



## Nature of stability of Mg<sub>4</sub> and many-body forces

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### ABSTRACT

The precise *ab initio* calculations of the tetramer Mg<sub>4</sub> were performed at the all-electron CCSD(T)/aug-cc-pVQZ level. The dissociation energy in respect to all possible dissociation channels at different levels of accuracy, from SCF till CCSD(T), but with the same large basis set, was calculated. Except the SCF method, in all approximations Mg<sub>4</sub> was found stable. The many-body decomposition of the interaction energy was performed. From it follows that the three-body forces are not only a single factor of stabilization, but the dominant factor of the many-body expansion. The three-body interactions favor the promotion of the 3s-valence electrons to the 3p orbitals with the subsequent *sp*-hybridization.

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### 1. Introduction

Noble gas atoms have the closed-shell electronic structure and interact only by the weak van der Waals (dispersion) forces. 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. On the other hand, the alkaline-earth elements Be, Mg, Ca, etc., have closed upper electronic subshell, (ns)<sup>2</sup>, 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 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 [1]. The crucial role of the three-body forces in the stabilization of the Be<sub>n</sub> clusters was revealed at the SCF level a long ago [2,3]. Then it was established at the Møller–Plesset perturbation theory level up to the fourth order (MP4(SDTQ)) [4,5]. The detailed MP4(SDTQ) studies of the trimers Be<sub>3</sub>, Mg<sub>3</sub>, and Ca<sub>3</sub> in Refs. [6,7] demonstrated that it is the three-body interactions that stabilized these trimers.

The alkaline-earth atoms have closed electronic shells and do not possess multipole moments. Therefore the induction forces between them are equal to zero and its the exchange and dispersion forces of the third and higher orders that give contributions to the nonadditive energy [1]. It is important to study the many-body decomposition for tetramers and reveal the role of three- and four-body forces in their stability.

Among alkaline-earth clusters the magnesium clusters have a weakest binding. There are many publications devoted to calculations of Mg<sub>4</sub> [1,8–20]. 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. From all calculations of the atomization energy it follows that Mg<sub>4</sub> is a stable tetramer. The only exception was the study by Jalbout [19]. From results based on the DFT calculations he came to conclusion that Mg<sub>4</sub> is unstable in respect to the dissociation into two dimers Mg<sub>2</sub> and claimed that Mg<sub>4</sub> is not likely to be formed under normal condition in nature [19]. We note that Mg<sub>2</sub> is bound by very weak van der Waals forces, while the tetramer is characterized by the covalent bonding, and these conclusions are tested in the calculation reported here.

In this paper, we calculated the binding energy of Mg<sub>4</sub> at the CCSD(T) level with the quite large aug-cc-pVQZ basis set [21] taking into account all electrons, including inner-shell electrons. All possible dissociation channels were studied at different levels of theory. We performed the many-body decomposition of the binding energy and analyzed each many-body contribution to the tetramer stability. For study the dependence of the binding energy

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on the cluster size, we calculated at the same level of theory the magnesium dimer and trimer. The last data are also needed for obtaining the appropriate dissociation channels.

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

All presented results were performed using MOLPRO 2008.1 suite of program [22], with the basis set aug-cc-pVQZ, taken directly from EMSL Basis Set Exchange web site [21]. The potential energy surfaces (PES) were calculated by means of the Coupled Cluster method at the CCSD(T) level [23,24] with all electrons involved (without the frozen-core approximation). The electron density distribution was studied by the Natural Bond Orbital (NBO) analysis [25,26] at the MP4(SDQ) level, using the *Gaussian 03 Revision D.02* suite of programs [27].

In all variational methods only the total energies are calculated. The interaction energy is found as a difference of the total energy of the system  $E(N)$  and the energies of the isolated subsystems, in our case of isolated atoms,

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

it can be represented as a finite many-body decomposition

$$E_{\text{int}}(N) = E_2(N) + E_3(N) + \dots + E_N(N). \quad (2)$$

The many-body contributions are convenient to obtain using the recurrent procedure described in Ref. [1],

$$E_2(N) = \sum_{a<b} E(ab) - a_{2N}^1 E_1(N), \quad (3)$$

$$E_3(N) = \sum_{a<b<c} E(abc) - a_{3N}^1 E_1(N) - a_{3N}^2 E_2(N), \quad (4)$$

$$E_4(N) = \sum_{a<b<c<d} E(abcd) - a_{4N}^1 E_1(N) - a_{4N}^2 E_2(N) - a_{4N}^3 E_3(N), \quad (5)$$

⋮

where the coefficients in Eqs. (3)–(5) are given by expression:

$$a_{mN}^k = \frac{(N-k)!}{(N-m)!(m-k)!}. \quad (6)$$

## 3. Results and discussion

For comparison and for obtaining all dissociation channels we calculated not only  $\text{Mg}_4$ , but also the smaller clusters. In Table 1 the total and binding energies of  $\text{Mg}_n$  ( $n = 1-4$ ), calculated at the all-electron CCSD(T)/aug-cc-pVQZ level, are represented. The obtained value for the  $\text{Mg}_4$  binding energy,  $E_b = 32.6$  kcal/mol, is in an agreement with published *ab initio* values, e.g.  $E_b = 31$  kcal/mol obtained in Ref. [12] by the MRCI method and  $E_b = 31.5$  kcal/mol obtained in Ref. [15] by the MP-R12 method. If in the magnesium dimer the binding energy is relatively small, in the trimer and tetramer its value rapidly increases. What is important, the binding energy per atom also essentially increases in the row  $\text{Mg}_2$ ,  $\text{Mg}_3$  and  $\text{Mg}_4$ . In comparison with the dimer,  $E_b/N$  is 3.5 times larger in

**Table 1**  
Total ( $E_0$ ) and binding ( $E_b = -E_{\text{int}}$ ) energies of magnesium clusters calculated at the all-electron CCSD(T)/aug-cc-pVQZ level; total energies in Hartrees, binding energies in kcal/mol.

	$R_0$ (Å)	$E_0$ (CCSD(T))	$E_b$	$[E_b/N]$
Mg	–	–199.6802915	–	–
$\text{Mg}_2$	3.79	–399.3632206	1.654	0.827
$\text{Mg}_3$	3.33	–599.0548734	8.777	2.926
$\text{Mg}_4$	2.86	–798.7731644	32.603	8.150

$\text{Mg}_3$  and 10 times larger in  $\text{Mg}_4$ . This increase stems from the many-body forces. We will discuss it below.

In Table 2, we calculated the dissociation energy in respect to the four possible dissociation channels at different levels of accuracy, from SCF till CCSD(T), all with the same large basis set, aug-cc-pVQZ. Except for the SCF method, in all approximations  $\text{Mg}_4$  was found stable, contrary to the conclusions made by Jalbout [19]. As it can be expected, the dissociation energy increases in the row of the dissociation channels corresponding to the consecutive decrease of the cluster size:  $\text{Mg}_3 + \text{Mg}$ ,  $2\text{Mg}_2$ ,  $\text{Mg}_2 + 2\text{Mg}$  and  $4\text{Mg}$ .

All studied magnesium clusters are not stable at the SCF level; they are stabilized by the electron correlation energy, which at large distances is equivalent to the dispersion energy, but at the equilibrium distance cannot be separated from the exchange forces. The binding energy of the dimer,  $\text{Mg}_2$ , is very small;  $\text{Mg}_2$  can be attributed to the molecules of the van der Waals type. Adding of the third atom leads to a large increase of the binding energy in trimers. This is evidently the effect of the three-body forces, which are absent in dimers. In the tetramer,  $\text{Mg}_4$ , the binding becomes much larger. It 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 (2) for  $\text{Mg}_4$ .

The many-body contributions to the interaction energy were calculated at the all-electron CCSD(T)/aug-cc-pVQZ level using the recurrent formulae (3)–(5). The following decomposition was obtained:

$$E_{\text{int}}(\text{Mg}_4) = E_2(4) + E_3(4) + E_4(4) = 24.36 - 67.75 + 10.78 = -32.61 \text{ kcal/mol}. \quad (7)$$

From these data follows that the three-body forces are not only a single factor of stabilization, but the dominant factor of the many-body expansion. The four-body contribution, as two-body one, is repulsive. Nevertheless, the binding in  $\text{Mg}_4$  is stronger than in  $\text{Mg}_3$ , where the repulsive four-body forces are absent. This paradox is resolved very simple, if we take into account that in  $\text{Mg}_4$  we have four different attractive three-body contributions, while in  $\text{Mg}_3$  there is only one. In the expression for the three-body energy [1]

$$E_3(N) = \sum_{a<b<c} \varepsilon_{abc}, \quad (8)$$

$$\varepsilon_{abc} = E(abc) - E_1(abc) - E_2(abc). \quad (9)$$

The sum (8) contains four terms – number of different combinations of three objects from four objects:  $4!/3! = 4$ .

The three-body interactions favor the promotion of the 3s-valence electrons to the 3p orbitals and the *sp*-hybridization. Even in the earlier studies of  $\text{Mg}_4$  by Bauschlicher et al. [10,11], the stability of  $\text{Mg}_4$  was attributed to the promotion of atomic electrons from 3s to 3p orbital leading to the *sp*-hybridization. Authors made a conclusion that the ratio of *p*-populations in different tetramers is in an agreement to the ratio of their dissociation energies. But their Mulliken population analysis was performed at the SCF level, for which the isolated atoms are not populated at the excited orbitals. Whereas, at an electron correlation level, because of the *p*-population in the isolated atoms, we cannot expect that the amount of the *p*-population in clusters can be used as a quantita-

**Table 2**  
Energy of the dissociation of  $\text{Mg}_4$  with respect to different dissociation channels, energies in kcal/mol.

Method	$D_e$			
	$\text{Mg}_3 + \text{Mg}$	$\text{Mg}_2 + \text{Mg}_2$	$\text{Mg}_2 + 2\text{Mg}$	$4\text{Mg}$
SCF	–11.322	–15.210	–17.245	–19.280
MP2	29.758	35.562	37.192	38.821
MP4(SDTQ)	27.348	33.727	35.748	37.768
CCSD(T)	23.826	29.296	30.949	32.603

**Table 3**  
The NBO atomic orbital population at the all-electron MP4(SDQ) level.

	3s	3p	4s	3d	4p	4f
Mg	1.89	0.10	–	–	–	–
Mg <sub>2</sub>	1.88	0.11	–	0.01	–	–
Mg <sub>3</sub>	1.84	0.14	0.01	0.01	–	–
Mg <sub>4</sub>	1.74	0.21	–	0.02	0.01	0.01

tive measure of the bond strength, although qualitatively they can be connected.

In Table 3, we represent the valence NBO populations for magnesium clusters calculated at the all-electron MP4(SDQ)/aug-cc-pVQZ level. As follows from Table 3, the inclusion of the electron correlation effects in isolated atoms leads to an essential population of the vacant (in the SCF approximation) 3p orbitals. Interatomic interactions lead to a further increase of the population of excited atomic orbitals. An increment of 3p-population in the dimers is small and it does not produce the covalent bonding; Mg<sub>2</sub> is binding by the weak van der Waals forces. In the trimers and especially in tetramers the significant 3p-population leads to the sp-hybridization, and the nature of binding should be attributed to the covalent bonding.

#### 4. Conclusions

The precise *ab initio* calculations demonstrated that Mg<sub>4</sub> is stable in respect to all possible dissociation channels. The conclusions, based on the DFT calculations [19], about the thermodynamically instability of Mg<sub>4</sub> are wrong. The possible reasons for unreliability of DFT calculations in this case are unclear. The DFT methods have serious problems in the case of unclosed electronic shells when the total spin  $S \neq 0$ , see Refs. [28,29], but for the close-shell systems, as in the case of Mg<sub>4</sub>, they usually provide quite reasonable results.

The binding energy per atom,  $E_b/N$ , essentially increases with the cluster size. Namely:  $E_b/N$  is 3.5 times larger in Mg<sub>3</sub> and 10 times larger in Mg<sub>4</sub> than it is in Mg<sub>2</sub>. This is an evident manifestation of many-body forces. It was revealed that the tetramers are stabilized by the three-body forces, as it takes place in the case of the trimers. The three-body interactions favor the promotion of the 3s-valence electrons to the 3p orbitals with the subsequent sp-hybridization.

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