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Theoretical study of the electron affinities of the alkaline-earth tetramers possessing T_d symmetry: Be$_4$ and Mg$_4$

Abstract The electron affinities of beryllium and magnesium tetramers are calculated at the ROMP2 level employing the Dunning-type aug-cc-pVQZ basis set. The vertical electron detachment energy (VEDE) amounts to 1.685 eV for Be$_4^-$ and 0.943 eV for Mg$_4^-$. The decomposition of the VEDE into physical components and an atomic orbital population analysis are used to elucidate the nature of the outer electron binding in these anions.

Keywords Electron affinity · Magnesium and beryllium · Clusters · Chemical bonding · Orbital population · Intermolecular forces

Introduction

The alkaline-earth elements Be, Mg, Ca, etc., have a closed electronic subshell $(ns)^2$, but form solids with quite a large cohesive energy. The cohesive energy in 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/atom), Na (1.10 eV/atom) and Cu (1.0 eV/atom). On the other hand, the dimers of Be, Mg and Ca are very weakly bound by 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 drastically changed in many-atom clusters, evidently indicating a manifestation of many-body effects. The crucial role of 3-body forces in the stabilization of the alkaline-earth

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clusters was established theoretically at the Møller–Plesset perturbation theory level up to the fourth order (MP4(SDTQ)) in Ref. [1–3].

The study the binding of an excess electron to clusters of the alkaline-earth elements is important as an instructive example of unusual properties of complexes of atoms possessing closed electron shells. Such theoretical studies of beryllium and magnesium dimers and trimers at the MP4(SDTQ) and CCSD(T) levels (for the beryllium clusters up to the CCSDT level [4]) were performed in Refs. [4, 5]. It was revealed that the electron affinities are of the right magnitude to be observed with standard photodetachment techniques. The vertical electron detachment energy (VEDE) amounts to 0.405 eV for Be$_2^-$ and 1.599 eV for Be$_3^-$ [4], and is equal to 0.298 eV for Mg$_2^-$ and 0.839 eV for Mg$_3^-$ [5]. The smaller magnitude of the EAs in Mg$_n$ in comparison with Be$_n$ can be explained by the different behavior of 3 p-orbitals and 2 p-orbitals occupied by the excess electron in magnesium and beryllium anions, respectively [5]. The only factor of stabilization of the excess electron in Be$_2^-$ is the relaxation energy, whereas in Mg$_2^-$ it is the correlation energy. Both the Be$_3^-$ and Mg$_3^-$ anions are stabilized by relaxation as well as correlation energies, although in anions these energies cannot be separated from the exchange energies. Both beryllium and magnesium negatively charged dimers and trimers must be attributed to the valence-bound anions.

The dimers and trimers discussed above are non-polar, their first non-vanishing multipole moment is a quadrupole moment. In molecules possessing T_d point symmetry, the first two multipole moments—dipole and quadrupole are equal to zero. The first non-vanishing multipole moment in these molecules is an octopole [6]. According to the calculations by Gutsev and Adamowicz [7], the CF$_4$ molecule with T_d geometry does not attach an electron in its ground state. The adiabatic electron affinity (AEA) has been determined to be clearly negative, −1.22 eV. However, the SF$_4$ molecule calculated at the non-local LSDA level attaches an additional

electron and has a positive AEA of 2.56 eV [8] that is in accordance with the experimental value 2.35 eV [9]. A very high value for the electron affinity of the AlF_4 molecule with T_d geometry, AEA = 7.96 eV, was quoted in Ref. [10].

To the best of our knowledge, no studies have been performed for the electron affinity of the Be_4 cluster. Mg_4 clusters were studied recently employing the density functional method (DFT) by Acioli and Jellinek [11–13] in connection with the important problem of the onset of metallic behavior of the Mg_n clusters. They studied clusters with $n = 2$–22. For large clusters, the DFT method is quite appropriate because the aim was to obtain a qualitative result. For a quantitative investigation of the excess electron binding, the one-electron DFT approach is not sufficient. For this purpose, many-electron methods with more precise account of the electron correlation effects must be applied.

In this paper, we present the results of calculations at the Møller–Plesset perturbation theory level (MP2) of the electron affinity of the Be_4 and Mg_4 tetramers with tetrahedral geometry. A comparative discussion of the nature of the excess electron binding in these clusters is also presented.

Methodology

The electron affinity (EA) in the ground electronic state is defined as

$$\Delta E_e = E_o(N) - E_o(N+1) \qquad (1)$$

where E_o is the ground electronic state energy of neutral (N electrons) and anion ($N+1$ electrons) systems. For molecules or clusters, depending on the internuclear distances at which $E_o(N)$ and $E_o(N+1)$ are calculated, three kinds of EA are defined:

tion code enclosed in the *Gaussian-03* suite. The reliable calculation of EAs demands the use of extended basis sets with many diffuse functions [15–17]. We used the Dunning-type augmented correlation-consistent polarized-valence basis sets (aug-cc-pVQZ) including 6 s, 5 p, 4 d, 3 f, and 2 g contracted Gaussians [18].

The initial calculations indicated that, in contrast to the alkaline-earth dimer and trimer anions [4, 5], for the tetramer anions in the Møller–Plesset approach based on the unrestricted Hartree–Fock method (UMP), the spin contamination [19] is no longer negligible and cannot be removed by the spin projection procedure of the Gaussian suit. This leads to unreliable results at the UMP2 and UMP4 levels. For these reasons we employed the restricted open-shell Møller–Plesset method (ROMP2) based on the restricted open-shell Hartree–Fock functions [20, 21] that is free from the spin contamination.

The atomic orbital population study was performed using the natural bond orbital (NBO) analysis [19]. For anion calculations at the ROMP2 level, the α-orbital and β-orbital populations were summed.

Results and discussion

The results of the calculations are shown in Table 1. The difference between the three types of EAs are small for both calculated tetramers Be_4 and Mg_4. The reason lies in the small difference between the equilibrium distances for neutral and anionic tetramers. On the other hand, the values of EAs are high enough. The VEDE is 1.684 eV for Be_4^- and 0.943 eV for Mg_4^-. As we mentioned before, we did not find any published calculations of the EA for Be_4. From the calculations of Mg_4 and Mg_4^- at the DFT level [11], the AEA can be extracted. Its value 1.01 eV is close to our value of AEA = 0.941 eV.

Vertical electron affinity (VEA)	Both energies in Eq. 1 are calculated at the equilibrium structure of the neutral system
Adiabatic electron affinity (AEA)	Energies in Eq. 1 are calculated at the equilibrium structures of the neutral and charged systems, respectively
Vertical electron detachment energy (VEDE)	Energies in Eq. 1 are calculated at the equilibrium structure of an anion

The calculations were carried out with the *Gaussian-03* suite of programs [14]. Figures for the HOMOs and LUMOs were generated by the *Gaussview-03* visualiza-

As was demonstrated in Ref. [4], for studying the nature of binding of the excess electron in anions it is useful to decompose the EA into three components

Table 1 Total ground state energies (a.u.) and electron affinities (eV) calculated at the ROMP2 levels with the aug-cc-pVQZ basis set[a]

	Be_4		Be_4^-	Mg_4		Mg_4^-
SCF	−58.359206		−58.388793	−798.439784		−798.452835
ROMP2	−58.579827		−58.641498	−798.602866		−798.637434
$r_o(A)$[b]	2.06		2.04	3.04		3.01
VEA		1.678			0.938	
AEA		1.678			0.941	
VEDE		1.685			0.943	

[a] For the neutral clusters, the calculations at the ROMP2 levels correspond to the RMP2 approach
[b] The equilibrium distance was calculated at the ROMP2 level

Table 2 Decompositions of the binding energy of the neutral tetramers (**a**) and the VEDE of their anions (**b**), energy in eV

(a)				(b) VEDE			
Be^4, T_d	1.832	2.859	4.691	Be_4^-, T_d	0.386	0.428	0.871	1.685
Mg^4, T_d	−0.467	1.751	1.284	Mg_4^-, T_d	0.135	0.265	0.543	0.943

$$\Delta E_e = EA = \Delta E_e^{KT} + \Delta E_{relax}^{SCF} + \Delta E_e^{corr} \qquad (2)$$

The Koopmans approach is defined within the framework of the SCF method in which both energies in Eq. 1 are calculated with the same SCF orbitals corresponding to the neutral system. According to Koopmans theorem (KT) [22], the difference between the HF energies is equal to the negative of the relevant orbital energy. For the VEA, the Koopmans contribution is determined as

$$\Delta E_e^{KT}(VEA) = E_o^{SCF}(N) \\ - E_o^{SCF}(N+1)_{non\text{-}relax} \\ = -\varepsilon_e(A_n) \qquad (3)$$

where $\epsilon_e (A_n)$ is the energy of the vacant orbital for the neutral system at the ground state equilibrium geometry occupied by the attached electron in an anion. The VEDE in the KT approximation is also determined according to Eq. 3, but at the anion equilibrium geometry. The KT approximation does not take relaxation effects into account and includes the electrostatic and exchange interactions only to the first order of the perturbation theory.

The remainder of the binding energy at the SCF level, we denote as the relaxation energy

$$\Delta E_{relax}^{SCF} = \Delta E_e^{SCF} - \Delta E_e^{KT}, \qquad (4)$$

which stems from the relaxation of the orbitals of the neutral system in the field of the attached electron. consists mostly of the induction (polarization) energy, but also contains the exchange energy, which at the cluster interatomic distances cannot be separated from the induction energy.

The electron correlation contribution is defined following the general definition of Lõwdin [23] and depends upon the correlation method used. At the ROMP2 level, it is defined as

$$\Delta E_e^{corr}(ROMP2) = \Delta E_e^{ROMP2} - \Delta E_e^{SCF}. \qquad (5)$$

At large distances, where the exchange effects are negligible, the correlation contribution to the binding energy reduces to the dispersion energy, see calculation for the alkaline-earth dimers in Ref. [1].

In Table 2, we represent the binding energies and their decomposition for neutral tetramers and the decomposition of the VEDE for anions. A comparison of the data shown in Table 2a with the binding energies of dimers and trimers [1] demonstrates that the binding energies of Be and Mg clusters increase systematically with the enlargement of clusters. The binding energies of Be_4 and Mg_4 per atom–atom bond are several times higher than those calculated for trimers. The bonding in tetramers is dominated by the correlation-energy contribution. The SCF interactions in Be_4 are attractive, while Mg_4 is unstable at the SCF level. However, the repulsive SCF interactions in Mg_4 are significantly reduced compared to smaller clusters. Binding energies correlate well with electron-affinity properties, manifested by the systematic increase of VEDE as the cluster grows. (Compare data of Table 2b and Ref. [5].) Both processes—the formation of the neutral complex and the electron attachment may be enhanced by electron delocalization due to many-body interactions, although this should be a subject of special study.

The decomposition of the VEDE into three components, according to Eq. 2, is presented in Table 2b. For Be_4^- all three components provide substantial contribu-

Table 3 Atomic orbital populations $n_l(A)$ in neutral and anionic beryllium and magnesium tetramers obtained by natural bond orbital (NBO) analysis at the ROMP2 level with the aug-cc-pVQZ basis set, and the atomic orbital distribution of the excess electron, Δe_l Eq. 6

	2 s	2 p	3 s	3 d	4 d	4 f
(a) Beryllium						
Be_4	1.56	0.40			0.01	0.01
Be_4^-	1.66	0.46	0.09	0.02		0.01
$\Delta e_l(Be)$	0.10	0.06	0.09	0.02	−0.01	

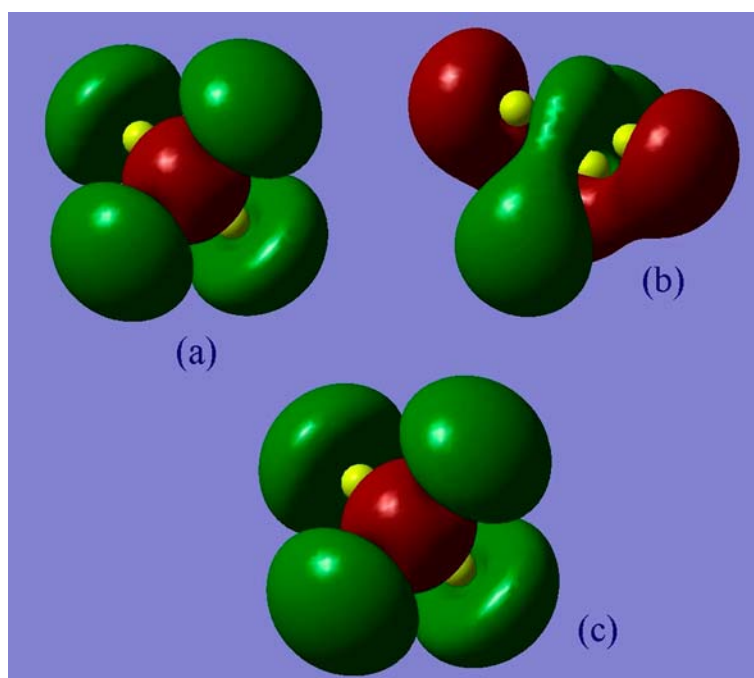|	3 s	3 p	4 s	3 d	5 p	4 f
(b) Magnesium						
Mg_4	1.87	0.10			0.01	0.01
Mg_4^-	1.92	0.20	0.11	0.01		0.01
$\Delta e_l(Mg)$	0.05	0.10	0.11	0.01	−0.01	

Fig. 1 The lowest unoccupied molecular orbitals in the ground state of Be_4. **a** LUMO, symmetry A_1. **b** LUMO + 1, symmetry T_2. **c** The highest occupied molecular orbital (HOMO), symmetry A_1, in the ground state of Be_4
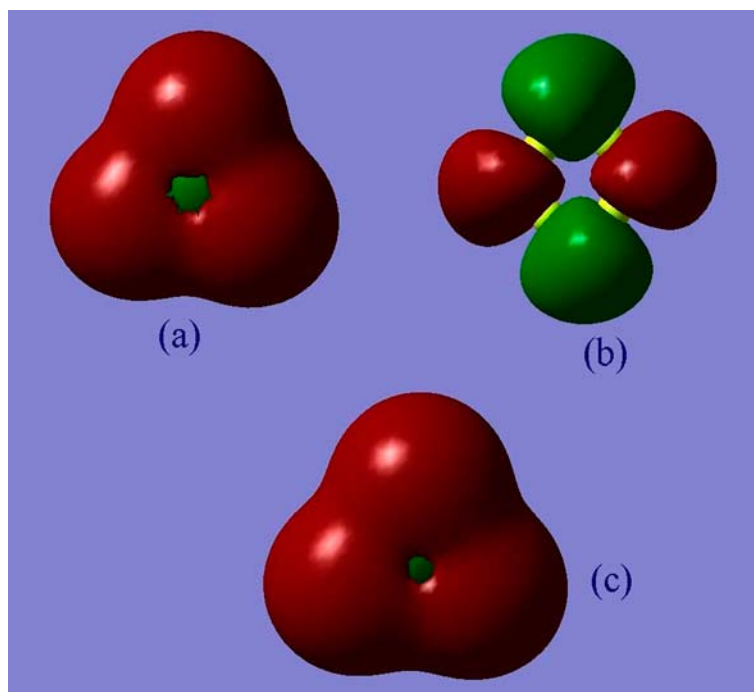
tions, although the electron correlation contribution is largest. For Mg_4^- the electron correlation also yields the major contribution to the binding energy of the excess electron. The relative contribution of the Koopmans component for Mg_4^- is smaller than in Be_4^-. As we noted in the introduction, the first non-vanishing multipole moment in tetrahedral molecules is the octopole, therefore the direct electrostatic interaction has to be very small. The main contribution to ΔE_e^{KT} constitutes induction forces and exchange and overlap effects.

The atomic orbital population was studied by the NBO analysis, which is more precise and well founded than the Mulliken population analysis. In Table 3, we show the atomic orbital populations for beryllium and magnesium neutral and anionic tetramers. The atomic orbital populations in the neutral alkaline-earth dimers and trimers are discussed in detail in Refs. [1, 3]. Whereas in the isolated atoms at the SCF approximation only the ns subshell is populated (it is closed $(ns)^2$), correlation effects and interatomic interactions induce

Fig. 2 The lowest unoccupied molecular orbitals in the ground state of Mg_4. **a** LUMO, symmetry A_1. **b** LUMO + 1, symmetry T_2. **c** The highest occupied molecular orbital (HOMO), symmetry A_1 in the ground state of Mg_4^-

the population of the np shell. This gives rise to sp-hybridization in the alkaline-earth clusters. In this study we are interested in the nature of the anion stabilization. Therefore, it is important to study the distribution of the excess electron among the atomic states. It is described as the difference between the anionic and neutral atomic orbital populations

$$\Delta e_l(A) = n_l(A_n^-) - n_l(A_n) \tag{6}$$

This difference is also shown in Table 3.

As follows from Table 3, the sum over all orbitals occupied by additional electron in anions is

$$\sum_l \Delta e_l(\text{Be}) = 0.26, \qquad \sum_l \Delta e_l(\text{Mg}) = 0.26 \tag{7}$$

The excess electron is equally distributed among all four atoms, the value 0.26 instead of 0.25 is caused by round-off error. Multiplying the values of $\Delta_L(A)$ in Table 3 by four, we obtain the orbital population of the outer electron in anions A_4^-

$$\Delta e_l(\text{Be}_4^-): 2s^{0.40} 2p^{0.24} 3s^{0.36} 3d^{0.08}$$
$$\Delta e_l(\text{Mg}_4^-): 3s^{0.20} 3p^{0.40} 4s^{0.44} 3d^{0.04} \tag{8}$$

Thus, the excess electron is distributed among s-orbitals and p-orbitals with a small contribution of d-orbitals. Note that the contribution of p-orbitals in Mg_4^- in the comparison with Be_4^- is twice as large.

The alkaline-earth anions may evidently be considered as valence-bound and the excess electron must occupy one of the valence vacant orbitals in the neutral cluster. In Fig. 1 and 2 plots of two lowest unoccupied molecular orbitals (LUMO and LUMO + 1) in neutral tetramers and highest occupied molecular orbital (HOMO) in anions are shown. From the symmetry of the orbitals, it follows that in both anions the outer electron occupies the LUMO of neutral tetramers. Let us mention that in Be_3^- it occupies the LUMO + 1 [4].

As follows from the orbital population analysis and the molecular orbital diagrams, see Fig. 1, the anionic tetramers must be attributed to the valence-bound anions. This is the reason that the EAs of clusters possessing an octopole moment as the first non-vanishing multipole moment are about 10^2 larger than the EAs of the dipole-bound anions [24].

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