtained by the NBO analysis [29,30]. The NBO valence population in atoms was also calculated. At the SCF level, which corresponds to the population in the Periodic Table of Elements, the following, well known, orbital population is valid:

Be : $1s^2 2s^2$;   Mg : $1s^2 2s^2 2p^6 3s^2$;   Ca : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$.

According to Table 5, the electron correlation partly populates np-valence orbitals even in the isolated atoms. In trimers and tetramers the amount of np-population increases considerably, especially in beryllium clusters. The largest increase of the excited orbital population takes place in the beryllium tetramer $-2p^{0.44}$. The population of np-orbitals favors the sp-hybridization [37] of the alkaline-earth atoms providing the covalent bonding in trimers and tetramers.

The crucial role of the sp-hybridization in the explanation of stability of alkaline-earth tetramers was stressed in some earlier studies [8,9]. Bauschlicher et al. [8], basing on the SCF Mulliken population analysis, 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 tetramers. The authors [8] found the ratio of np-population in different tetramers proportional to the ratio of their dissociation energies. However at an electron correlation level because of the np-population in the isolated atoms, we cannot expect such proportionality and this is confirmed by the data presented in Tables 2 and 5. For instance, in Be$_4$, in comparison with Mg$_4$, the np-population is twice larger, while the binding energy is three times larger; the np-populations in Mg$_4$ and Ca$_4$ are practically the same, while their binding energies differ almost in 1.5 times.

We also should keep in mind that some of atom–atom interactions, which enhanced the excited orbital population, do not provide the bonding. This is confirmed by the valence orbital population for the alkaline-earth dimers and trimers found at the SCF level [5,6]. The NBO analysis at the SCF level gives rather non-negligible np-population especially for trimers. But at the SCF level the dimers and trimers are not stable. As follows from the analysis above, the stability of cluster depends upon the interplay of different components of the many-body energy, see Tables 3 and 4.

It is worth-while to discuss the connection of the three-body interactions, which stabilized the considered atomic clusters, with so-called Efimov's three-particle states [38,39], see also the review [40]. In 1970 Efimov analyzing a three-particle system came to conclusion that if the two-particle interaction can be divided on a short-range non-resonance part with the effective range r_o and a long-range resonance part with the scattering length a, then the presence of the third particle leads to some effective resonance interaction among the three particles, which does not depend on the nature of two-particle forces. This interaction produces a large number of stable three-body states, if the scattering length of the resonance interaction is large, $a \gg r_o$. After more than 35 years from this theoretical prediction, the Efimov three-particle states were revealed experimentally in an ultracold gas of cesium atoms [41].

From the description above it follows that the Efimov states are produced by long-range three-body resonance interactions with large a, while the three-body forces in stable clusters have not a resonance character and their range is determined by the relatively small cluster dimensions, about 5 bohr. Thus, the three-body forces, stabilizing the clusters considered in our study are not the Efimov three-body interactions.

4. Conclusion

In comparison with very weakly bound dimers, the binding energy per atom in the larger alkaline-earth clusters is drastically

increases. For instance, E_b/N in Be_3 is 7 times larger and in Be_4 is 18.4 times larger than in Be_2, see Table 2. This is evidently a manifestation of many-body interactions. As follows from our results, within the framework of the many-body decomposition the three-body forces are the single factor of the tetramer stability and the dominant factor in the many-body decomposition. The two- and four-body forces are repulsive. The attractive contribution to the three-body energy stems from the three-body SCF component, which has the electron exchange origin. The three-body exchange mixed electrons of three atoms involved in the exchange. This benefits the promotion of ns-electrons to np-orbitals.

The NBO population analysis reveals a relatively large np-population in trimers and tetramers, especially in beryllium clusters. The largest increase of the valence np-orbital population is revealed in Be_4 and equals $2p^{0.44}$. The population of np-orbitals leads to the atomic sp-hybridization. The hybridized orbitals enhance the overlap in the bond region increasing the strength of the bond [37] and provide the covalent bonding in trimers and tetramers.

On the other hand, the strength of bonding is not proportional to the amount of the np-population; compare the data in Tables 2 and 5. Let us stress that not all atom–atom interactions, which enhanced the np-population, lead to binding. The alkaline-earth dimers and trimers have a non-negligible np-population already at the SCF level, [5,6] although in this approximation they are not stable. The cluster stability depends upon the interplay of different components of many-body forces. The main factors of stabilizations are the three-body exchange forces. The attractive two-body dispersion forces are suppressed by the repulsive two-body exchange.

Acknowledgements

References

[1] W. Kolos, F. Nieves, O. Novaro, Chem. Phys. Lett. 41 (1976) 431.
[2] J.P. Daudey, O. Novaro, W. Kolos, M. Berrondo, J. Chem. Phys. 71 (1979) 4297.
[3] I.G. Kaplan, J. Hernández-Cóbos, I. Ortega-Black, O. Novaro, Phys. Rev. A 53 (1996) 2493.
[4] I.G. Kaplan, Adv. Quantum Chem. 31 (1999) 137.
[5] I.G. Kaplan, S. Roszak, J. Leszczynski, J. Chem. Phys. 113 (2000) 6245.
[6] I.G. Kaplan, S. Roszak, J. Leszczynski, Adv. Quantum Chem. 40 (2001) 257.
[7] I.G. Kaplan, Intermolecular Interactions: Physical Picture, Computational Methods and Model Potentials, Wiley, Chichester, England, 2006.
[8] C.W. Bauschlicher Jr., P.S. Bagus, B.N. Cox, J. Chem. Phys. 77 (1982) 4032.
[9] G. Pacchioni, J. Koutecky, Chem. Phys. 71 (1982) 181.
[10] P.S. Bagus, C.J. Nelin, C.W. Bauschlicher Jr., Surf. Sci. 156 (1985) 615.
[11] R.J. Harrison, N.C. Handy, Chem. Phys. Lett. 123 (1986) 321.
[12] C.M. Rohlfing, J.S. Binkley, Chem. Phys. Lett. 134 (1987) 110.
[13] M.M. Marino, W.C. Ermler, J. Chem. Phys. 86 (1987) 6283.
[14] T.J. Lee, A.P. Rendell, P.R. Taylor, J. Chem. Phys. 93 (1990) 6636.
[15] F. Reuse, S.N. Khanna, V. de Coulon, J. Buttet, Phys. Rev. B 41 (1990) 11743.
[16] V. Kumar, R. Car, Z. Phys. 19 (1991) 177.
[17] W. Klopper, J.J. Almlöf, Chem. Phys. 99 (1993) 5167.
[18] P.V. Sudhakar, K. Lammertsma, J. Chem. Phys. 99 (1993) 7929.
[19] C.W. Bauschlicher Jr., H. Partridge, Chem. Phys. Lett. 300 (1999) 364.
[20] R. Sekine, K. Tanaka, J. Onoe, K. Takeuchi, H. Nakamatsu, Adv. Quantum Chem. 37 (2000) 237.
[21] P.H. Acioli, J. Jellinek, Phys. Rev. Lett. 89 (2002) 213402.
[22] F. Jalbout, THEOCHEM 629 (2003) 7.
[23] J.S. Lee, Phys. Rev. A 68 (2003) 043201.
[24] C.C. Diaz, I.G. Kaplan, S. Roszak, J. Mol. Model. 11 (2005) 330.
[25] Basis set EMSL web site. <https://bse.pnl.gov/bse/portal>.
[26] H.J. Werner, P.J.R. Knowles, R. Lindh, F.R. Manby, M. Schütz, P. Celani, T. Korona, A. Mitrushenkov, G. Rauhut, T.B. Adler, R.D. Amos, A. Bernhardsson, A. Berning, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, E. Goll, C. Hampel, G. Hetzer, T. Hrenar, G. Knizia, C. Köppl, Y. Liu, A.W. Lloyd, R.A. Mata, A.J. May, S.J. McNicholas, W. Meyer, M.E. Mura, A. Nicklaß, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, U. Schumann, H. Stoll, A.J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, A. Wolf, MOLPRO 2008.1, A Package of Ab Initio Program.
[27] K. Raghavachari, G.W. Trucks, J.A. Pople, M. Head-Gordon, J. Chem. Lett. 157 (1989) 479.
[28] P.J. Knowles, C. Hampel, H.-J. Werner, J. Chem. Phys. 99 (1993) 5219.
[29] F.W. Biegler-König, R.F.W. Bader, T.H. Tang, J. Comput. Chem. 3 (1982) 317.
[30] K.B. Wiberg, C.M. Hadad, T.J. LePage, C.M. Breneman, M.J. Frisch, J. Phys. Chem. 96 (1992) 671.
[31] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03 Revision D.02, Gaussian, Inc., Wallingford CT, 2004.
[32] I.G. Kaplan, R. Santamaria, O. Novaro, Mol. Phys. 84 (1995) 105.
[33] C.F. Bunge, J.A. Barrientos, A. Vivier-Bunge, Atom. Data Nucl. Data Tables 53 (1993) 113.
[34] P.-O. Löwdin, Adv. Chem. Phys. 2 (1959) 207.
[35] B.M. Axilrod, E. Teller, J. Chem. Phys. 11 (1943) 299.
[36] J. Muto, Proc. Phys. Math. Soc. Jpn. 17 (1943) 629.
[37] R. McWeeny, Coulson's Valence, third ed., Oxford University Press, Oxford, 1979.
[38] V. Efimov, Phys. Lett. B 33 (1970) 563.
[39] V. Efimov, Comments Nucl. Part. Phys. 19 (1990) 271.
[40] E. Braaten, H.-W. Hammer, Phys. Rep. 428 (2006) 325.
[41] T. Kraemer et al., Nature 440 (2006) 315.