Superatom Orbitals, Orbital Splitting and Structure Prediction of Pure Alkali Metal Clusters

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Jellium model achieved great success in predicting stable clusters with closed electronic shells and zero spin. In order to explain the stability of open shell clusters, it is necessary to consider the case of non-degenerate energy levels. In this paper the energy levels in nine low-lying Li$_{19}$ clusters are analysed systematically through superatomic orbital splitting effect. It is found that for originally degenerate orbitals like five 1D orbitals, the more the orbital extends in the direction of the cluster extension, the lower the energy of the orbital becomes. It is found that this relationship can be applied to explain the stability of Li$_{14}$ and predict the shape as prolate, oblate or sphere and magnetic moment of clusters. 11 out of 16 predicted shapes of Li$_n$($n = 3 - 18$) are consistent with the results obtained by the principle of minimum energy.

I. INTRODUCTION

Jellium model assumes that the movement of valence electrons in simple metal clusters is carried out in a uniform potential [1, 2]. The quantum states of valence electrons in the cluster follows the configuration of $1S^2 - 1P^6 - 1D^{10} - 2S^2 - 1P^{14} - 2P^6 - \cdots$, with S, P, D, F the angular momentum. This way, these clusters, also known as superatoms, mimic the chemical behaviour of single atom [3-8]. Jellium model predicts that superatoms with full electronic shells are endowed with extra stability, giving the magic numbers of 2, 8, 18, 20, 34, 40, 54, 76, while combination of cluster consists of 8 electrons, responsible for a gap as high as 3.72 eV between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [9]. Tetrahedral Al$_{20}$ cluster is of special stability, of which the electronic shell can be viewed as $1S^2 - 1P^6 - 2S^2 - 1D^{10}$ [10]. Experimental measured HOMO-LUMO gap is 1.77 eV, greater than that in C$_{60}$ [11]. 40-electron Al$_{13}$ cluster is known for mimicking holo- gen atoms, the stability of which originates from closed 2P shell [12].

Despite the great success that spherical jellium model has achieved on the explanation of stability possessed by closed shell superatoms, the limitation of magic number hinders the diversity of physical and chemical properties of clusters [13]. Here we propose that when orbitals are split into several subgroups, extra stability can also be achieved if electrons happen to fully or halfly occupy one subgroup. In this work, we report the splitting of originally degenerate superatom orbitals through our investigation of orbitals in Li$_{19}$ clusters, the number of electrons $n = 19$ is exactly between magic numbers 18 and 20. When a transition metal cation is located in the center of an octahedral cage of oxygen anions, due to the electric repulsion produced by ligands, its d orbitals splits into two sets, which is the core idea of crystal field theory [14].

Orbitals in superatoms, e.g., 1P and 1D, will also split into several groups, only the intrinsic dirving force is not ligand’s electric field but the deformation of cluster shape. Lithium, the simplest alkali metal with electronic shell of 1s$^2$, is an ideal prototype for simple metal [4, 5, 15, 16]. Li$_{19}$ cluster owns 19 electrons, and its electrons can fully occupy orbitals from 1S to 1D, providing convenience for analysis of electronic orbitals. Based on a combined searching strategy and DFT calculation, the optimal configuration of Li$_{19}$ cluster is obtained along with eight low-lying iso- mers. The superatomic orbitals are studied and it is found that their electronic configurations can be divided into two types, corresponding to two different cluster shapes, prolate ellipsoid and oblate ellipsoid, respectively. Clusters in the shape of oblate ellipsoid have the electronic configuration of $1S^2 - 1P^6 - 1D^4 - 2S^2 - 1D^{14}$ - $2P^6 - \cdots$, while clusters in the shape of prolate ellipsoid have the configuration of $1S^2 - 1P^6 - 1D^4 - 2S^2 - 1D^{14} - 2P^6 - \cdots$. It is found that for originally degenerate orbitals, the more the orbital extends in the direction of the cluster extension, the lower the energy becomes. It is found that this relationship can be applied to explain the stability of Li$_{14}$ and predict the shape as well as magnetic moment of alkali clusters. Our results based on superatomic orbital splitting effect analysis is a powerful tool and theoretically sound for explaining and predicting the structure and stability of simple alkali metal clusters.

II. COMPUTATIONAL DETAILS

A large number of initial isomers are generated by the following methods in order to carry out an unbiased search for the global-minimum structures of Li$_{19}$:

1. Crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO) software package developed by Yanchao Wang et al [17].
2. Blending smaller clusters. Place several smaller clusters (19 lithium atoms in total) at random relative position, which simulates the formation of large clusters through collision of small clusters.

3. Constructing geometrically symmetric system. We randomly fabricated polygons with high mathematical symmetry and fit lithium atoms in geometric vertex properly.

All Electron Relativistic methods were subsequently performed for further geometric optimization with Dmol3 package in MaterialsStudio. The Perdew and Wang’s 1991 exchange and correlation functional (PW91) functional [18] was continually selected since the quality has been verified by our previous work in V@Li_n superatom clusters [7]. The highest precision basis set of double numerical plus polarization with addition of diffuse functions (DNP+) was chosen. Cut-off energy and the self-consistent field (SCF) convergence tolerance were both set as Fine. The frequencies of the configurations were calculated and there are no imaginary frequencies for the obtained configuration with lowest energy. For odd or even number of valence electrons, the potential spin multiplicity may be 2, 4, 6, 8... or 1, 3, 5, 7..., respectively. Each possible spin multiplicity of the clusters was tested and value with the lowest energy is picked.

III. RESULTS AND DISCUSSION

A. Identification of Geometric Configurations

Although a large variety initial structures were obtained from the above three different methods, the lowest energy structure obtained by further DFT optimization of these initial configurations are indeed the same. We listed 9 isomers with distinct geometry in FIG. 1 sorted by energy from low to high.

The ground state structure for \( \text{Li}_{19} \) clusters is an oblate cage with three lithium atoms inside as marked \( \text{A} \) in FIG. 1, which is consistent with the result predicted by Sung using simulated annealing method [6]. According to the jellium model, alkali metal clusters with closed-shell electronic configurations usually adopt high symmetry geometries [19]. Since \( \text{Li}_{19} \) cluster has total 19 valence electrons, which is between two magic number of 18 and 20, it is in line with expectations that structure of the \( \text{Li}_{19} \) has low \( C_{2v} \) symmetry and does not tend to form a spherical shape. Another intriguing structure is \( \text{E} \) with the symmetry of \( D_{5h} \). Its shape is a prolate cage-like structure with a morphology similar to that of Chinese lanterns. Four atoms sit on its central axis, encircled by three staggered 5-membered rings. C and H structures evolve from E and I structures respectively with one atom moves from the top or bottom of the original structures to their side. These two isomers C and H are considered as the transitional structures because they are because it is somewhere in between prolate ellipsoid and oblate ellipsoid. Binding energies of oblate C and H are lower than their parent structures E and I, respectively, indicating that \( \text{Li}_{19} \) is more inclined to form oblate ellipsoid clusters. This structural characteristic is also verified by the most stable isomer A with the oblate structure.

B. Superatom Orbitals in \( \text{Li}_{19} \)

Orbital analysis reveals that \( \text{Li}_{19} \) clusters possess superatom orbitals and mimic the s, p, d orbitals of simple atom. As each lithium atom provides one delocalized electron, the number of effective valence electrons is 19. Despite having a open shell, it is found that molecular orbitals of \( \text{Li}_{19} \) clusters can be discussed under jellium model. FIG. 2 displays orbitals of three typical structures: \( \text{A} \), \( \text{C} \) and \( \text{E} \) as representatives of oblate cluster, transition shape cluster and prolate cluster respectively. All these three sets of orbitals show a lot of similarities to the atomic orbitals. The spherical 1S orbital is followed by the dumbbell-shaped 1P orbital, then comes the petal-like 1D orbital together with 2S orbital. The identification of orbitals relies on the orientation of the coordinate axes, which is determined by the following method: we take advantage of co-planar 1D_{xy}/1D_{xz}/1D_{yz} to fix x-y plane, thus the direction perpendicular to the plane is z axis.

As one might note the orbital alignment sequences of three isomers in FIG. 2 differ from one another. For the most stable configuration of pure \( \text{Li}_{19} \) marked as \( \text{A} \), 1D orbitals split into three groups, 1D_{xy}/1D_{xz}/1D_{yz} with the lowest energy, followed by 1D_{xz}/1D_{yz} with the second lowest energy, and 1D_{x^2} with the highest energy. 1P orbitals also split into two groups...
FIG. 2. The molecular orbitals (MOs) and MO energy level diagrams of the pristine Li19 cluster for structure C, E and A respectively. The color bar on the scale axis represents the energy range covered by corresponding sets of MOs. The shapes of MOs are drawn outside the scale axis, and the type and number of each MOs are marked nearby. To represent the energy level order for non-degenerate orbitals, the orbitals drawn before are lower in energy while the orbitals in the same radial position have similar energies. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels are marked by dotted lines.

The energy of $1P_x/1P_y$ is lower than the energy of $1P_z$. The more the orbital stretches in the $z$ direction, the higher the energy become. For prolate configuration E, the sequence of splitted orbitals is dramatically opposite. 1D orbitals with lowest energy are $1D_{2z}$, followed by $1D_{xz}/1D_{yz}$, and highest energy level orbitals are $1D_{xy}/1D_{x^2−y^2}$. The situation is same in 1P orbitals. The more the orbital stretches in the $z$ direction, the higher the energy become. For prolate configuration E, the sequence of splitted orbitals is dramatically opposite. 1D orbitals with lowest energy are $1D_{2z}$, followed by $1D_{xz}/1D_{yz}$, and highest energy level orbitals are $1D_{xy}/1D_{x^2−y^2}$. The situation is same in 1P orbitals. The more the orbital stretches in the $z$ direction, the lower the energy become. For prolate ellipsoid $\alpha < 0$ while for oblate ellipsoid $\alpha > 0$. As in FIG. 4, geometry A, B, D, F are oblate ellipsoids with $\alpha$ ranging from 0.33 to 0.47, geometry E, G, I are prolate ellipsoids with $\alpha$ ranging from -0.29 to -0.19. By such classification, we can draw the conclusion that oblate clusters have the orbital sequence of $1S^2−1P^6−1D_{2z}−1D_{xz}/1D_{yz}−2S^2−1D_{x^2−y^2}−1D_{xy}^4$, while prolate clusters have the sequence of $1S^2−1P^6−1D_{2z}−1D_{xz}/1D_{yz}−2S^2−1D_{x^2−y^2}−1D_{xy}^4$. For originally degenerate orbitals, the more the orbital extends in the direction of the cluster extension, the lower the energy becomes (e.g. energy of $1D_{2z}$ is lower than $1D_{xz}/1D_{yz}$ in prolate cluster because $1D_{2z}$ has a greater lob in $z$ axis).

C. Prediction of Stability

Furthermore, orbital splitting effect can be generalized to explain the stabilities of alkali metal systems with ellipsoidal structures, such as the Li$_{14}$ cluster. In the literature [15], the
FIG. 3. Energy level of superatom orbitals of Li$_{19}$ clusters where solid lines with different colors represent different energy levels. Orbitals with strange shapes that cannot be classified as known orbitals are classified as Non-Classical.

FIG. 4. Fitting results of the flattening of seven lithium clusters, atoms inside the cluster have a weight of 0 in the fit. $\alpha = (a - b)/a$ describes the flattening of the ellipsoid and $R_s$ is the squared norm of the residual.
stability of the Li\(_{14}\) cluster is explained as the combination of two Li\(_{10}\) clusters with super-covalent bonds, mimicking fluorine molecule. However, superatomic orbitals of Li\(_{14}\) from 43(LUMO)-48 do not correspond to any orbital of fluorine molecule according to our molecular orbital analysis. Within the view of orbital splitting effect, the structure and stability can be successfully interpreted. As illustrated in FIG. 5, the prolate structure of Li\(_{14}\) will lead to the split of 1D energy levels. As a result, 1D\(_{z}\) lies at the lowest energy levels, following the next higher energy of 1D\(_{xz}/yz\) MOs. The 1D\(_{z}\) and 1D\(_{xz}/yz\) are all doubly occupied resulting in a large HOMO-LUMO gap of 1.60 eV. This interpretation based on splitted orbitals clearly shows the nonspherical clusters can achieve good stability without meeting the requirement of magic number.

As shown in FIG. 6 when \(n = 3(4)\), electrons can halfly (fully) fill 1P\(_z\) orbital, so the shape of cluster should be prolate. When \(n = 5\), three electrons halfly occupy three degenerate 1P orbitals, so the cluster will be spherical. When \(n = 6\), electrons can either halfly occupy 1P\(_{xy}\) orbitals with fully occupied 1P\(_z\) in prolate configuration or fully occupy 1P\(_{xy}\) orbitals with empty 1P\(_z\) in oblate configuration. Since fully occupied HOMOs are more stable, the cluster will be prolate. When \(n = 11\), the cluster will be prolate because in this case there will be only one electron in the HOMOs instead of three when the cluster is oblate. To sum up, for prolate clusters, numbers match electron configuration are \(n = 3, 4, 9, 10, 11, 14, 15, \cdots\). For a cluster with oblate shape, the occupancy agrees with \(n = 6, 7, 12, 16, 17, \cdots\). For spherical clusters, preferred numbers are \(n = 5, 8, 13, 18 \cdots\). The results are summarized in TABLE I.

![FIG. 5. Calculated energy levels and electronic orbitals in Li\(_{14}\) clusters.](image)

**D. Prediction of Geometric Structure**

It should be pointed out that the orbital splitting effect of Li\(_{19}\) cluster proposed here can be extended to describe and predict the geometric shapes of the pure alkali metal species with other size. Based on previous discussion, the electron configuration of oblate, prolate and spherical jellium clusters can be theoretically predicted, and we are able to fill electrons in properly to connect the shape of cluster with the number of valence electrons \((n)\). The rule of filling electrons are proposed in analogy with single element atoms:

1. In all possible electron configurations, the term with fully occupied (degenerate) HOMOs has the lowest energy. This rule is based on the experimental fact that high peaks in mass spectrum correspond to closed superatom shells \([21, 22]\).

2. When a closed shell cannot be achieved, the configuration with halfly occupied (degenerate) HOMOs has the lowest energy.

3. When previous goals can’t be satisfied, considering the fact that repulsion of electrons may raise the energy, we suppose HOMOs with less electrons occupied has lower energy.

| \(n\) | prolate | oblate | spherical |
|------|---------|--------|-----------|
| 3    | √       |        | √         |
| 4    | √       |        | √         |
| 5    | √       |        | √         |
| 6    | √       |        | √         |
| 7    | √       |        | √         |
| 8    | √       |        | √         |
| 9    | √       |        | √         |
| 10   | √       |        | √         |

Once the configuration is determined, the magnetic moment of each cluster equal to the number of unpaired electrons (FIG. 7). Compared with DFT calculated results, the prediction reproduced odd-even oscillation of magnet moments. In particular, the predicted magnetic moment of Li\(_{13}\) clusters is 5\(\mu_B\), in good agreement with the DFT theory calculations. It seems that we have overestimated the magnet moment in Li\(_5\) while underestimated that in Li\(_{16}\), the reasons will be analysed later.

![FIG. 7. Predicted magnetic moments for Li\(_n\) clusters compared with the results calculated by DFT.](image)
When considering the lowest energy structures of Liₙ clusters (FIG. 8), in line with expectations, most of the shapes satisfy our prediction. When \( n = 3 \), instead of forming an equilateral triangle, Li₃ forms an isosceles triangle which can be viewed as a prolate structure stretched from an equilateral triangle in order to make the cluster more stable. Li₄ \((n = 4)\) has a tendency to be prolate so it will not form a regular tetrahedral (a square) which is close to spherical (oblate). For Li₁₀, Li₁₁, Li₁₄ and Li₁₅, the optimized equilibrium structures are prolate ellipsoid with their orbital configurations matching FIG. 6 perfectly.

The most stable structures of Li₆ and Li₇ are all oblate ellipsoids, namely, Li₆ and Li₇ are squared pyramidal and pentagonal bipyramid respectively, which are consistent with theoretical prediction.

Li₈, Li₉, and Li₁₈ clusters have quite spherical shape and with high \( D_{3h} \), \( I_h \), \( C_s \) symmetry respectively. Li₁₃ has 5 parallel 1D orbitals resulting in a high magnetic moment of \( 5\mu_B \), as forecasted in FIG. 7. We can see that the model of orbital splitting can be successfully applied to interpret the structure and stability of other alkali metal clusters and the model is likely to be extended to \( n > 18 \) clusters after taking into account of 1F, 2S, 2P... orbitals. It is also expected to be useful for the study of other types of doped metal clusters.

Although the geometric structures of the pure lithium clusters is overwhelmingly consistent with our predictions, there are also a few deviations. These exceptions may arise due to the multiple factors that determine the cluster structure. First of all, Jahn-Teller distortion is known to reduce the symmetry of small clusters and cause a low spin state [24]. Li₅ was set to be a high spin sphere with \( 3\mu_B \) but transformed to be a prolate spheroid with \( 1\mu_B \). Li₉ was predicted to be prolate but turned out spherical with no explicit \( z \) direction. Likewise, Li₁₂ transformed from a prolate spheroid to a tri-axial ellipsoid with \( a < b < c \) which leads to nondegeneration of the 1D \( xz \) and \( yz \). The final electron configuration for Li₁₂ is \( 1S^2 - 1P_x^2 - 1P_y^2 - 1P_z^2 - 1D_{2x}^2 (HOMO) - 1D_{2z} (LOMO) \). Moreover, Hund’s rule is reported to favour high spin state in cluster [25, 26], which may be responsible for prolate Li₁₆ with \( 2\mu_B \). In addition, we ignored the intercalation of 2S orbitals. It has been calculated that 2S inserted between \( 1D_{2x}^4 \) and \( 1D_{2z}^4 \) in Li₁₉ while it inserted between 1P and 1D in Li₈. Li₁₇ is a prolate ellipsoid which has 2S orbitals intercalated in 1D \( xy/x^2-y^2 \), causing an orbital configuration of \( 1S^2 - 1P_x^2 - 1P_y^2 - 1D_{x}^2 - 1D_{y}^2 - 1D_{z}^2 - 1D_{xy}^2 - 1D_{xz}^2 - 1D_{yz}^2 (HOMO) - 1D_{xy} (LOMO) \). There only exist a small gap (0.148 eV) between HOMO and LUMO. It is predictable that

FIG. 6. Preferred electron occupation for (a) prolate, (b) oblate and (c) spherical clusters.
IV. CONCLUSION

In conclusion, our work offered a method to predict the magnetic moment and shape of alkali clusters through the analysis of superatom orbitals. The molecular orbitals of nine low-lying Li$_{19}$ clusters have been calculated, identified and compared. It has been found that clusters in the shape of oblate ellipsoid have the electronic configuration of $1S^2 - 1P^6 - 1D_{xy} - 1D_{yz} - 2S^2 - 1D_{z^2} - 1D_{x^2-y^2}$, while clusters in the shape of prolate ellipsoid have the sequence of $1S^2 - 1P^6 - 1D_{x^2} - 1D_{y^2} - 1D_{z^2} - 1D_{x^2-y^2} - 2S^1$. For originally degenerate orbitals, the more the orbital extends in the direction of the cluster extension, the lower the energy becomes. The applications of the orbital splitting are promoted in two following ways. The stability of the Li$_{14}$ cluster are explained in the framework of orbital splitting effect without resorting to the SVB model. Meanwhile, it is proposed that the orbital splitting effect can be used to predict the shape and magnetic moment of clusters. 11 out of 16 predicted shapes of Li$_n$($n = 3 - 18$) are consistent with the results obtained by the principle of minimum energy.

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