# Electronic shell structure of simple metal heteroclusters

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By studying two small heteroclusters, $Na_6Mg$ and $Na_8Mg$, we propose that the electronic shell structure which was previously observed in pure alkali-metal clusters should also exist in an alkali-metal cluster with a single divalent atom such as Mg. The calculations are performed self-consistently using pseudopotentials within the local-density approximation. We find that the charge distribution is delocalized with no evidence for directional bonding. A central Mg in a Na cluster primarily affects the $s$ states and thus slightly modifies the set of shell closing numbers.

Recent progress made in cluster physics has contributed to our understanding of these atomic aggregates. From a series of experiments on alkali-metal clusters of sodium and potassium,[1,2] it is found that clusters having particular numbers of atoms $n$ ($n = 8$, 20, 40, 58, 92, ...) are distinctively more abundant in the mass spectrum and have relatively larger ionization potentials compared with clusters with $n + 1$ atoms. These properties have been explained by the existence of electronic shells associated with the delocalized valence electrons in these clusters.[1–3] The physical properties of the alkali-metal clusters are different from those of semiconductor[4] or noble-gas[5] clusters where cluster stability is closely related to the number of directional bonds or the geometrical closed-packing patterns of atomic spheres, respectively.

It is believed that for alkali-metal clusters the valence electrons contributed by constituent atoms are essentially itinerant and able to screen the atomic potentials as in the case of the bulk metals. However because the electrons are confined to the cluster they occupy discrete electronic levels.[1] When the number of valence electrons in a cluster is just enough to completely fill a certain electronic level (shell), this cluster displays the properties described above. Quantitative theoretical studies have been performed using a jellium model for clusters over a large range of sizes.[3,6,7] This model assumes nearly free electrons and yields reasonably good agreement with experiment. Calculations with more realistic potentials and atomic arrangements for alkali-metal clusters of limited sizes support the delocalized result for the valence electrons[8–11] and give eigenvalues ($n \geq 13$) with orderings which are almost identical to the jellium results.[9] In contrast, conventional chemical bonding principles may not be adequate for understanding these systems.[12]

New questions arise when one tries to understand metallic heteroclusters. Of central importance is the extent to which electronic shell structure still exists and whether the electrons start to form localized bonds. Experiments have shown that mixed clusters of sodium and potassium have similar characteristics to pure sodium or potassium clusters.[2,13] This is not surprising because they belong to the same column of the Periodic Table and both are free-electron-like metals in the bulk. However, if the foreign atom is a divalent element such as magnesium, which is also a free-electron-like metal in the bulk, it is interesting to see whether the core charge can be screened and how the binding mechanism changes in these mixed clusters.

In this paper, we report a calculation for two prototype small clusters $Na_6Mg$ and $Na_8Mg$ in fixed geometries. Recent photoionization measurements[13] of $K_nMg$ ($n < 20$) heteroclusters show an abundance maximum at $K_8Mg$ which has ten valence electrons per cluster. Because this new peak does not coincide with any of those observed before,[1,2] this has been used to question[13] the validity of the shell description and the jellium model for metal clusters. However, the theoretical results reported here indicate that the electrons remain delocalized in both $Na_6Mg$ and $Na_8Mg$ and that the energy levels are still consistent with the angular momentum quantum states of the cluster as whole.[1] The presence of the magnesium potential at the center lowers the energies of the $s$ states and changes the level ordering in part of the energy spectrum. Both $Na_6Mg$ and $Na_8Mg$ turn out to be closed-shell systems. The theoretical results also suggested that for larger mixed clusters $Na_nMg$, which are currently beyond our computational capability, the jellium model may still be a usable approximation. By introducing a different atom at the center of a cluster, it is possible to vary the shell closing numbers. This may be valuable for future applications.

The equilibrium geometries of some small $Li_nMg$ clusters ($n \leq 6$) have been calculated[14] theoretically, and for $Li_6Mg$, a body-centered octahedral structure was found to be most stable. However, the charge distribution and energy level relations were not examined. Here we assume the same equilibrium structure for the $Na_6Mg$ cluster based on the assumption of a similar role for sodium as for lithium in these clusters. With eight electrons per cluster in an itinerant-electron system, the energy levels up to $1p$ level could be filled. The other cluster studied is $Na_8Mg$ with ten electrons per cluster. We believe this cluster has similar physical properties of $K_8Mg$. The

TABLE I. The calculated binding energy and equilibrium separation between Mg and Na for $Na_6Mg$ and $Na_8Mg$ in a body-centered octahedral and body-centered cubic structure, respectively.

|          | Bind energy (eV/cluster) | $d_{Mg-Na}$ (Å) |
|----------|--------------------------|-----------------|
| $Na_6Mg$ | 6.52                     | 2.91            |
| $Na_8Mg$ | 9.00                     | 3.10            |

model structure consists of a sodium cube with a central magnesium atom for $Na_8Mg$. The distance between the sodium and magnesium atoms are varied in both systems to find the energy minimum.

The calculation is performed using *ab initio* pseudopotentials[15] within the local-density functional formalism[16] and the supercell method[17] where the cluster is repeated in real space on a simple cubic lattice with a lattice constant of 21.8 a.u. A symmetrized plane-wave basis set with energy up to 4 Ry is employed for the eigenfunction expansion. With this plane-wave set the total energy is expected to be converged to within 20 mRy according to our tests. For the exchange-correlation energy, the functional form of Perdew and Zunger[18] is employed. The Kohn-Sham equation is solved iteratively for the $\Gamma$ point in the Brillouin zone reciprocal to the supercell lattice until the potential changes become less than 2 mRy.

Table I lists the binding energy and the equilibrium separation between the magnesium and sodium atoms calculated for $Na_6Mg$ and $Na_8Mg$, respectively. The magnesium and sodium separations are 10–15% smaller than the average of the nearest-neighbor distances of bulk magnesium and sodium.

Figure 1(a) shows the valence charge density for a $Na_6Mg$ cluster with $d_{Mg-Na}=3.0$ Å which is close to the equilibrium separation of $d_{Mg-Na}=2.91$ Å. The cross section plotted is the central plane of the octahedron. Figure 1(b) and 1(c) show the charge density for the two occupied energy levels, respectively. The charge densities for both states exhibit slight variations along different directions and show no evidence of directional bonding. The lowest occupied level $1s$ in Fig. 1(b) is not an atomic $3s$ valence state of the central magnesium. When the magnesium is moved off center, shown later, the wave-function characteristics of this state are little affected. Since the electrons are fairly delocalized, it is still adequate to use the notation of the electronic shell model to label the energy levels, i.e., $1s, 1p, \ldots$.

The charge contour plots for the $Na_8Mg$ cluster with $d_{Mg-Na}=3.0$ Å (the calculated energy minimum is at $d_{Mg-Na}=3.10$ Å) and the charge-density difference between $Na_8Mg$ and $Na_9$ clusters are shown in Fig. 2. We have assumed a similar cluster structure for $Na_9$ as in the case of $Na_8Mg$ with the central magnesium atom replaced by a sodium atom. The plane shown has the central Mg atom and four Na atoms on it and is equivalent to the (110) plane of the bcc crystal. Again, a delocalized charge distribution is found for $Na_8Mg$ in Fig. 2(a).

Compared with the $Na_9$ cluster, the extra charge of $Na_8Mg$ is centered at the origin with an almost spherical shape as shown in Fig. 2(b). Each individual state is somewhat affected by the replacement of the central atom since both the number of electrons and the pseudopotential have been changed. The net effect is reflected in a more attractive potential at the center which does not depend strongly on direction as would be expected from directed bonding.

Table II lists the energy levels for $Na_6Mg$ and $Na_8Mg$, respectively, for a nearest-neighbor distance of 3.0 Å which is near the equilibrium separations between the magnesium and sodium atoms. The two sets of energy levels display similar trends although they correspond to different cluster sizes and structures. A comparison with the energy levels of a pure sodium cluster $Na_9$ is also made in Table II. The $s$ levels have been significantly lowered, but other states are less affected. This is be-
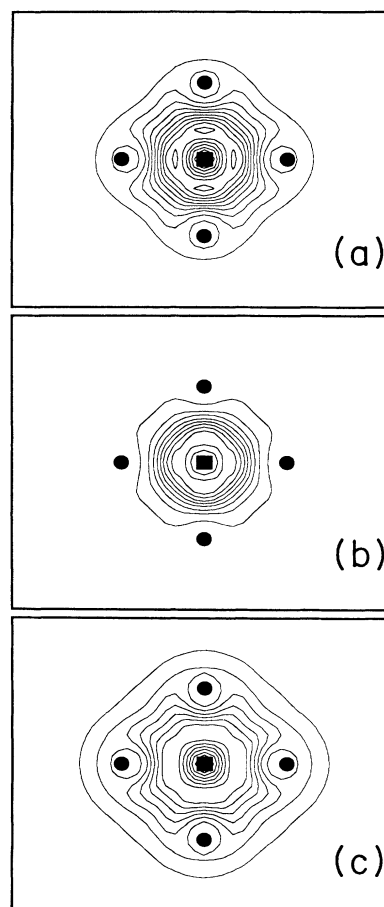


FIG. 1. Charge contour plots of $Na_6Mg$ ($d_{Mg-Na}=3.0$ Å) for the central plane of the octahedron. The total charge densities and charge distributions for occupied states $1s$ and $1p$ (averaged over $p_x$, $p_y$, and $p_z$) are plotted in (a), (b), and (c), respectively. The contour spacings are 15.0 in (a) and 10.0 in (b) and (c), respectively, in units of electrons per supercell with a cell volume of about 1760 Å$^3$. Solid circles and squares represent Na and Mg atoms, respectively.
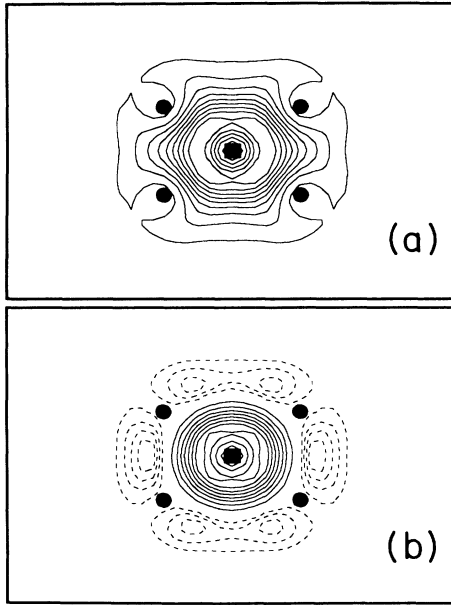
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FIG. 2. (a) Charge contour plots for Na$_8$Mg with $d_{Mg-Na}=3.0$ Å. The contour spacing is 15.0 in units of electrons per supercell with the cell volume of about 1535 Å$^3$. (b) Charge differences between Na$_8$Mg and Na$_9$ with contour spacings of 10.0 for the positive values (solid line) and 1.0 for the negative values (dashed line) in the same units as in (a). Solid circles and squares represent Na and Mg atoms, respectively.



FIG. 3. Wave functions of $1s$ (a) and $1p_z$ (b) states for Na$_6$Mg with the magnesium off center (arbitrary scale). The dashed lines are negative values. The plane plotted is the same as that in Fig. 1. Solid circles and squares represent Na and Mg atoms, respectively.

cause the magnesium pseudopotential at the center, being more attractive than the sodium potential influences most strongly those states with large amplitude near the center of the cluster. Hence the $s$ states which have a nonzero wave function at the origin experience a relatively large attraction. As a consequence, the energy gap separating the $2s$ and $1d$ states becomes as large as 0.8 eV in Na$_8$Mg compared with 0.2 eV in Na$_9$ (Table II), and the gap between $1p$ and $2s$ remains large ( ~0.9 eV). These results indicate that both $Na_8M_g$ and Na$_6$Mg (with ten and eight electrons, respectively) are clusters with closed electronic shells.

The existence of any nonspherical components of the potential usually causes splittings of the degenerate energy levels of spherical systems. For cubic symmetry, the $1d$ state will split into two groups of levels which are twofold (with the charge concentrated along the axes) and threefold (with the charge concentrated between the
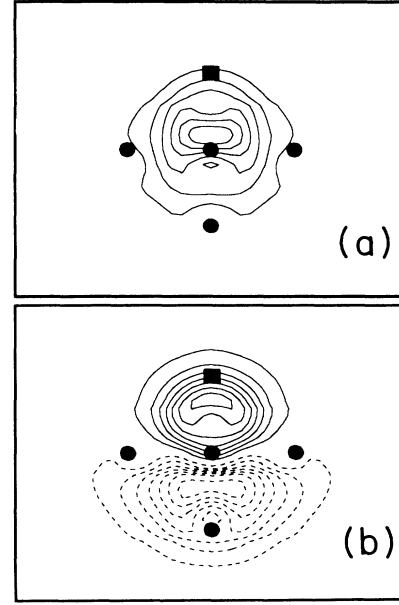
axes) degenerate, respectively. For Na$_8$Mg at a $d_{Mg-Na}$ equal to the bulk nearest-neighbor distance of Na (3.66 Å), this splitting is only 0.2 eV and is very close to those found in Na$_{13}$ (fcc) and Na$_{15}$ (bcc) at the same nearest-neighbor distance.[9] This indicates that the presence of the Mg atom hardly changes the weak nonspherical part of the potential, which again gives little evidence of directional bonding. At the equilibrium $d_{Mg-Na}$ for Na$_8$Mg, this splitting decreases and becomes negligible.

We have also performed a jellium calculation for Na$_{58}$Mg using the $r_s$ values of bulk Na and Mg with Mg at the center. As is expected, all the $s$-levels are lowered with respect to other energy levels. In particular, the $3s$ level, which is 0.2 eV above the $2d$ level in Na$_{58}$ with the ordering of . . . ,$2p,1g,2d,3s,$ . . . , becomes lower than the $2d$ level and is only 0.2 eV above the $1g$ level. The new ordering is . . . ,$2p,1g,3s,2d,$ . . . , in Na$_{58}$Mg. Hence, the previous shell closing number of 58 for Na clusters with $1g$ levels filled is likely to be replaced by 60.

TABLE II. The energy levels (in eV) of Na$_6$Mg, Na$_8$Mg, and Na$_9$ at a nearest-neighbor distance of 3.0 Å in a body-centered octahedral or a body-centered cubic structure. Degeneracies are noted. Numbers shown in parentheses are separations from the lower adjacent levels.

|           | Na$_6$Mg        | Na$_8$          | Na$_9$          |
|-----------|-----------------|-----------------|-----------------|
| $1s$ (2)  | $-4.99$         | $-5.77$         | $-4.95$         |
| $1p$ (6)  | $-2.78$ (2.21)  | $-3.50$ (2.27)  | $-3.42$ (1.53)  |
| $2s$ (2)  | $-2.04$ (0.74)  | $-2.56$ (0.94)  | $-2.10$ (1.32)  |
| $1d$ (6)  |                 | $-1.78$ (0.78)  | $-1.91$ (0.19)  |
| (4)       |                 | $-1.75$ (0.03)  | $-1.84$ (0.07)  |

Since at this point our conclusions are based on results for two highly symmetric clusters, it might be argued that by reducing the symmetry of the clusters, one may no longer be able to assign the energy levels using this electronic shell model. To test whether the quantum shell structure is more generally appropriate, a calculation for $Na_6Mg$ has been carried out in which the central magnesium atom is exchanged with one of the sodium atoms at the corner. The symmetry group is now reduced to $D_{2h}$ instead of the full cubic symmetry. From the topology of the wave functions we can still identify the energy levels with the shell states, i.e., $1s$, $1p$, $2s$,.... Figure 3 shows the wave functions for the two lowest occupied energy levels. Their global features imply that they are in fact the $1s$ and $1p_z$ states, respectively. The peak position of the $1s$ state is not near the position of the magnesium atom [Fig. 3(a)]; instead, it is only displaced from the center of the cluster toward the magnesium atom by a small amount. This indicates that the magnesium atom donates its electrons to the global electron gas of the whole cluster. Hence, the use of the shell model description for $Na_x Mg$ clusters is further justified. The total energy increases by 1.19 eV when the magnesium is off center. This supports our earlier argument that the magnesium at the center maximizes the binding energy.

In summary, by studying the two specific clusters $Na_6Mg$ and $Na_8Mg$ we have demonstrated that shell structure should exist in the energy spectra of the heteroclusters $Na_n Mg$ ($n \geq 6$). The charge distributions of these clusters remains delocalized, and this suggests a jellium approximation should be appropriate to study larger clusters. Both of these conclusions contradict those interpretations of Kappes et al.[13] of their experimental observations. As in the case of pure alkali-metal clusters, many physical properties of these mixed clusters are expected to be size dependent with characteristics related to the total number of electrons. However, shell closing numbers will be slightly different because of the lowering of the $s$ states.

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