
Comparative Study of the Electron Affinities of Beryllium and Magnesium Dimers and Trimers

I. G. KAPLAN, C. C. DÍAZ

Instituto de Investigaciones en Materiales, UNAM, Apdo. Postal 70-360, 04510 México, D. F., México

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ABSTRACT: The electron affinities of magnesium dimers and trimers are calculated at the MP4(SDTQ) and CCSD(T) levels employing the Gaussian 03 suit of programs and the Dunning-type aug-cc-pVQZ basis set. The vertical electron detachment energy (VEDE) is 0.298 eV (0.269 eV) for Mg_2^- and 0.839 eV (0.840 eV) for Mg_3^- at the MP4(SDTQ), and CCSD(T), levels. The comparative analysis of the nature of the excess electron binding and its atomic-state distribution in small beryllium and magnesium anions are performed. © 2005 Wiley Periodicals, Inc. *Int J Quantum Chem* 104: 468–474, 2005

Key words: electron affinity; magnesium and beryllium clusters; orbital population; chemical bonding; intermolecular forces

Introduction

During the past decade, most publications on the molecular anions were devoted to so-called dipole anions [1–9]. For a short critical account of these studies, especially of the wrong Møller–Plesset type 2 (MP2)-dispersion decomposition used in Refs. [4–7], see our recent publication [10].

Some of the nonpolar molecules with high point symmetry have a trend to repel an additional electron. At least, as was shown in Ref. [11], the CF_4

molecule does not attach an electron in its ground state. For the adiabatic electron affinity, a large negative value of -1.22 eV has been obtained. The molecule CF_4 possesses T_d point-group symmetry. In tetrahedral molecules, the first nonvanishing multipole moment is the octopole [12]. It is important to study the anion formation in nonpolar molecules characterizing by a quadrupole moment in their ground state and molecules with T_d geometry with an octupole moment, as well.

In this context, it is interesting to study the beryllium and magnesium dimers and trimers that possess a quadrupole moment. The Be and Mg atoms, as all alkaline-earth elements, have the closed outmost ns^2 subshell; in other words, they have no valence electrons in the ground state. In

Correspondence to: I. G. Kaplan; e-mail: kaplan@zinalco.iimatercu.unam.mx

accordance with this circumstance, the dimers of alkaline–earth elements have a weak van der Waals bond because are bonded by the dispersion forces. In contrast, the trimers are characterized by a much stronger bonding with a complex nature [13, 14]. In the case of Be_3 and Mg_3 , the dispersion attraction is almost completely compensated by the two-body exchange repulsion, and it is the three-body forces that bind these trimers and promote the ns – np transition giving rise to sp hybridization.

The first qualitative calculations of the electron affinities (EAs) of small Be_n and Mg_n clusters ($n = 2$ – 4) were carried out by Jordan and Simons [15–18]. These investigators found that the studied anions are stable with rather large EAs for the beryllium anions and much smaller EAs for the magnesium anions, see also the more precise calculations of Be_2^- by Bauschlicher and Partridge [19]. Most subsequent calculations of beryllium and magnesium clusters focused on neutral clusters. The only exception, to the best of our knowledge, are the calculations of Mg_n^- anions in Ref. [20].

The precise calculations of EAs of beryllium dimer and trimers were recently performed up to the complete coupled-cluster single–double–triple (CCSDT) level [10]. The decomposition of the binding energy of the attached electron into three components—Koopmans, relaxation, and correlation—which can easily be interpreted quantum chemically, have allowed us to elucidate the nature of anion formation in beryllium clusters.

During the past several years, the magnesium anions attract great attention stimulated by the measurements of the photoelectron spectra of Mg_n^- ($n = 3$ – 35) by Bowen and collaborators [21]. It was observed that the s – p band gap is closed at certain cluster sizes signaling the onset of metallic behavior. The theoretical studies of this phenomenon were performed by Jellinek and Acioli [22–24] within the framework of the density functional method.

In this study we calculate the EAs of Mg_2 and Mg_3 at different levels of accuracy up to the MP4(SDTQ) and CCSD(T) levels. A reliable calculation of EAs demands the use of large basis sets with many diffuse functions [25]. We employed the Dunning-type augmented correlation consistent polarized valence basis set (aug-cc-pVQZ) [26–28]. The comparative analysis of the nature of the excess electron binding and its atomic-state distribution, in small beryllium and magnesium anions, is also presented.

Methodology and Calculation Results

In variational methods (as well as in the Møller–Plesset perturbation approach), the binding energy is defined as a difference between total energies. In the anion case, the binding energy of an attached electron (the electron affinity) is equal to

$$\Delta E_e \equiv EA = E_n(N) - E_a(N + 1), \quad (1)$$

where N denotes a neutral molecule or cluster and $N + 1$ denotes an anion; n and a label the electronic states of neutral and charged systems, respectively. For the ground electronic state, Eq. (1) is written as

$$\Delta E_e = E_o(N) - E_o(N + 1). \quad (2)$$

Depending on the internuclear distances at which $E(N)$ and $E(N + 1)$ are calculated, three kinds of EA can be defined:

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 the charged system.

Figure 1 presents the typical disposal of the potential curves for a neutral and a stable anionic dimer. The stable anionic dimer usually has the energy of the minimum, which is deeper than the neutral dimer, and the value of its equilibrium distance is reduced in comparison with the neutral dimer, that is, $R_{o,A_2^-} < R_{o,A_2}$. For this disposal of potential curves, as follows from Figure 1, the electron affinities must satisfy the inequality:

$$\text{VEDE} > \text{AEA} > \text{VEA}. \quad (3)$$

Let us point out that the inequality (3) is not a rigorous theorem. It can be violated in the case of another potential curve disposal.

The calculations were carried out with the Gaussian 03 suite of programs [29] at the MP4(SDTQ) and CCSD(T) levels. Geometry optimization of ground-state structures for neutral and anionic species was performed at each level of calculation. Two basis sets were tried: the triply split valence basis set [6-311+G(3d2f)] [30–32] and the

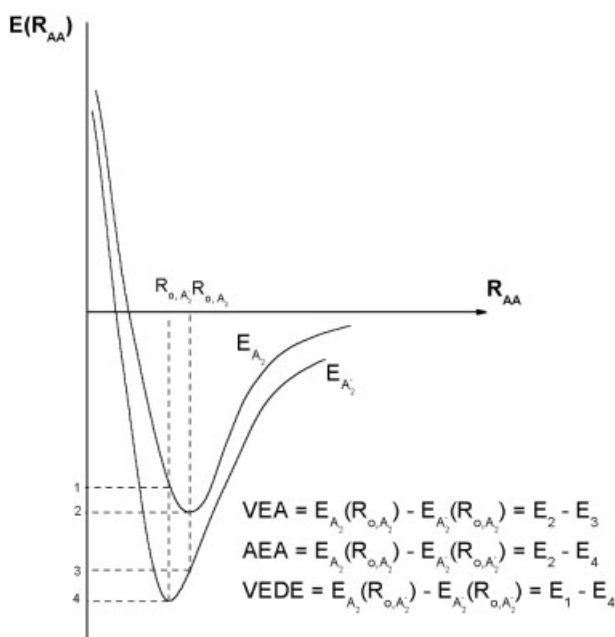


FIGURE 1. Electron affinities for a typical disposal of the potential curves for neutral and anionic dimers. 1

- $E_{A_2}(R_{o,A_2^-})$; 2 – $E_{A_2}(R_{o,A_2})$; 3 – $E_{A_2^-}(R_{o,A_2})$; 4
- $E_{A_2^-}(R_{o,A_2^-})$.

augmented correlation consistent Dunning-type basis set [aug-cc-pVQZ] taken from the EMSL basis set library website [33]. As shown in Ref. [10], the 6-311+G(3d2f) basis set gives a good accuracy and can be used in calculations of EAs of beryllium clusters. For magnesium anions, this basis set does not give reliable results at high correlation levels;

we employed the larger and refined aug-cc-pVQZ basis set, having 7s, 6p, 4d, 3f, and 2g contracted gaussians [33].

In the anion calculations, the unrestricted Hartree–Fock (UHF) reference functions were used, and the spin contamination was monitored at the UHF and CC levels. To eliminate the spin contamination in the MP calculations, the spin projection procedure [34], embedded in the Gaussian suite, was employed.

The electron density distribution was studied within the population analysis based on the natural orbitals [35, 36]. The analysis of orbital population was performed for the MP4(SDQ) generalized density using the NBO option provided by the Gaussian suite.

Results obtained at different levels of theory are presented in Table I. For comparison, Table II presents similar data for the neutral and anionic beryllium clusters taken from Ref. [10], the KT values for Be_3 and Be_3^- are corrected. In Tables I and II, the values of the EAs found in the Koopmans approach are also presented. This approach corresponds to the self-consistent field (SCF) method, in which both energies in Eqs. (1) or (2) are calculated with the same SCF orbitals. According to the Koopmans theorem (KT) [37], 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

$$\Delta E_e^{\text{KT}}(\text{VEA}) = E_o^{\text{SCF}}(N) - E_o^{\text{SCF}}(N + 1)_{\text{nonrelax}} = -\varepsilon_e(A_n), \quad (4)$$

TABLE I

Total ground-state energies (a.u.) and electron affinities (eV) of magnesium clusters, calculated at different levels of theory with the aug-cc-pVQZ basis set.

| | KT | UHF | UMP2 | UMP4(SDTQ) ^a | CCSD(T) ^b |
|-----------------|--------|-----------|-----------|-------------------------|----------------------|
| Mg_2 | | –399.2258 | –399.2790 | –399.2946 | –399.2980 |
| Mg_2^- | | –399.2154 | –399.2835 | –399.3027 | –399.3056 |
| VEA | –0.258 | –0.117 | 0.083 | 0.156 | 0.126 |
| AEA | | –0.285 | 0.123 | 0.220 | 0.205 |
| VEDE | –0.213 | –0.083 | 0.221 | 0.298 | 0.269 |
| Mg_3 | | –598.8298 | –598.9265 | –598.9515 | –598.9550 |
| Mg_3^- | | –598.8389 | –598.9533 | –598.9810 | –598.9838 |
| VEA | –0.043 | 0.277 | 0.681 | 0.755 | 0.713 |
| AEA | | 0.249 | 0.729 | 0.804 | 0.785 |
| VEDE | 0.001 | 0.425 | 0.772 | 0.839 | 0.840 |

^a UMP4(SDTQ) Mg–Mg distances for Mg_2 , 3.90 Å, and Mg_2^- , 3.21 Å, for Mg_3 , 3.32 Å, and Mg_3^- , 3.12 Å.

^b CCSD(T) Mg–Mg distances for Mg_2 , 3.98 Å, and Mg_2^- , 3.26 Å, for Mg_3 , 3.36 Å, and Mg_3^- , 3.10 Å.

TABLE II

Total ground-state energies (a.u.) and electron affinities (eV) of beryllium clusters calculated at different levels of theory with the 6-311+G(3d2f) basis set [10].

| | KT | UHF | UMP2 | UMP4(SDTQ) | CCSD(T) | CCSDT |
|------------------------------|--------|-----------|-----------|------------|-----------|-----------|
| Be ₂ ^a | | -29.13358 | -29.20130 | -29.22932 | -29.23688 | -29.23767 |
| Be ₂ ⁻ | | -29.14632 | -29.21784 | -29.24395 | -29.24878 | -29.25005 |
| VEA | -0.249 | 0.357 | 0.442 | 0.392 | 0.316 | 0.332 |
| AEA | | 0.347 | 0.450 | 0.398 | 0.324 | 0.337 |
| VEDE | -0.203 | 0.402 | 0.467 | 0.405 | 0.327 | 0.341 |
| Be ₃ ^b | | -43.71493 | -43.84610 | -43.88146 | -43.88698 | |
| Be ₃ ⁻ | | -43.74074 | -43.90252 | -43.93759 | -43.93972 | |
| VEA | 0.107 | 0.684 | 1.462 | 1.482 | 1.377 | |
| AEA | | 0.702 | 1.535 | 1.527 | 1.435 | |
| VEDE | 0.121 | 0.754 | 1.589 | 1.599 | 1.488 | |

^a CCSD(T) Be–Be distances for Be₂, 2.528 Å, and Be₂⁻, 2.434 Å, except for the CCSDT column, where CCSDT Be–Be distances for Be₂, 2.511 Å, and Be₂⁻, 2.433 Å, are used.

^b CCSD(T) Be–Be distances for Be₃, 2.221 Å, and Be₃⁻, 2.113 Å.

where $\varepsilon_e(A_n)$ is the energy of the vacant orbital for the neutral system at its ground state occupied by the attached electron in an anion. The VEDE in the KT approximation is also determined according to Eq. (4), but at the anion equilibrium geometry.

As follows from Table I, there is a gradual increase of the negative ground-state energy, E_0 , with an increasing account of electron correlation in employed methods for both neutral and anionic clusters. These results manifest a good convergence and stability of employed calculation methods for neutral and anionic magnesium clusters. The obtained values of EAs are quite large at all levels of theory. The VEDE is equal to 0.298 eV for Mg₂⁻ and 0.839 eV for Mg₃⁻ at the MP4(SDTQ) level and is slightly less at the CCSD(T) level (VEDEs for Mg₃⁻ are almost the same), although they are about two times smaller than the EAs for beryllium clusters (see Table II). As follows from Table II, where for the Be₂ represented the EAs at the more precise CCSDT level, the MP4(SDTQ) calculations overestimate the EAs, whereas the CCSD(T) approximation underestimates the values of EAs. Thus, we may suggest that the reliable values of the magnesium clusters EAs are located between values presented in the last two columns of Table I. At the SCF level, the Mg₂ and Mg₃ clusters, in contrast to the beryllium case, repel an excess electron. Only at electron correlation levels, the anions Mg₂⁻ and Mg₃⁻ become stable.

The relatively large values of EAs for Mg₂ and Mg₃ are an indication that the excess electron can be considered to be valence bound, as it takes place in

the beryllium anions [10]. In the following section, we analyze the nature of binding in anions in more details.

Decomposition of the Electron Affinities and Discussion

As was demonstrated in Ref. [10], to study the binding of the excess electron in anions, it is useful to decompose its binding energy (EA) into three components

$$\Delta E_e = EA = \Delta E_e^{\text{KT}} + \Delta E_{\text{relax}}^{\text{SCF}} + \Delta E_e^{\text{corr}}. \quad (5)$$

The KT approximation [see Eq. (4)] does not take relaxation effects into account and includes only the electrostatic and exchange interactions at the first order of the perturbation theory (it corresponds to the Heitler–London approximation). The remainder of the binding energy at the SCF level, we denote as the relaxation energy

$$\Delta E_{\text{relax}}^{\text{SCF}} = \Delta E_e^{\text{SCF}} - \Delta E_e^{\text{KT}}, \quad (6)$$

which stems from the relaxation of the orbitals of the neutral system in the field of the attached electron. $\Delta E_{\text{relax}}^{\text{SCF}}$ consists mostly of the induction (polarization) energy, but it contains also the exchange energy that cannot be separated from the induction energy.

TABLE III
Decomposition of the VEDE (eV) in the ground state of Be and Mg anions at the MP4(SDTQ) level.

| | ΔE_e^{KT} | $\Delta E_{\text{relax}}^{\text{SCF}}$ | ΔE_e^{corr} | VEDE |
|-------------------------|--------------------------|--|----------------------------|-------|
| Be_2^- | -0.203 | 0.605 | 0.003 | 0.405 |
| Be_3^-, D_{3h} | 0.121 | 0.633 | 0.845 | 1.599 |
| Mg_2^- | -0.213 | 0.130 | 0.381 | 0.298 |
| Mg_3^-, D_{3h} | 0.001 | 0.424 | 0.414 | 0.839 |

The electron correlation contribution is defined following the general definition of Löwdin [38]

$$\Delta E_e^{\text{corr}} = \Delta E_e - \Delta E_e^{\text{SCF}} \quad (7)$$

and depends on the correlation method used. If the MP4(SDTQ) method is employed,

$$\Delta E_e^{\text{corr}}[\text{MP4(SDTQ)}] = \Delta E_e^{\text{MP4(SDTQ)}} - \Delta E_e^{\text{SCF}}. \quad (8)$$

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. [13]. The relaxation energy at large distances reduces to the classical induction energy.

We are interested in the study of the binding of the excess electron in anions; so, it is natural to study the VEDE for the corresponding anion (in Ref. [10], decomposition (5) was applied to the VEA). Table III presents the decomposition of the VEDE at the MP4(SDTQ) level for the beryllium and magnesium anions, using Eqs. (6) and (8) and the data from the calculations presented in Tables I and II. Let us discuss the conclusions according to the binding, which follows from Table III, separately for dimers and trimers.

Dimers. In both anionic dimers, the electrostatic and exchange interactions, ΔE_e^{KT} , play a destabilizing role. Evidently, these anions are not quadrupole bound; rather, they are valence bound. The only factor of stabilization of the excess electron in Be_2^- is the relaxation energy, which includes induction and exchange energies. It is large enough to stabilize Be_2^- at the SCF level. The contribution of the correlation energy is negligible. In Mg_2^- , the relaxation energy is considerably smaller than the repulsive ΔE_e^{KT} , causing instability of the Mg_2^- anion at

the SCF level. The main factor of stabilization of the excess electron in Mg_2^- is the correlation energy.

Trimers. Both Be_3^- and Mg_3^- are stabilized by the relaxation and correlation energies. At large distances these energies reduce to the induction and dispersion energies between the excess electron and the neutral trimers, but at distances in anions they cannot be separated from the exchange and overlap effects. In the Be_3^- anion, ΔE_e^{KT} makes a contribution (about 10%) to its stability, and the correlation effects play a more important role than in the Mg_3^- anion. Both anionic trimers are valence bound.

It is instructive to study the atomic orbital population in anions and to compare it with the atomic orbital population in neutral clusters. At present, it can be performed by the natural bond orbital (NBO) analysis, which is more precise and substantiated than the Mulliken population analysis. Table IV presents the atomic population for beryllium and magnesium neutral and anionic dimers. The atomic population in the neutral alkaline-earth dimers and trimers is discussed in detail in Refs. [13, 14]. Whereas in the isolated atoms at the SCF approximation, only the ns subshell is populated, in this case, it is closed, $(ns)^2$; the correlation effects and interatomic interactions induced the population of the np shell. This suggests the possibility of the sp hybridization in alkaline-earth clusters. In the present study, we study the nature of anion stabilization and it is important to study the distribution of the excess electron among the atomic states. For this we need to find the difference

$$\Delta e_1(A) = n_1(A_n^-) - n_1(A_n). \quad (9)$$

From the data presented in Table IV, we find

$$\text{Be}_2^-; \quad \Delta e_1(\text{Be}): 2s^{-0.01}2p^{0.46}3s^{0.00}3p^{0.03}3d^{0.02};$$

$$\sum_l \Delta e_l = 0.50.$$

$$\text{Mg}_2^-; \quad \Delta e_1(\text{Mg}): 3s^{-0.03}3p^{0.48}4s^{0.01}3d^{0.02}4p^{0.03};$$

$$\sum_l \Delta e_l = 0.51.$$

The attached electron mostly occupies the p -type orbitals; its total p -population is $2p^{0.92} 3p^{0.06}$ in Be_2^- and $3p^{0.96} 4p^{0.06}$ in Mg_2^- (a part of the p -population in Mg_2^- that exceeds unity has the $3s$ -origin). Thus,

TABLE IV

Atomic population n_i in neutral and anionic beryllium and magnesium dimers obtained by the natural bond orbital (NBO) analysis at the MP4 level with the 6-311+G(3d,2f) basis set for Be₂ (Be₂⁻) and the aug-cc-pVQZ basis set for Mg₂ (Mg₂⁻).

| | a. Beryllium | | | | |
|------------------------------|--------------|------|------|------|------|
| | 2s | 2p | 3s | 3p | 3d |
| Be ₂ | 1.80 | 0.19 | 0.01 | — | — |
| Be ₂ ⁻ | 1.79 | 0.65 | 0.01 | 0.03 | 0.02 |
| | b. Magnesium | | | | |
| | 3s | 3p | 4s | 3d | 4p |
| Mg ₂ | 1.88 | 0.11 | — | — | — |
| Mg ₂ ⁻ | 1.85 | 0.59 | 0.01 | 0.02 | 0.03 |

the density distribution of the attached electron in the beryllium and magnesium dimers is very similar. The difference in binding and following from it the difference in EAs (according to Tables I and II, the EAs in magnesium clusters are about twice as small as similar EAs in the beryllium clusters), is connected with the different behavior the 2*p*- and 3*p*-orbitals [17]. The 3*p*-orbital is more diffuse and more spatially extended than the 2*p*-orbital. This results in less bonding of the excess electron in Mg_{*n*} in comparison with Be_{*n*}.

Conclusions

Calculations of the EAs of Mg₂ and Mg₃ up to the MP4(SDTQ) and CCSD(T) levels with the Dunning-type aug-cc-pVQZ basis set show good convergence and stability of employed methods for both neutral and anionic magnesium clusters. It has been demonstrated that the 6-311+G(3d2f) basis set, which gives good accuracy for the beryllium anions [10], does not give reliable results for the Mg₃⁻ anion. This is the reason that the aug-cc-pVQZ basis set was employed. The vertical electron detachment energy (VEDE) is 0.298 eV (0.269 eV) for Mg₂⁻ and 0.839 eV (0.840 eV) for Mg₃⁻ at the MP4(SDTQ), and CCSD(T), levels. The smaller magnitude of the EAs in Mg_{*n*} in comparison with Be_{*n*} can be explained by the different behavior of 3*p*- and 2*p*-orbitals occupied by the excess electron in magnesium and beryllium anions, respectively.

The only factor of stabilization of the excess electron in Be₂⁻ is the relaxation energy, whereas in

Mg₂⁻, it is the correlation energy. Both the Be₃⁻ and Mg₃⁻ anions are stabilized by the relaxation and correlation energies, although in anions these energies cannot be separated from the exchange energies. Both anionic dimers and trimers are valence bound.

Investigation of the EAs of the beryllium and magnesium tetramers having *T_d* ground-state geometry is now in progress.

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