

Real-space representation of electron localization and shell structure in jelliumlike clusters

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Results of first-principles calculations on pure and doped aluminum clusters are analyzed using the electron localization function (ELF) to obtain a real-space representation of the electronic shell structure. Our results provide a quantitative analysis of the bonding nature and localization of charge in jelliumlike metal clusters and show that similar to atoms, ELF reproduces the electronic shell structure of clusters in real space.

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It is believed that the electronic shell structure in metal clusters is a consequence of the free-electron-like nature of the bonding in these systems, and that a jellium model¹ provides a valid starting point from which the theory of cluster stability and electronic shells can be constructed. Clusters of predominantly *sp* bonded metals,² viz., alkali, divalent (group IIB), trivalent (group III), and noble metals, as well as their alloys, are found to exhibit jelliumlike behavior. Therefore, understanding of the jelliumlike clusters constitutes the core of cluster science. Although great progress has been made both theoretically and experimentally, two basic questions still remain: (1) The success of the jellium model provides *confidence* that electrons may be free-like even in small clusters. This is a basic assumption in the jellium model. How free-like do electrons really behave in jellium-type clusters? Can we find some *direct evidence* for the free-electron behavior in jelliumlike clusters? (2) The most striking feature of jellium clusters is the shell structure of electrons, which is traditionally associated with the filling of the energy levels having $2(1s^2)$, $8(1s^2 + 1p^6)$, $18(1s^2 + 1p^6 + 1d^{10})$, $20(1s^2 + 1p^6 + 1d^{10} + 2s^2)$, . . . valence electrons. Can this be represented in the real space?

In this report, we explore these questions by using the electron localization function (ELF) analysis,³ which was introduced in quantum chemistry as a measure of the parallel-spin correlation by defining conditional probability of finding an electron in the neighborhood of another electron with the same spin. It uniquely identifies regions of space where electrons are well localized such as in covalent bonds or lone pairs and can clearly distinguish the free-electron behavior. Savin and co-workers^{4,5} expressed ELF equivalently in terms of the excess of the local kinetic energy density (D) due to the Pauli principle

$$\text{ELF} = \frac{1}{1 + [D/D_h]^2}, \quad (1)$$

where

$$D = \frac{1}{2} \sum_i |\nabla \phi_i|^2 - \frac{1}{8} \frac{|\nabla \rho|^2}{\rho}, \quad (2)$$

$$D_h = \frac{3}{10} (3\pi^2)^{2/3} \rho^{5/3} = c_F \rho^{5/3}. \quad (3)$$

The second term on the right-hand side of D is the Weizsäcker functional,⁵ which represents the kinetic energy of electrons with bosonlike behavior such as in covalent bonds. D_h is the kinetic energy density of a homogeneous electron gas at a density equal to the local density (ρ) and ϕ_i is the Kohn-Sham orbital. This form is more suitable for applications in density-functional approaches such as those adopted here. From the definition of ELF, it can take values in the range $0 \leq \text{ELF} \leq 1$, 1 corresponding to perfect localization, 0.5 for perfect delocalization, and 0 for very-low-density regions. For a single electron or paired electrons of antiparallel spins, the excess kinetic energy is diminished and correspondingly ELF has a value close to 1. For a free-electron gas (jellium), ELF equals 0.5 at any density. Therefore, ELF provides a quantitative criterion to study the jelliumlike behavior in metal clusters and the variation of the bonding nature in different regions on an absolute scale. This is very important, because in clusters, there could be significant variations in bonding with size as well as due to different bond lengths and/or atom distribution. A graphical representation of ELF provides a vivid description of electron localization in space, instead of an atom-centered description such as in Mulliken population analysis.

We consider here pure and doped clusters of aluminum such as Al_6 , Al_{12}Si , Al_{12}C , Al_{55} , and Al_{54}Si , which are good representatives of jelliumlike behavior. The simulations have been performed with the Vienna *ab initio* simulation code,⁶ which uses ultrasoft pseudopotentials⁷ and a plane-wave basis. The minimization of the free energy is done over the atomic and electronic degrees of freedom using the conjugate gradient iterative technique.⁸ A simple cubic supercell is used with 15 Å edge length for Al_6 , Al_{12}Si , and Al_{12}C clusters, and 28 Å for Al_{55} and Al_{54}Si . In such a big supercell we use the Γ point to represent the Brillouin zone. The exchange-correlation energy is calculated within the generalized gradient approximation⁹ (GGA). The calculations are performed with high precision using a cutoff of 170, 225, and 429 eV for pure Al and doped clusters with Si and C, respectively. The convergence criterion for energy and force are 10^{-5} eV and 0.001 eV/Å, respectively. The structure optimization is symmetry unrestricted.

The optimized structure of Al_6 is a distorted octahedron with an average bond length of 2.76 Å and binding energy of 2.14 eV/atom, which is slightly higher than an earlier GGA result of 1.89 eV/atom with D_{3d} symmetry.¹⁰ Al_{12}Si and Al_{12}C have symmetric icosahedron structures with Si/C at

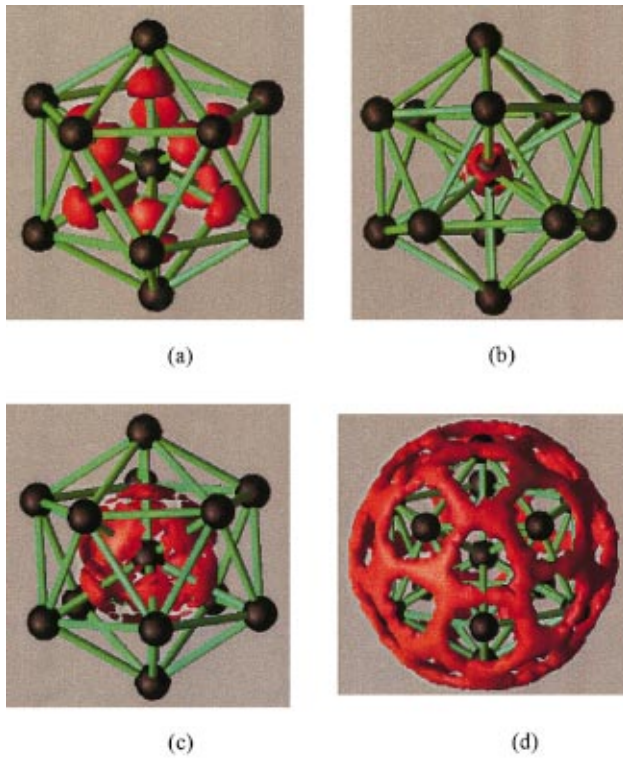


FIG. 1. (Color) Constant electronic charge density surfaces for the excess (a) and depletion (b) of charge in Al_{12}Si as compared to the overlapping densities of Al_{12} and Si atoms, respectively. (c) and (d) are the corresponding constant charge density surfaces for Al_{12}C . The values of charge in the four cases (a)–(d) are 0.052, 0.055, 0.038, and 0.048 electrons/ \AA^3 , respectively. Red color is for charge density and black balls represent ions.

the center. The center-vertex and vertex-vertex nearest-neighbor bond lengths are 2.64 and 2.77, and 2.54 and 2.67 \AA , respectively, which are in good agreement with previous results.^{11–15} For Al_{55} and Al_{54}Si , we studied icosahedral (*i*), decahedral (*d*), and cuboctahedral (*c*) isomers. In the case of Al_{55} , a recent GGA study¹⁰ reported the truncated decahedron to be of lowest energy. However, the optimization was constrained by symmetry. Our results show that the relaxed *i* isomer is 0.3 and 1.50 eV lower in energy than the fully relaxed truncated *d* and *c* isomers, respectively. The distortion from an ideal *i* structure is significant and is in agreement with an earlier report.¹⁶ However, for the *d* and *c* isomers, deviations from perfect symmetry are smaller. Substitution of a silicon atom at the center of Al_{55} also gives the *i* isomer to be 0.34 and 1.51 eV lower in energy than the truncated *d* and *c* isomers, respectively, as well as a reduction in strain. Most importantly, there is a gain of 1.44 and 1.42 eV for the *i* and *d* isomers of Al_{55} in contrast to strain energy of 0.5 eV for a silicon impurity in bulk Al.^{17–20}

The electronic structure of Al_6 , Al_{12}Si , Al_{12}C , and Al_{54}Si clusters has closed-shell features as expected from the jellium model at 18, 40, and 166 valence electrons with highest occupied and lowest unoccupied molecular orbital (HOMO-LUMO) gaps of 0.65, 1.90, 2.01, and 0.34 eV, respectively. The large gap for Al_{12}Si and Al_{12}C makes these clusters behave more like superatoms. This behavior of carbon is very unusual as it appears to behave like a metal atom. In order to understand the bonding nature in these clusters, we calculate (Fig. 1) the excess and depletion of electronic



FIG. 2. (Color) Contour plots and isosurfaces (denoted by iso) of ELF. *h* represents the horizontal plane [see panel (b)] and *v*, the vertical plane perpendicular to *h* and having only the central atom. In isosurfaces, red color is for ELF, and the black balls, for ions.

charge density due to doping. This is obtained by subtracting the overlap of charge densities of the Al_{12} cluster and the Si or C atom at the respective positions as in $\text{Al}_{12}X$, $X=\text{Si}$ or C from the self-consistent charge density of the $\text{Al}_{12}X$ cluster. It is seen that Si loses electrons [Figs. 1(a) and 1(b)] with the excess charge distributed in bonds between the Si and the vertex Al atoms. However, in Al_{12}C [Figs. 1(c) and 1(d)], there is a depletion of charge in the outer part of the cluster and an excess between the carbon and aluminum atoms. Therefore, we find that although the electronegativities of Si and C atoms are higher than that for an Al atom, the valence electrons are distributed inside the whole cluster, with high densities along the bonds joining Si or C with the aluminum atoms. Is this behavior jelliumlike?

In order to distinguish the character of bonding (covalent or metallic), we show in Fig. 2 the ELF for Al_{12}Si and Al_{12}C clusters. For comparison, we also show ELF for bulk aluminum in the [100] crystalline plane. It clearly illustrates the jellium behavior of bulk aluminum in the regions between the ions. The maximum value of ELF is 0.63 and therefore, the deviation from the jellium behavior is small. We use this result as a reference for understanding the behavior in clusters. Figure 2(b) shows the orientation of the plane (labeled as plane h) containing the central and four other vertex ions (rectangle). The plane perpendicular to h is labeled as plane v , which contains only the central ion. The contour plots of ELF through planes h and v are also shown in Fig. 2 as well as the isosurfaces, labeled as iso, for $\text{ELF}=0.9$. In both clusters, we see that in regions (labeled as J in the contour plots) between the vertex and the central ions, ELF has values close to 0.5 and it displays the jelliumlike behavior with nearly delocalized charge distribution. Therefore, bonding in both the clusters is *metallic*, which can be regarded as the *direct evidence* for the free-electron-like behavior. Outside the vertex ions, electrons are highly localized with a maximum value of ELF to be 0.94 and 0.92 for Al_{12}Si and Al_{12}C , respectively, which suggests that the surface valence electrons in Al_{12}Si are more localized than those in the Al_{12}C cluster. A similar result of high value of ELF has been recently obtained for Al surfaces²¹ with a maximum value of 0.86 and 0.73 for the (110) and the closest-packed (111) surfaces, slightly off the outermost surface plane. Therefore, on the cluster surface, electrons are much more localized as compared to corresponding crystal surface.

The importance of ELF for understanding the electronic shell structure of atoms has been clearly demonstrated in real space^{3,22} for several elements including heavy and other first-series transition metals. As an example, ELF clearly shows six peaks separated by five minima, corresponding to six electronic shells in Rn as one can expect from the highest occupied principle quantum number state, $6p^6$. For Al_6 , Al_{12}Si , Al_{12}C , and Al_{54}Si , states with, respectively, 1, 2, 2, and 3 principle quantum numbers are occupied. Accordingly, we expect 1, 2, 2, and 3 shells in ELF, respectively. This is indeed true as shown in Figs. 3(a)–3(d). The center of the cluster is shown by the dotted line. The Jahn-Teller distortions in Al_6 and Al_{54}Si make ELF asymmetric. An interesting finding is that even in Al_6 , the value of ELF at the center is close to 0.5 and therefore, the behavior is very close to jellium nature.

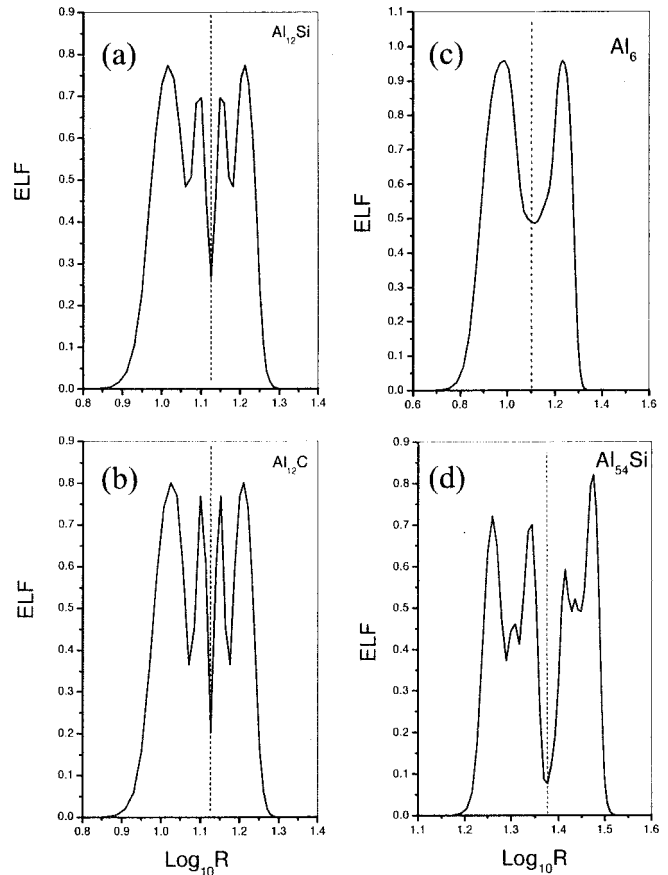


FIG. 3. Real-space representation of shell structures. The dotted line specifies the center of the cluster. We plot ELF along the diagonal direction of the cubic supercell, and the radial distance (R) is measured from a cubic cell corner.

lium nature. In fact, the ionization potential (IP) measurement revealed the onset of sp hybridization in Al_n clusters beginning at $n=5$.²³ It is to be noted that there is no atom at the center of Al_6 . For other clusters, the value of ELF at the center is low due to the very low charge density in the core region of an atom in the pseudopotential framework. In all the clusters, the ELF has the highest value outside the vertex ions.

In summary, our studies on several jelliumlike clusters using ELF provide a direct and quantitative evidence for free electrons as well as the localized nature of electrons in metal clusters in an easily understandable and visually informative way. Similar to atoms, we find the shell structure in real space for metal clusters. We hope that such an analysis would be very fruitful for other systems such as clusters of silicon, where there appears to be a change in the bonding character as a function of size.

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- ¹W. A. de Heer and W. D. Knight, *Solid State Physics* (Academic, New York, 1987), Vol. 40.
- ²D. Boatsos, N. Karoussos, D. Lenis, P. P. Raychev, R. P. Roussev, and P. A. Terziev, *Phys. Rev. A* **62**, 013203 (2000), and references therein.
- ³A. D. Becke and K. E. Edgecombe, *J. Chem. Phys.* **92**, 5397 (1990).
- ⁴B. Silvi and A. Savin, *Nature (London)* **371**, 683 (1994).
- ⁵A. Savin, R. Nesper, S. Wengert, and T. F. Fässler, *Angew. Chem. Int. Ed. Engl.* **36**, 1809 (1997).
- ⁶G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993); **49**, 14 251 (1994).
- ⁷D. Vanderbilt, *Phys. Rev. B* **32**, 8412 (1985).
- ⁸M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.* **64**, 1045 (1992).
- ⁹J. P. Perdew, in *Electronic Structure of Solids*, edited by P. Ziesche and H. Eschrig (Akademic, Berlin, 1991).
- ¹⁰R. Ahlrichs and S. D. Elliott, *Phys. Chem. Chem. Phys.* **1**, 13 (1999).
- ¹¹S. N. Khanna and P. Jena, *Phys. Rev. Lett.* **69**, 1664 (1992).
- ¹²X. G. Gong and V. Kumar, *Phys. Rev. Lett.* **70**, 2078 (1993).
- ¹³V. Kumar, S. Bhattacharjee, and Y. Kawazoe, *Phys. Rev. B* **61**, 8541 (2000).
- ¹⁴A. P. Seitsonen, K. Laasonen, R. M. Nieminen, and M. L. Klein, *J. Chem. Phys.* **103**, 8075 (1995).
- ¹⁵The carbon atom is much smaller than aluminum. In order to check whether it is optimally bonded in the *i* structure, we displaced the C atom from the central position. However, upon optimization, it converges again to the symmetric *i* structure, in agreement with the results reported in Ref. 14. Our Al-C and Al-Al bond lengths agree with the values 2.57 and 2.69 Å obtained in Ref. 14 using the gradient corrected exchange and correlation method. Also the binding energy in Ref. 14 was 36.6 eV, in close agreement with 36.94 eV obtained by us.
- ¹⁶J.-Y. Yi, D. J. Oh, J. Bernholc, and R. Car, *Chem. Phys. Lett.* **174**, 461 (1990); J.-Y. Yi, D. J. Oh, and J. Bernholc, *Phys. Rev. Lett.* **67**, 1594 (1991).
- ¹⁷D. E. Turner, Z. Z. Zhu, C. T. Chan, and K. M. Ho, *Phys. Rev. B* **55**, 13 842 (1997).
- ¹⁸This different behavior is due to the smaller size of the silicon atom. Note that the relaxed *i* isomer has the mean nearest-neighbor Al-Si and Al-Al bond lengths to be 2.65 and 2.79 Å, respectively. This improves bonding between the aluminum atoms in the *i* or *d* structures but creates strain in an fcc lattice. This is also reflected from a smaller gain (1.2 eV) in the *c* isomer.
- ¹⁹The gain in energy for Al₅₄Si is only slightly smaller than 1.59 and 1.61 eV in the case of *i* and *d* Al₂₂Si (Ref. 13), respectively. Our results, therefore, suggest that silicon substitution should continue to be favorable for larger *i/d* aluminum clusters. This also agrees with the observed stability of aluminum-based quasicrystals with silicon doping (Ref. 20). The HOMO-LUMO gaps for the *i*, *d*, and *c* isomers of Al₅₄Si are 0.34, 0.46, and 0.33 eV, respectively, and are significantly smaller than 0.82 eV for the lowest energy *d* Al₂₂Si and comparable to 0.23 eV for the *i* Al₂₂Si isomer. Therefore, the gain in energy is predominantly due to the *i* structure.
- ²⁰See articles in the *Proceedings of the Fourth International Conference on Quasicrystals, St. Louis, 1992*, *J. Non-Cryst. Solids* **153&154**, (1993).
- ²¹L. De Santis and R. Resta, *Surf. Sci.* **450**, 126 (2000).
- ²²M. Kohout and A. Savin, *Int. J. Quantum Chem.* **60**, 875 (1996).
- ²³K. E. Schriver, J. L. Persson, E. C. Honea, and R. L. Whetten, *Phys. Rev. Lett.* **64**, 2539 (1990).