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## On the existence and stability of small $K_nMg$ clusters

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**Abstract.** *Ab initio* many-body perturbation theory has been used to study the existence and stability of small  $K_nMg$  clusters. Significant differences are shown to exist between experimental results and different theoretical models. Further experimental data are clearly needed to resolve central questions on heteroatomic clusters.

### 1. Introduction

Recent years have witnessed a remarkable progress in the experimental and theoretical studies of atomic and molecular clusters (Jena *et al* 1987, Sugano *et al* 1987, Benedek *et al* 1988, Chapon *et al* 1989). Much of the work has been confined to homonuclear alkali-metal clusters and clusters of semiconducting elements. However, published work on heteroatomic metal clusters remains relatively scarce, in spite of the importance of such clusters in addressing such questions as the influence of electron shells, the electronegativity difference and the role of the foreign atom. In particular,  $K_nMg$  clusters are interesting systems because, as pointed out by Kappes *et al* (1985), a magnesium atom put into a potassium cluster large enough to manifest 's-p band mixing' should contribute two electrons and one core to the system and provides a good test to the jellium model (Knight *et al* 1984, Chou *et al* 1984, Kappes *et al* 1985). Experimental data by Kappes *et al* (1985) indicate that  $K_6Mg$  is the smallest  $K_nMg$  heterocluster present in 'significant' amounts and the first abundance maximum is reached at  $K_8Mg$ . In particular, these experiments served to falsify the jellium model of a metal cluster. In a Letter to the Editor, Baladron *et al* (1987) have claimed that a very natural modification of the jellium-background model can explain the results of Kappes *et al* (1985) and that very small  $K_nMg$  clusters are absent in the mass spectra due to a positive heat of solution of the Mg atom in the  $K_n$  cluster. Ballone *et al* (1989) have presented an *ab initio* molecular dynamics study of the ground state, finite temperature, dynamical and electronic properties of  $Na_{20}$  and  $Na_{10}K_{10}$  microclusters. They found that the electronic configuration largely reflects that predicted by the shell model. Molecular dynamics calculations by Heiz *et al* (1990) indicate that the heteroatom (Zn, Cd or Hg) does not penetrate into a  $Na_n$  cluster with  $n = 6$ . This article is thus concerned with a study of the existence and stability of small  $K_nMg$  clusters from an *ab initio* point of view and is a natural extension of our published results on  $K_n$  and  $K_nNa$  clusters (Ray and Altekar 1990, Ray and Berry 1990). As before, electron correlation effects have been studied by invoking the concepts of many-body perturbation theory (MBPT).

## 2. Theory

In MBPT, the energy is given by the linked-diagram expansion (Bartlett and Silver 1974, Bartlett 1981, Goldstone 1957, Lowdin 1965a,b)

$$\Delta E = E - E_0 = E_1 + E_{\text{corr}} = \sum_{n=0}^{\infty} \langle \Phi_0 | [V(E_0 - H_0)^{-1} V]^n | \Phi_0 \rangle_L \quad (1)$$

where  $\Phi_0$  is the single-determinant self-consistent-field (SCF) wavefunction,  $H_0$  is the sum of one-electron Fock operators,  $E_0$  is the sum of SCF orbital energies,  $V = H - H_0$  is the perturbation, where  $H$  is the usual electrostatic Hamiltonian. We have chosen  $\Phi_0$  to be the unrestricted Hartree-Fock (UHF) wavefunction. The subscript L indicates the limitation to linked diagrams. Though one can include various categories of infinite-order summations from (1), the method is usually limited by termination at some order of perturbation theory. In this work, we have carried out complete fourth-order calculations which consist of all single-, double-, triple- and quadruple-excitation terms. This is known to be very reliable in the computation of bond energies (Hehre *et al* 1986).

## 3. Computational results and discussions

One of the primary considerations involved in *ab initio* HF/MBPT calculations is determination of the type of basis set to be used. Gaussian-type basis sets used in *ab initio* molecular orbital computations usually involve some compromise between computational cost and accuracy. For potassium and magnesium, we have used the 3-21G basis set due to Dobbs and Hehre (1986) and Hehre *et al* (1986). In this basis set, functions that comprise the valence shell are split into two (inner and outer) parts, while the inner shell atomic orbitals are each represented by single basis function. Each of the inner shell atomic basis functions is represented by three Gaussian functions; the inner and outer parts of the valence basis functions are represented by two and one Gaussians, respectively.

We first performed (UHF) calculations for the KMg-K<sub>3</sub>Mg clusters and geometries were optimized by total energy minimization with the use of analytical gradient techniques (Hehre *et al* 1986). Geometries were not optimized for all the clusters at the MP4 level, because of excessive computational requirements; however, optimized geometries for KMg and K<sub>2</sub>Mg at the MP4 level indicated that our bond lengths and bond angles are expected to be accurate within 10%. All the computations were carried out on an IBM 4381 computer using the GAMESS program written by Schmidt *et al* (1987) and on a Cray X-MP/24 computer using the GAUSSIAN 86 program written by Frisch *et al* (1986). The optimum geometry for a given cluster was then used to calculate the fourth-order perturbation theory energy eigenvalue (table 1). We first discuss the optimum geometries of the K<sub>n</sub>Mg clusters (figure 1).

The optimized KMg dimer has a significantly higher bond length of 4.99 Å as compared to the K<sub>2</sub> dimer which has a bond length of 4.22 Å. The doublet ground state is a very weakly bound structure with a binding energy per atom of only 0.011 eV at the fourth-order many-body perturbation theory level. For the triatomic clusters, we optimized three structures and the best structure was found to be an acute isosceles triangle with the Mg atom at the vertex. This structure was also found to be the

Table 1. Ground state energies of  $K_n$ Mg clusters.

Total no. of atoms	State	UHF total energy (au)	MP2 total energy (au)	MP4 total energy (au)	Atomization energy per atom (eV)
2	$C_{\infty V} \ ^2A_1$	-794.6216	-794.6399	-794.6521	0.013
3	$C_{\infty V} \ ^1A'$	-1390.7573	-1390.7907	-1390.8067	0.024
3	$C_S \ ^1A'$	-1390.7573	-1390.7906	-1390.8066	0.023
3	$C_S \ ^1A'$	-1390.7697	-1390.8005	-1390.8190	0.136
4	$C_{2V} \ ^2B_2$	-1986.9326	-1986.9582	-1986.9753	0.124
4	$C_{\infty V} \ ^2A_1$	-1986.9315	-1986.9544	-1986.9702	0.089
4	$C_{\infty V} \ ^2A_1$	-1986.9301	-1986.9497	-1986.9626	0.038
4	$C_{2V} \ ^4B_2$	-1986.9292	-1986.9512	-1986.9647	0.052
5	$C_{2V} \ ^1A_1$	-2583.0724	-2583.1172	-2583.1425	0.176
5	$C_S \ ^1A'$	-2583.0806	-2583.1299	-2583.1564	0.252
5	$C_{2V} \ ^1A_1$	-2583.0675	-2583.1144	-2583.1381	0.152
6	$C_S \ ^2A'$	-3179.2462	-3179.2831	-3179.3038	0.185
6	$C_S \ ^2A'$	-3179.2261	-3179.2863	-3179.3115	0.220
7	$C_S \ ^1A'$	-3775.3520	-3775.4433	-3775.4731	0.222
7	$C_{2V} \ ^1A_1$	-3775.3819	-3775.4623	-3775.4946	0.305
7	$C_S \ ^1A'$	-3775.3898	-3775.4729	-3775.5038	0.341
8	$C_S \ ^2A''$	-4371.5666	-4371.6383	-4371.6653	0.327
9	$C_S \ ^1A'$	-4967.7246	-4967.8508	-4967.8784	0.473

most stable structure for  $K_2$ Na cluster and disagrees with the results of Fantucci *et al* (1989) for  $Na_2$ Mg and  $Li_2$ Mg clusters. For the  $K_3$ Mg clusters, we optimized several structures with the Mg atom at different positions as shown in figure 1, but the most stable conformer has the shape of a rhombus with the magnesium at the peripheral position. The high stability of the rhombic structure is due to Jahn-Teller distortion.

For the  $K_4$ Mg clusters, we replaced the centre K atom with a Mg atom in three neutral  $K_5$  clusters (Ray and Altekar 1990). The most stable structure was found to be a bi-triangular structure with the Mg atom at the apex of the base triangle. Again, this structure is different from the most stable  $Na_4$ Mg and  $Li_4$ Mg clusters found by Fantucci *et al* (1989). For the  $K_5$ Mg clusters, two geometries were studied: one was a pentagonal pyramid with the Mg atom at the apex and the other a triangular bipyramid with the Mg atom at the centre of the base. The second structure was found to be the most stable structure.

The  $K_6$ Mg cluster, with eight valence electrons, is considered to be a stable structure in a closed shell configuration and we considered three structures: a square bipyramid, a hexagon and a prism, with the Mg atom at the centre of the structure. The most stable structure was found to be the prism which disagrees with the results of Fantucci *et al* (1989) for  $Li_6$ Mg and  $Na_6$ Mg clusters. Zhang *et al* (1987) also assumed that a body-centred octahedral structure is the most stable structure for the  $Na_6$ Mg cluster. For the  $K_7$ Mg cluster, we optimized only one geometry, by adding a Mg atom to the centre of the most stable  $K_7$  cluster, the pentagonal bi-pyramid and for the  $K_8$ Mg cluster, a Mg atom was added to the centre of the cubic  $K_8$  structure.

We now return to the central question of the existence and stability of small  $K_n$ Mg clusters. For this purpose, we first define the atomization energy per atom of a cluster from

$$AE = [nE(K) + E(Mg) - E(K_nMg)]/(n + 1) \quad (2)$$

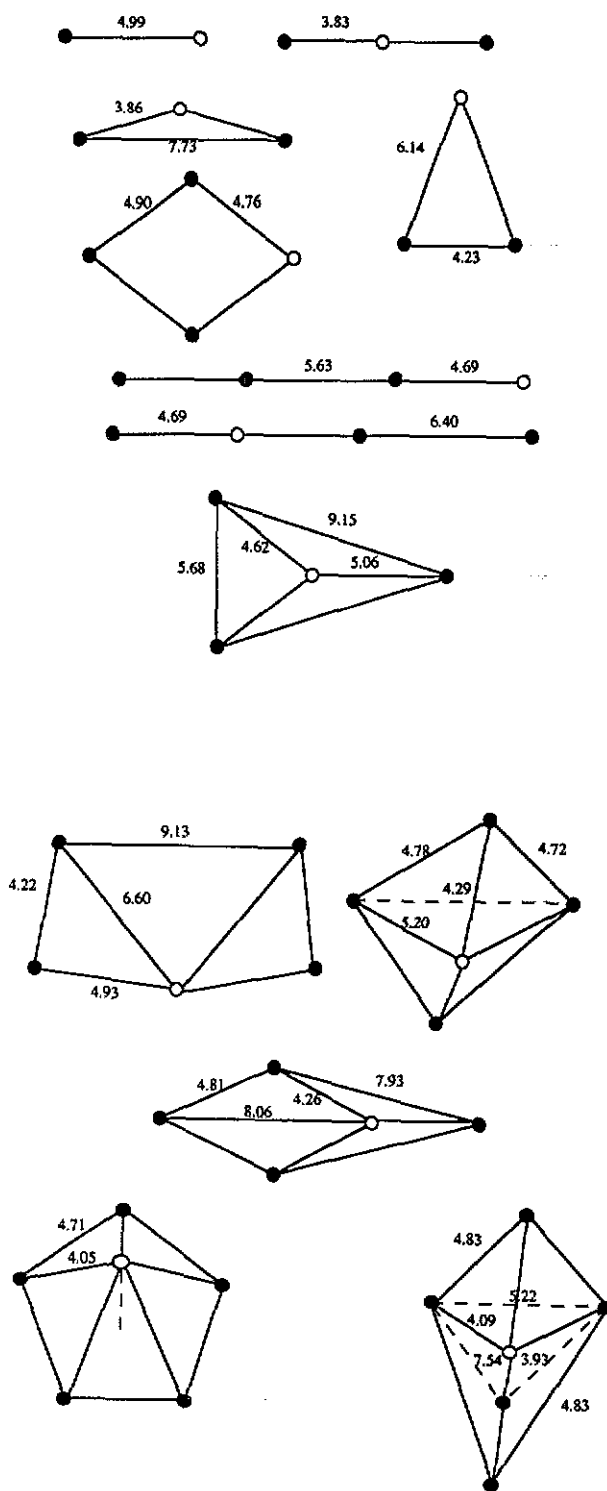


Figure 1. Ground state geometries of  $K_nMg$  clusters. Distances given in Å.

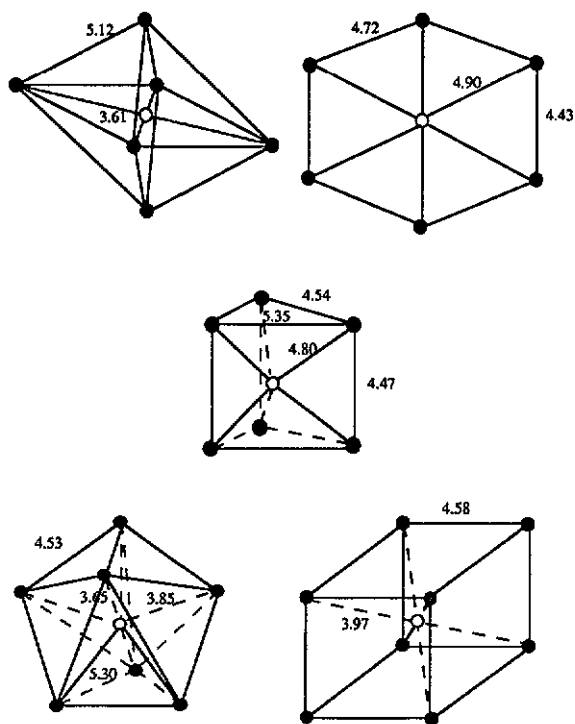


Figure 1. (Continued)

Table 2. Estimated total energies and atomization energies of the most stable  $K_nMg$  clusters.

Total no. of atoms	Total energy (au)	Atomization energy per atom (eV)
2	-794.6550	0.053
3	-1390.8231	0.172
4	-1986.9800	0.156
5	-2583.1615	0.280
6	-3179.3153	0.237
7	-3775.5081	0.357
8	-4371.6701	0.343
9	-4967.8820	0.483

where  $E(K)$  is the energy of a K atom,  $E(Mg)$  is the energy of a Mg atom and  $E(K_nMg)$  is the energy of the optimized  $K_nMg$  cluster. The plotted values of  $\Delta E$  against the total number of atoms in figure 2 clearly indicate that all the clusters are bound implying existence and that the characteristic odd-even alternation for homonuclear alkali-metal clusters (Ray 1989, Ray and Altekar 1990) persists for mixed potassium-magnesium clusters. In particular,  $K_6Mg$  and  $K_8Mg$  clusters are very stable. The atomization energy per atom ranges from 0.011 eV for the weakly bound  $KMg$  structure to 0.473 eV for the stable structure of  $K_8Mg$ . This implies a range of 0.022 to 4.257 eV for the total atomization energy for the range of clusters studied. Thus although the atomization energies are of the order of 1 eV or less for  $K_nMg$

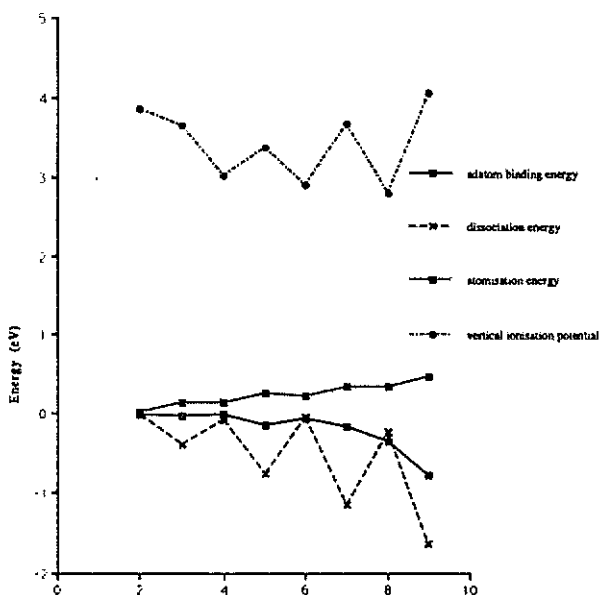


Figure 2. Atomization energies, adatom binding energies, dissociation energies and vertical ionization potentials of  $K_nMg$  clusters: full lines and squares, adatom binding energy; broken line and crosses, dissociation energy; dotted line and squares, atomization energy; and chain line and full dots, vertical ionization potential.

( $n \leq 6$ ) clusters, it is not clear that the prevailing thought in the literature that the Mg atom does not penetrate into a  $K_n$  cluster for  $n < 6$ , is quite correct. To estimate the total correlation energy, we used the expression given by Bartlett and Shavitt (1977) and the results are given in table 2. It is noted that our general conclusions about atomization energies remain valid. We then calculated the adatom binding ('heat of the solution') of the Mg atom in the  $K_n$  cluster from

$$E_{ad} = E(K_nMg) - E(K_n) - E(Mg). \quad (3)$$

Here a negative value of  $E_{ad}$  indicates stability against dissociation into a  $K_n$  cluster and a Mg atom. As indicated in figure 2, our computed values at the fourth-order many-body perturbation theory level shows that all the clusters are stable and that the adatom binding increases monotonically and significantly beyond  $n \geq 5$ . This is in direct contrast with the results of Baladron *et al* (1987) who found that  $E_{ad}$  is positive for  $n < 3$ . Baladron *et al* (1987), in fact, pointed out that the modified jellium-background model might be less adequate for very small values of  $n$ . To analyse the stabilities further, we then computed the energy gained in adding a potassium atom to an existing cluster from

$$E_k = E(K_nMg) - E(K_{n-1}Mg) - E(K) \quad (4)$$

where a negative value of  $E_k$  for a cluster  $K_nMg$  implies stability against dissociation into a  $K_{n-1}Mg$  cluster and a K atom. Again, at the MP4 level, all  $E_k$ s are negative and distinct odd-even alternation is noticed, with large oscillations as  $n$  increases.

In figure 2, we have plotted the vertical ionization potentials defined by

$$VIP = E^+ - E \quad (5)$$

where  $E^+$  is the total energy of the ionized cluster at the neutral geometry against the total number of atoms. Inasmuch as vertical ionization potentials are not equivalent to experimental appearance potentials, we do however observe odd-even alternations and find that the  $K_8$ Mg has a higher ionization potential than  $K_6$ Mg. The higher ionization potential of the more stable ten-electron system  $K_8$ Mg plotted against the lower ionization potential of the less stable eight electron system  $K_6$ Mg can, to some extent, be rationalized within the jellium model but disagrees with the experimental results of Kappes *et al* (1985).

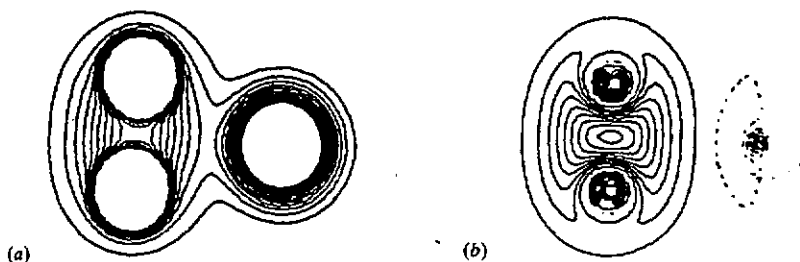


Figure 3. (a) Total one-electron density contour plots of  $K_2$ Mg. (b) Difference one-electron density contour plots of  $K_2$ Mg.

In figure 3, we have plotted the total one-electron density and difference one-electron density for  $K_2$ Mg cluster in the plane containing the Mg atom. The difference one-electron density has been calculated as the difference between one-electron density of the cluster and the superposition of the one-electron density of the non-interacting atoms. In the total one-electron density plots, one notices regions of higher and lower electron densities and clearly the one-electron densities are delocalized. The increment between successive contours is 0.0002 in units of  $\text{Bohr}^{-3/2}$ . As far as the difference densities are concerned, we do see some evidence of two-centre bonds.

In summary, as far as small  $K_n$ Mg clusters are concerned, there are clear disagreements between the experimental observations of Kappes *et al* (1985) and the contradictory theoretical predictions of the jellium model and results based on Hartree-Fock theory followed by extensive correlation corrections. Further experimental work on these clusters followed by more elaborate theoretical models are clearly necessary to resolve these discrepancies.

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