Inhomogeneous contraction of interatomic distances in metallic clusters:
Calculations for Cs$_n$ and OCs$_n$

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(Received 11 March 1991)

The equilibrium geometrical structures of Cs$_n$ and OCs$_n$ clusters have been obtained by a method that, in the framework of density-functional theory, describes the ion-electron interaction by means of a pseudopotential that is spherically averaged about the cluster center. In the size range studied (up to $n = 78$ and 70, respectively) the clusters present well-separated atomic layers for which the distances to the two closest neighbors of each atom have been analyzed, showing that there is an inhomogeneous shrinking of the geometrical structure, in the sense that the distances obtained for atoms in the inner layers are lower than those for the outer ones. The analysis of the growing of the clusters suggests that the equilibrium geometries are those for which any atom of the aggregate has its closest neighbor at a distance lower than the nearest-neighbor distance of the pure bulk metal. For small ($n \leq 20$) pure clusters, geometries of high symmetry have been found, which are completely modified by the presence of the oxygen impurity. A regular octahedron is formed around the oxygen atom in most cases.

I. INTRODUCTION

Metallic clusters are remarkable examples of finite quantum systems. The size dependence of some of their properties, for example, the abundance spectra and the ionization potentials (IP), is well understood, for the case of simple metallic elements, in the framework of the jellium model, which is an extension of the free-electron model of bulk metals. In the case of clusters, the quantum states of the valence electrons are determined by the self-consistent mean field produced by the finite positive ion distribution, considered as continuous (jellium model), and the electron-electron interaction. For clusters with number of atoms $n$ smaller than 100, the assumption of a homogeneous spherical jellium distribution allows the reproduction of experimentally found local maxima in the abundances, magic numbers, which coincide with those clusters with completely filled electronic shells and with the next empty shell well separated in energy. The corresponding ionization potentials present a step-like behavior when we pass from the magic cluster $n$ to its neighbor $n + 1$, in agreement with experiment, although the calculated drops are, in general, greater than the measured ones. Several refinements of this self-consistent spherical model have been proposed, such as the inclusion of spheroidal distortions and the use of diffuse positive distributions.

Recently, experimental results on the abundances have been obtained by Martin and co-workers for large clusters of OCs$_n$, with $n \leq 600$ (Ref. 8) and Na$_n$, with $n \leq 1500$ (Refs. 9 and 10), which have been explained by means of an inhomogeneous jellium model. A positive density that is higher than the bulk average value is needed at the center of the cluster in order to produce the bunching of the electronic levels necessary to give the right sequence of magic numbers. Martin and co-workers found it impossible to predict the experimental values of the most abundant clusters, for $n \geq 100$, with a homogeneous distribution, although both distributions give the same sequence for the light clusters, $n \leq 100$. The calculated ionization potentials for the centrally compressed spherical background present also steps at those magic numbers observed experimentally for large clusters and a reduction of step size in the IP values for light clusters, $n \leq 100$.

In this contribution we present an analysis of the equilibrium geometries obtained for Cs$_n$, with $3 \leq n \leq 78$ and OCs$_n$, $3 \leq n \leq 70$, using a model that, in the framework of density functional theory, includes also the ionic structure of the aggregate, transcending the jellium model but retaining the spherical assumption for the external potential. The ion-electron interaction for the valence electrons is thus approximated by the spherical average of the pseudopotential (SAPS method). Some results concerning the cohesive energies, electronic structure, ionization potentials, embedding energy of the oxygen atom, and general geometrical trends have already been published. We have compared the IP's for OCs$_n$ with the experimental values, showing that the SAPS scheme reproduces the general trend and the drop after a magic number, those drops greater than the experimental ones. The inadequacy of the homogeneous jellium model to describe the expected sequence of magic numbers of Cs$_n$ was discussed in Ref. 13, where we have shown that
the inclusion of the ionic structure gives the expected sequence for pure clusters (expected from trends in the measured ionization potential and the experimental one for suboxide OCs clusters). In the present work we analyze the ion-ion distances in the clusters and the detailed geometrical structure showing that an inhomogeneous shrinking is obtained from our calculations in agreement with the conclusions of T. P. Martin's group. Also, a recent SAPS calculation for aluminum clusters Alₙ, 3 ≤ n ≤ 25, explains the deviations of the predicted values of the polarizability within the homogeneous jellium model from the experimental results as due to the actual contraction of the small Alₙ clusters. Finally, we point out that lattice contractions have been measured in Au and Pt clusters, and also that a size-dependent contraction of the nearest-neighbor distances for clusters isolated in solid argon has been measured for Ag and Cu clusters, thus indicating that the effect could be a general property of any metallic cluster.

II. THE MODEL

The model used to calculate the electronic and geometrical structures of the clusters has been presented in detail elsewhere and we stress here only the main points. For an initial geometry of the cluster, the Kohn-Sham equations of density-functional theory are self-consistently solved, using the local-density approximation for the exchange-correlation energy. Afterward the ionic coordinates are moved, with a steepest-descent method and preserving the self-consistency between the ionic positions and the electronic density, to obtain the equilibrium geometry and the corresponding ground-state total energy E. To avoid trapping in a local minimum several initial random geometries are considered (40 for pure clusters and 70 for the OCs). An empty-core pseudopotential is used to describe the ion-electron interaction with a core radius, rₐ(Cs) = 2.74 a.u., which leads to the experimental ionization potential in the free-atom limit for the same density functional method. The total ionic potential of the cluster is spherically averaged around the center of mass of the cluster. This is equivalent to using the spherically averaged electronic density in the calculations and it is the most drastic approximation of our model which must be more accurate the bigger the cluster becomes. However, the exact ion-ion repulsion is included in the calculations, which makes the total energy a function of the precise location of the atoms. For OCs all the electrons of the oxygen atom are considered in the calculation and the positive nuclear charge is always located at the center of mass of the cluster reinforcing the spherical symmetry assumed for the aggregate.

The results of our calculations reproduce the electronic shell effects associated with the local maxima in the abundance spectrum of OCs. The sequence of single-electron shells obtained (1s, 2s, 1p, 3s, 2p, 1d, 1f, 4s, 3p, 1g, 2d) produces, once the electronic configuration of the ion O²⁻ (1s²2s²2p⁶) is considered, the following closing-shell numbers: n = 4, 10, 20, 34, 36, 42, 60. When the near degeneracy of the 4s-1f and 1g-3p shells is taken into account, the relative high stability of clusters with

![FIG. 1. Mean radius and standard deviation as functions of n \(1/3\) for the atomic layers of Csₙ clusters. The straight lines, \(R_i\), given by Eq. (1), separate the three regions defined in the clusters. \(R_i\) corresponds to the radius of the homogeneous spherical jellium. The vertical arrows indicate the largest clusters with a central atom and one and two atomic layers, respectively.](image1)

n = 10, 20, 36, and 60 due to electronic effects arises from the SAPS calculations, in agreement with the experimental results. For pure Cs clusters the sequence obtained (1s, 1p, 1d, 2s, 1f, 2p, 1g, 2d, 3s, 1h) presents three shells nearly degenerate in energy (2d, 3s, and 1h), so the following sequence of magic numbers was predicted: n = 8, 18, 20, 34, 40, and 58, in accordance with the results for other alkali-metal clusters.

III. THE GROWING OF THE CLUSTERS

The main trends of the geometrical structures of Csₙ and OCsₙ are summarized in Figs. 1 and 2, respectively.

![FIG. 2. The same quantities as in Fig. 1 now for the Cs atoms in OCs clusters. The oxygen atom is in the cluster center. The vertical arrow indicates the biggest cluster with only two atomic shells.](image2)
The atoms are arranged in spherical layers around the cluster center; these layers are clearly separated in the radial direction and the atoms within each one show a small relative dispersion in the radial coordinate. The mean radius of each atomic shell and the standard deviations are given in the figures. The corresponding number of atoms in each layer has been given in Figs. 4 and 9 of Ref. 13. The radial distribution of the ions and the electronic densities are given in Fig. 3 for some selected clusters, Cs20, OCs20, Cs60, and OCs60, of which the first three have closed electronic shells (the actual geometry obtained for Cs20 will be given in Fig. 8). The atomic layering is clearly shown and also the corresponding correlation with the oscillations in the electronic density. It is also remarkable that the presence of the oxygen impurity produces only a small modification of the outer maximum of the electronic density, which is located at \( r = 9 \) a.u. for \( n = 20 \) and at \( r \approx 14 - 15 \) a.u. for \( n = 60 \). This indicates that the atomic layer surrounding the oxygen atom produces a very strong screening of the impurity and consequently its effect on the outer part of the cluster becomes less noticeable. The screening effect is even more notorious for those clusters which have nearly identical radial distributions of the Cs atoms in the pure and in the OCs\(_n\) cases. Such is the case for \( 26 \leq n \leq 32 \) (with the only exception of \( n = 29 \)), a group of aggregates which, in the pure case, have no central atom and an inner shell of six Cs atoms (only five for \( n = 29 \)), the same radial distribution as the one obtained for the corresponding OCs\(_n\). For these clusters, a minimum value of the calculated embedding energy \( \Delta H(n) = E(\text{OCs}_n) - E(\text{Cs}_n) - E(\text{O}) \) of oxygen in Cs\(_n\) is obtained, as was discussed in Ref. 13. In Fig. 4 two pairs of aggregates are given for comparison: Cs26, OCs26 and Cs32, OCs32. The oxygen produces a very small change in the electronic density of the outer part of the clusters \( (r \geq 5 \) a.u.) and a small shrinking of the ionic distributions in the radial direction. This last effect is more noticeable for the internal shell of six atoms, as the outer part of the cluster only slightly modified because of the strong screening produced by the innermost shell. In the region of larger sizes an analogous situation is expected for Cs73 and Cs76. The radial distributions of these clusters show an outer shell of six atoms and a vacancy at the central site. However, we have not extended our calculations to those sizes for OCs\(_n\) and we do not have the corresponding data to be compared. The strong ionic bonding of the oxygen is also responsible for the large shrinking obtained for Cs6 (an octahedron with an edge of 9.5 a.u.) when the impurity is embedded: OCs6 is also an octahedron, with the oxygen at its center, but now the value of the edge is 7.96 a.u. For those OCs\(_n\) aggregates whose internal geometry is also that of OCs60, the value of the edge oscillates between 7.7 and 7.8 a.u. These results contrast with the expansion of the geometrical structure when a Cs atom is located at the center: Cs7 is a centered octahedron with an edge of 11.1 a.u.

For pure cesium the population of each atomic layer increases with the total number of atoms and the cluster strongly reconstructs as it grows. The growth can be de-

![Figure 3](image-url)

**FIG. 3.** Radial distribution of the atoms and electronic densities for Cs20, OCs20, Cs60, and OCs60. The units for the electronic density are \( n_0 = 1/\Omega(\text{Cs}) \), where \( \Omega(\text{Cs}) \) is the volume per atom in the pure bulk metal. The stars indicate Cs atoms and the circle the oxygen. The vertical arrow in the plots for pure Cs clusters indicates the homogeneous jellium radius \( R = r_n n^{1/3} \).
scribed such that new shells appear in the innermost region of the cluster when certain conditions are met. This can be appreciated in Fig. 1, where we have indicated with two vertical arrows the biggest clusters with one central atom and one and two additional atomic layers, Cs$_{18}$ and Cs$_{63}$, respectively. For Cs$_{18}$ the distance between the central atom and any atom in the surface layer becomes slightly larger than the nearest-neighbor distance in bulk Cs, $d_{NN} = 9.893$ a.u. Our calculation indicates that the cluster Cs$_{19}$ reconstructs its geometry in such a way as to avoid neighbor interatomic distances larger than $d_{NN}$. This is achieved by locating the added atom in the interior of the cluster (see the geometrical structures obtained for Cs$_{18}$ and Cs$_{19}$ in Fig. 7) instead of placing it on the surface, a situation which would have increased the cluster radius (and distances between neighbors) further. For Cs$_{63}$ the situation is analogous to that of Cs$_{18}$. Now the central atom is surrounded by an atomic shell of 19 atoms at a mean radius nearly identical to that of Cs$_{18}$ and again clearly larger than $d_{NN}$. The next cluster, Cs$_{64}$, has two atoms in the inner region, like Cs$_{19}$, forming a new shell that is populated as the cluster grows in size. This behavior is again an indication that neighbor interatomic distances greater than $d_{NN}$ are avoided in the equilibrium geometries of the clusters.

In the case of OCs$_n$, a stable inner structure, typically of six atoms arranged as a regular octahedron, is formed around the oxygen impurity for any cluster size.$^{13}$ This means that, in general, the geometrical structure of Cs$_n$ is strongly perturbed by the presence of the oxygen, as a comparison of Cs$_{60}$ and OCs$_{60}$ in Fig. 3 clearly shows. For these suboxide clusters the growth pattern differs from that in pure Cs. An intermediate Cs shell appears at OCs$_{47}$ midway between the surface shell and the inner core. The appearance of this new atomic shell can be explained by the same argument as in the case of pure Cs: From Fig. 2 the values of the radii of the two atomic shells of OCs$_{46}$ are 6.5 a.u. and 15±1.5 a.u., respectively, and this means that the minimum distance between a Cs atom in the inner part and another in the outer part is of the order of, or greater than, $d_{NN}$, because two atoms in different shells are never in the same radial direction (in this cluster); if it is assumed that no Cs atom in any finite aggregate can be located at a distance from all the other atoms that is clearly greater than $d_{NN}$, as the results for pure Cs suggest, a new intermediate shell should form in order to fulfill this condition. This intermediate layer bridges the two parts of the OCs$_n$ clusters and makes the radius of the surface layer increase faster (see Fig. 2). The number of atoms in the intermediate layer increases from 13 to 22 between OCs$_{48}$ and OCs$_{70}$, although with an oscillatory behavior. However, the corresponding shell radius is rather stable. In fact, for 60≤n≤70 the number of atoms in this layer oscillates only between 19 and 22 with a more stable value for the radius also.

**IV. THE INHOMOGENEOUS CONTRACTION**

In order to show the inhomogeneous shrinking of the interatomic distances of the clusters we have divided each

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**FIG. 4.** Radial distribution of the atoms and electronic densities for Cs$_{26}$, OCs$_{26}$, Cs$_{32}$, and OCs$_{32}$. Symbols and units are as in Fig. 3.
aggregate in several regions, each one including only one atomic shell, which are separated by the radii indicated by the straight lines in Figs. 1 and 2. For each atom within one of those regions we look for the two closest ions at any point in the cluster and not only inside its own atomic shell. Finally, the mean value of the distances to the nearest atom \( D_1 \) and of the distances to the two nearest atoms \( D_2 \) are obtained for the collection of atoms within the chosen regions. The regions considered are separated by the radii given by the following relationship:

\[
R_i(n) = a_i + b_i n^{1/3}, \quad i = 1, 2, 3
\]

where, for \( \text{Cs}_n \), \( b_1 = b_2 = b_3 = r_2 \) (\( r_2 \) is the Wigner-Seitz radius for bulk cesium, \( r_2 = 5.67 \) au.), \( a_1 = 0 \), \( a_2 = -8.0 \) au., \( a_3 = -16.0 \) au., and only the positive values of \( R_i(n) \) are considered. These radii clearly separate the atomic shells that actually exist in the Cs aggregates. Actually, only two radii are necessary to separate the three regions considered. The most external radius, \( R_1 = r_n n^{1/3} \), which is the radius of a cluster of \( n \) atoms in the spherical jellium model, is included only to illustrate the global contraction of the cluster volume with respect to a piece of the macroscopic metal with the same number of atoms. For \( \text{OCs}_n \), the three regions considered correspond to the following values of the coefficients in (1): \( b_1 = r_2 \), \( b_2 = b_3 = 0 \), and \( a_1 = 0 \), \( a_2 = 8.5 \) au., \( a_3 = 15.0 \) au.; in this case only two regions are considered for \( 9 \leq n \leq 45 \), and three regions are analyzed for \( 46 \leq n \leq 70 \). The results for the mean values and the standard deviations for the distances to the closest atom \( D_1 \) and to the two closest atoms \( D_2 \) are given in Figs. 5 and 6 for \( \text{Cs}_n \) and \( \text{OCs}_n \), respectively. Also the experimental value of the nearest-neighbor distance for bulk cesium, \( d_{\text{NN}} \), is given for comparison.

At this point it is important to notice that the two closest atoms (of a given one) mentioned here have not the same meaning as the nearest-neighbor and second-nearest-neighbor for a perfect crystal in solid state physics. As we show in the following, the interatomic distances for a Cs cluster are not as well defined as in a perfect crystal (that is, there is a larger dispersion). By means of \( D_1 \) and \( D_2 \), we are trying to obtain the average nearest-neighbor distance for atoms in the different regions defined above. Actually, an average over a larger number of closest atoms, \( D_3, D_4, \) etc., may be better. Ideally one should average over the first coordination shell, but the problem is that its population around an inner atom is different from that for a surface atom. To avoid these additional complications we stop with \( D_2 \), since we consider that it is enough for our purposes.

**A. Cs\(_n\) clusters**

In the case of \( \text{Cs}_n \), Fig. 5(a) shows that atoms in the inner parts of the cluster have their first neighbor closer than those atoms that are in the outer parts of the aggregate. The behavior of \( D_1 \) in the two zones \( 7 \leq n \leq 18 \) and \( 40 \leq n \leq 63 \) is due to the singular character of the central atom in these clusters. In the first zone there is only one atomic shell plus one atom at the center, and Fig. 5(a) shows that for \( 7 \leq n \leq 13 \) the closest atom to any one in the external shell is the central atom and vice versa, so the lines for \( D_1 \) corresponding to the outer shell (crosses) and to the central atom (stars) are practically identical. However, from \( \text{Cs}_{14} \) to \( \text{Cs}_{18} \) the atom closest to one in the surface is also on the surface at a distance which is lower than the mean radius of the atomic layer. Now the line corresponding to the central atom is clearly over the mean value \( D_1 \) for the external shell. The sudden drop in the value of \( D_1 \) at \( \text{Cs}_{19} \) is due to the formation of the new internal shell already described. For \( \text{Cs}_{18} \) the value of \( D_1 \) corresponding to the central atom is slightly larger than \( d_{\text{NN}} \) (see arrow in the figure), so the transition reflects the fact that the preferred equilibrium geometry is one in which the values of \( D_1 \) for any region of the cluster are always lower than \( d_{\text{NN}} \), as is the case for \( \text{Cs}_{19} \).

A similar behavior is obtained for \( D_1 \) in the range \( 40 \leq n \leq 63 \) in which there is also only one atom (the central one) in the innermost region defined by the radius \( R_3 \). For this region, \( D_1 \) increases with the cluster size, associated with the corresponding increment of the radius of the intermediate shell, and a sudden decrease occurs when a new inner shell of two atoms is formed at \( \text{Cs}_{64} \). However, in this size range the values of \( D_1 \) for the

![FIG. 5. (a) Mean distance to the nearest Cs atom and standard deviation, for the three regions defined in Fig. 1 for Cs\(_n\) clusters, as a function of \( n \). (b) Mean values of the distances to the two nearest Cs atoms for each of the regions. In both cases the horizontal arrow corresponds to the nearest-neighbor distance in pure bulk cesium, \( d_{\text{NN}} = 9.893 \) au.](image)
intermediate shell are lower (only in three cases are slightly larger) than those for the central atom. This is due to the contraction of this shell with respect to the case of single layered clusters, as can be shown when its population is considered. The number of atoms in this intermediate shell is 10 (for \( n = 40, 41, \text{and} \ 44 \)) and 12 (for \( n = 42, 43, 45, 46, \) and 50). The values of \( D_1 \) for the central atom are, in both cases, clearly lower than those corresponding to the central atom of Cs_{11} and Cs_{13}, respectively. The contraction is about 0.8 a.u. for most of the clusters considered. Also the values of \( D_1 \) corresponding to the intermediate layer are lower than those corresponding to the outer part of the single layered clusters, Cs_{11} and Cs_{13}, indicating that these intermediate layers are more closely packed. When the population in this intermediate shell is greater than 12, the corresponding values of \( D_1 \) for the two regions defined by \( R_2 \) and \( R_3 \) are clearly different, showing that for these clusters the closest atom to one in the intermediate shell is never the central one. A maximum value of 19 atoms surrounding the central one is reached at Cs_{80}, with a radius for the spherical shell of the order of \( d_{\text{NN}} \) like in the case of Cs_{18}, thus promoting the formation of a new internal shell for the larger clusters.

The values of \( D_1 \), and also of \( D_2 \) in Fig. 5(b), are fairly constant in the range studied except at the first steps of the formation of a new shell, for example, the most internal shell, for \( 64 \leq n \leq 78 \), which only has a number of atoms between 2 and 6. The oscillation in \( D_1 \) for the external shell of the light clusters, when \( n \leq 13 \), is smoothed by the inclusion of the distance to the second closest atom in \( D_2 \), Fig. 5(b), with the corresponding increment in the standard deviations. The reason is that for \( 7 \leq n \leq 13 \) the closest distance between atoms in the outer shell is, as mentioned above, bigger than the mean radius of the shell, being Cs_{13}, a centered icosahedron, the first cluster for which both distances are similar.

In Fig. 5(b) the values of \( D_2 \) also show the same effect of inhomogeneous contraction of the clusters. For those aggregates with a central atom, \( D_2 \) coincides with \( D_1 \) for the region that only contains the central atom due to the spherical arrangement of the layer surrounding the center of the cluster. It is important to point out that if the central atom had been included as part of its closest shell for the calculation of \( D_1 \) and \( D_2 \), the values obtained should not be very different from those quoted because of the small relative influence of one distance (with the value given in the figures) in the mean values of 7–19 (the populations of the shell closest to the central atom) distances. Actually, we feel that defining a region with only one atom is not satisfactory, as shown by the peculiar behavior of this region in Fig. 5. The reason for showing explicitly this one atom region is that it helps to understand the process of cluster growth.

Comparison of Figs. 5(a) and 5(b) shows that, for the atoms in the outer shell, the distance to the second closest atom is, in average, 0.25 a.u. greater than the distance to the first one. The same qualitative behavior is present in the intermediate shell; however, the effect is in this case weaker than before and the values for \( D_1 \) and \( D_2 \) are more stable, as is clearly indicated by the lower values of the standard deviations. The conclusion is that in this intermediate shell atoms are more homogeneously arranged than in the outer shell.

From Figs. 5(a) and 5(b) we can conclude that, in spite of the overlapping between the standard deviations that is present mainly for the larger aggregates, Cs atoms in finite clusters are closer than in the bulk material and that the atoms in the inner layers are more closely packed than the atoms of the surface. Of course, when cluster size increases it is expected that at least the distances in Figs. 5(a) and 5(b) corresponding to the internal layers should converge to the nearest-neighbor distance in bulk cesium, but what our results show is that this convergence is rather slow and that for \( n \leq 100 \) we are still far away from the bulk limit, because even for Cs_{13} more than half of the atoms of the cluster are located at its surface. It can be expected that, as the number of atoms in the internal part grows, an expansion toward the bulk distances should occur in the internal regions of the clusters.

**B. OC_{3n} clusters**

The results for OC_{3n} are given in Figs. 6(a) and 6(b) for the two distances \( D_1 \) and \( D_2 \) corresponding to the three regions in which the aggregates have been divided (see Fig. 2). In this case the strong ionic bonding due to the oxygen impurity gives as a result the very stable and compressed structure of the inner atoms of the clusters, the layer associated with the radius \( R_2 \). We shall discuss

**FIG. 6.** (a) and (b). The same quantities as in Figs. 5(a) and 5(b), now for the case of OC_{3n} clusters.
the actual geometrical structures of these regions in the next section. For these clusters only the distances between Cs atoms have been analyzed to obtain \( D_1 \) and \( D_2 \). All the information about the oxygen-cesium distances was already given in Fig. 2, in particular, the very stable radii of the innermost shells, which are around 5.3 a.u. in the case of octahedral structure, giving a value around 7.5 a.u. for the edge of the octahedron and, consequently, for the values of \( D_1 \) and \( D_2 \) corresponding to this internal Cs layer. The drop in the values of \( D_1 \) and \( D_2 \) between OCs\(_{34}\) and OCs\(_{35}\) is due to the formation of a pentagonal bipyramid, with seven atoms, as the inner structure of the cluster, instead of the octahedron. The former is also the inner shell for OCs\(_{36}\) and OCs\(_{37}\), whereas eight atoms forming a square antiprism is the geometry obtained for \( n = 38, 39, 40 \), and 42. The spike in the values of \( D_1 \) and \( D_2 \) for OCs\(_{41}\) is due to the new structure of the internal layer, now formed by nine atoms arranged as a triapped trigonal prism. Finally, for OCs\(_{45}\) a biccapped square antiprism (10 Cs atoms) is the geometry for the inner part before a transition, again to the octahedron, occurs at OCs\(_{46}\). These structures will be also commented in the next section. The mean values of \( D_1 \) and \( D_2 \) for the external shell are very similar to those obtained for Cs\(_{n}\); however, the intermediate shell, for 46 \( \leq n \leq 70 \), shows a contraction which is smaller than the one obtained for the pure case. A very significant overlapping of the standard deviations is present here, indicating the strong dispersion on the values of the distances used to calculate \( D_1 \) and \( D_2 \) for these two atomic shells. The number of atoms in the intermediate shell and its corresponding mean radii have values that are more stable (independent of \( n \)) than those of pure clusters.

The inhomogeneous contraction of the clusters is clearly shown by Figs. 6(a) and 6(b) just by comparing the values of \( D_1 \) and \( D_2 \) for the outer shells with those of the internal one, the latter being determined by the presence of the oxygen impurity. This influence of the oxygen on the compression of the internal shell is very clear even for those clusters for which the populations of the two atomic layers are identical to those of the pure clusters, \( n = 26 - 32 \), except \( n = 29 \), as can be seen by comparing Figs. 5 and 6: The values of \( D_1 \) and \( D_2 \) for the internal shell of these clusters are nearly one atomic unit lower in the case of OCs\(_{n}\) than for the pure clusters. However, the values for the external shell are not very much influenced by the impurity due to the strong screening produced by the inner layer. When \( D_1 \) and \( D_2 \) for this internal shell are compared with those for the most internal one in pure Cs\(_{n}\), 64 \( \leq n \leq 78 \), the conclusion can be drawn that the outer shells of the pure cluster produce an effect of compression that is analogous to the one due to the presence of the oxygen atom in the suboxide clusters. Finally, we point again that when the cluster size increases the distances \( D_1 \) and \( D_2 \) for the internal layers should converge to the bulk distance \( d_{\text{NN}} \), except perhaps in the first coordination shell around the oxygen impurity. Our results suggest that the inner structure, in most cases an octahedron, will probably remain stable even in the very large clusters.

V. THE EQUILIBRIUM GEOMETRICAL STRUCTURES

In a previous work\(^{13}\) we have pointed out that the well-known difficulty of determining the ground-state geometry of an atomic cluster, due to the large number of local minima in the energy hypersurface, is also present in the SAPS method. In fact, from our results we conclude there that the determination of the cluster geometry for a not too small cluster (e.g., Cs\(_{35}\)) is a nearly impossible task because of the huge number of local minima. However, many of these minima can be considered as small stable distortions of the ground-state geometry, because of the softness of the aggregates,\(^{2,25}\) and in that case we expect that the geometry associated with the energy minimum obtained in the SAPS method, starting from a relatively small number of random initial geometries, should be quite close to the true ground-state geometry within our method. This should be especially true for the smaller clusters and for the internal structure of the larger ones for which we present in this section some examples of their geometries. Two effects can be shown from the actual geometries obtained: The complete reconstruction of the pure clusters when they grow in size and also when the oxygen impurity is included in the cluster, and the formation of a compressed inner layer for large clusters.

Our results can be compared with other calculations that avoid the spherical average for the total ionic potential but are restricted to small clusters of light alkaline metals (Na, Li) (see the references quoted in Ref. 22). Unfortunately, direct experimental evidence on the geometrical structures of small clusters is very scarce and difficult to obtain for unsupported aggregates, although information about the actual geometries of the clusters can be extracted from the comparison of the experimental and calculated static electric polarizabilities,\(^{25}\) which is a measurable property strongly sensitive to the cluster shape. These polarizabilities can be calculated in the SAPS scheme\(^{16}\) once the geometry is obtained and then compared with the experimental data.

The geometries for Cs\(_n\) with 4 \( \leq n \leq 13 \) are identical to those of Na\(_n\) calculated by the same method and described in Ref. 22, with the only exception of Cs\(_8\) for which a centered pentagonal bipyramid is obtained instead of the square antiprism of Na\(_8\). Of course, the interatomic distances are different, and we have found that, at least for \( n \leq 13 \), they are 29–31 % greater than those of Na\(_n\),\(^{22}\) approximately the same relative variation of the corresponding nearest-neighbor distances of the bulk materials [\( d_{\text{NN}}(\text{Na}) = 6.917 \text{ a.u.} \) and \( d_{\text{NN}}(\text{Cs}) = 9.896 \text{ a.u.} \)]. Summarizing, the calculated geometries of Cs\(_n\) are the following: tetrahedron, \( n = 4 \); trigonal bipyramid, \( n = 5 \); octahedron, \( n = 6 \); centered octahedron (\( O_3 \), \( n = 7 \)); centered square antiprism (\( C_{4v} \), \( n = 8 \)); centered trigonal prism (\( D_{3h} \), \( n = 10 \)); centered square antiprism bicapped at the square faces (\( C_{4v} \), \( n = 11 \)); distorted and centeredicosahedron with one vertex lost, \( n = 12 \), and a perfect centeredicosahedron for \( n = 13 \) with a value for its edge of 9.9 ± 0.1 a.u. The structures for Cs\(_{10}\) and Cs\(_{11}\) are given in Fig. 7, together with those of larger clusters.
that present relevant properties of symmetry. Also, the corresponding geometries for OCs8 are given for comparison. Cs15 is a bicapped hexagonal antiprism with a central atom, Cs16 has a D3h symmetry and can be described as a centered trigonal prism with two atoms over each rectangular face and one more centered over each of the long edges of these faces, Cs18 is a centered pentagonal prism capped in all its faces preserving a fivefold symmetry, and Cs19 is the first cluster with two atoms in the inner part, its external structure being identical to the one of Cs18. Finally, Cs20 is given in Fig. 8 and its remarkable geometry (D3d) is completely different from the one obtained for Na2018 in which only two atoms are located inside the structure. A visualization of the effect of shrinking can be obtained from this last cluster by comparing the mean values of the edges of the inner and the outer polyhedra. An internal tetrahedral structure is also obtained for Cs10 with n = 21—25, and an octahedral one is formed in the inner region for n = 26—32 with the only exception of n = 29.

For the suboxide clusters OCs2n the geometries of the

\[ \begin{align*}
\text{Cs} & = 9,76 \\
\text{b} & = 10,5 \\
\text{c} & > 12,0 \\
\text{n} & = 10
\end{align*} \]

\[ \begin{align*}
\text{a} & = 7,6 \\
b & > 7,1 \\
c & = 10,0 \\
\text{n} & = 11
\end{align*} \]

\[ \begin{align*}
a & = 10,2 \\
b & = 8,9 \\
c & = 11,7 \\
\text{n} & = 15
\end{align*} \]

\[ \begin{align*}
\text{a} & = 9,9 \\
b & = 8,5 \\
c & = 7,8 \\
\text{n} & = 16
\end{align*} \]

\[ \begin{align*}
a & = 9,2 \\
b & = 10,2 \\
c & = 7,8 \\
\text{n} & = 18
\end{align*} \]

\[ \begin{align*}
a & = 9,6 \\
b & = 10,3 \\
c & = 7,65 \\
\text{n} & = 19
\end{align*} \]

\[ \begin{align*}
a & = 8,6 \\
b & = 10,7 \\
c & = 7,5 \\
\text{d} & = 7,8 \\
\text{n} & = 20
\end{align*} \]

FIG. 7. Equilibrium geometries for Cs2n (left-hand column) and OCs2n (right-hand column) for n = 10, 11, 15, 16, 18, and 19. Open and solid circles correspond to Cs and O atoms, respectively. For Cs10 the two internal atoms are linked by a line. The indicated distances are in atomic units.

Cs cover are completely modified by the presence of the O atom, except in those light clusters for which the central site is empty (n = 4, 5, 6). The presence of the oxygen atom produces a general contraction of the clusters, for example, the edge of the octahedron changes from 9.52 a.u. in the pure case to 7.96 a.u. for OCs6, indicating again the strong ionic bonding between the impurity and the Cs atoms. This contraction is also present for those Cs2n clusters with their internal layer formed by six atoms, as we have mentioned in Sec. III and was shown in Fig. 4. For the other clusters we obtain pentagonal bipyramid, n = 7; square antiprism, n = 8; trigonal bipyramid, n = 9 (this is the first cluster with two separated atomic layers, of six and three atoms, respectively, and its geometry is given in Fig. 9). The geometries for OCs10 and OCs11 are given in Fig. 7, where it is seen that the inner Cs layer has five atoms for both clusters but the corresponding structures are completely different (a square pyramid and a trigonal bipyramid, respectively) and the outer atoms can be considered as coordinated to each of the faces of those internal structures. OCs12 has also a trigonal bipyramid as internal geometry, but for 13 ≤ n ≤ 34 and 46 ≤ n ≤ 70 the internal structure is always an octahedron with the only exception being OCs51, for which a trigonal bipyramid is obtained. The structure of OCs14 was already given in Ref. 13: an octahedron with one Cs atom coordinated to each one of its eight

FIG. 8. Equilibrium geometry for Cs20. The distances are in atomic units.

FIG. 9. The structure of OCs20 (left) and of the internal region of OCs44, both formed by nine Cs atoms surrounding the O atom. The symbols and distances are as in Fig. 7. (d) is the mean value of the plotted edges.
faces \( (O_4) \), and those for \( n = 15, 16, 18, \) and 19 are plotted in Fig. 7. Particularly notorious is the distorted cuboctahedron for \( \text{OCs}_{18} \) which surrounds the inner icosahedron, preserving the global \( O_4 \) symmetry.

Some of the structures for the internal layers with a low number of atoms are given in Figs. 9–11 to show that our method is able to describe the influence of the external shells on the inner structure producing geometries different from those of the single layered clusters. In Fig. 9, \( \text{OCs}_9 \) and the nine Cs atoms of the inner shell of \( \text{OCs}_{44} \) are compared, showing a completely different geometry. Also, the internal shell of \( \text{OCs}_{44} \) is formed by nine atoms surrounding the oxygen, with a structure identical to that of \( \text{OCs}_9 \) but with different values for the distances quoted in Fig. 9(a). These are now the following: \( a = 7.8 \) a.u., \( b = a \), and \( b' = 8.6 \) a.u., indicating that the presence of the outer shell of Cs atoms produces a contraction of the radial distances of the atoms in the inner region of the cluster. Figure 10 gives the case of \( \text{OCs}_{40} \) and \( \text{OCs}_{45} \), both with 10 atoms surrounding the central one, which can be compared with \( \text{Cs}_{14} \) and \( \text{OCs}_{15} \) in Fig. 7; it is clear that the equilibrium geometries are determined by the actual environment of the clusters and that there is a complete reconstruction of the aggregate when the total number of atoms is modified. Two more examples of centered internal structures are given in Fig. 11 for \( \text{Cs}_{46} \) and \( \text{Cs}_{53} \) because of its symmetry properties. For \( n = 46 \), 12 atoms are arranged around the central one in a form which is different from the icosahedron of \( \text{Cs}_{13} \) or from the cuboctahedron. The structure of 15 atoms corresponding to \( \text{Cs}_{53} \) is a distorted cuboctahedron bicapped on its square faces and with a central atom, a structure which is different from the one obtained for pure \( \text{Cs}_{15} \) given in Fig. 7, showing again the influence of the external Cs atoms in the equilibrium geometries of the internal layer.

VI. SUMMARY

The geometrical structures found in our calculations indicate that atoms in the clusters are arranged in spheri-cal layers around the cluster center and that those geometries for which no atom has its closest neighbor at a distance clearly greater than \( d_{\text{NN}} \) (bulk nearest neighbor) are preferred as equilibrium geometries. The ionic bonding of the oxygen impurity strongly modifies the structural arrangement of \( \text{Cs}_n \) clusters and, on the other side, it produces a stable inner structure (mostly an icosahedron) around which the rest of the Cs atoms are located, also in spherical layers. In the growing of this external part the formation of a new intermediate shell seems to be ruled by the same condition as for pure clusters: no closest neighbor at a distance greater than \( d_{\text{NN}} \).

The geometrical arrangement of the aggregates in atomic spherical layers allows for the analysis of the interatomic distances for atoms located at different regions of the clusters. When the distances from one atom to its two closest atoms are considered, the values obtained show that the atoms in the inner parts of the clusters are more densely packed than those on the outer parts. This effect should be related to the fact that, for the size range studied, more than half of the atoms of the aggregates are located at the surface and then the strong surface tension produces the shrinking of the cluster, and what is remarkable is that, according to our calculations, it is an inhomogeneous one. It should be interesting to check these conclusions for other simple metal clusters.

ACKNOWLEDGMENTS

This work has been supported by Dirección General de Investigación Científica y Técnica of Spain (Grant Nos. PB 86-0654-C02-01 and PB 89-0352-C02-01) and by NATO.