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Communication: New insight into electronic shells of metal clusters: Analogues of simple molecules

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A new concept of super valence bond is proposed, of which superatoms can share both valence pairs and nuclei for shell closure thus forming delocalized super bonding. Using Li clusters as a test case, we theoretically find that metal clusters can mimic the behavior of simple molecules in electronic shells. It is found that Li_{14} , Li_{10} , and Li_8 clusters are analogues of F_2 , N_2 , and CH_4 molecules, respectively, in molecular orbital diagrams and bonding patterns. This new concept shows new insights in understanding the stability of clusters and designing the cluster-assembling materials. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4801860>]

Jellium model is widely used in studies of alkali-metal clusters.^{1–5} In this model, the valence electrons of a cluster are delocalized in the cluster volume and fill discrete energy levels. There are several degrees of sophistication of this model, among which the spherical Jellium model^{1,6} is widely accepted. The spherical Jellium model assumes a uniform background of positive charge of the cluster's atomic nuclei and the innermost electrons, in which valence electrons move and are subjected to an external potential. The infinitely deep spherical well and the harmonic well are the simplest forms of the potential, in which the former gives the series of magic numbers of 2, 8, 18, 20, 34, 40, 58, . . . , and the later gives the series of 2, 8, 20, 40, 70, . . .

Based on the Jellium model, atomic assemblings with magic number electrons can act as superatoms, and such a superatom concept has achieved great success in explaining the stability of pure metal clusters. For example, the experimental spectra of sodium clusters¹ reveal high peaks at 8, 20, 40 in agreement with both models. Moreover, stability of the metallic core of ligand-protected gold clusters⁷ can also be understood by the Jellium model. Superatom concept for a cluster has been extended to mimic any atom, based on electronic states and/or reactivity. This concept is in fact traceable to Mulliken's united atom approach.⁸ For example, Castleman *et al.* showed that metal clusters, such as Al_{13} , could behave as superatoms, with reactivity resembling halide or alkali atoms.^{9–11}

However, the smaller peaks in the experimental spectra of sodium clusters, e.g., $N = 10, 12, 14$, and 26 cannot all be understood in the framework of strictly spherical Jellium model,¹ where the cluster is far from spherical. To explain the smaller peaks, Clemenger¹² suggested an ellipsoidal shell model, of which stability of the smaller peaks can be explained at $0.04 < U < 0.08$. However, the parameter

U gives no direct physical picture, and the model is entirely structureless.

In this Communication we propose a new concept for bonding between superatoms and give a more generalized insight to the stability of non-spherical clusters. Rare gas atoms have filled electronic shells, and are chemically very inert. The other elements are active in atomic state but can compose stable molecules, in which each atom has filled electronic shells by sharing valence pairs, which is just the basic idea of valence bond (VB) theory. Magic numbers of superatoms ($N = 8, 20, 40, \dots$) can mimic the behavior of rare gas atoms in electronic shells. We found that the smaller peaks in mass spectra¹ may correspond to the superatomic molecules, i.e., superatoms can compose superatomic molecules by sharing valence pairs.

Lithium is the first alkali-metal, which can be considered as an ideal prototype for simple metals. Thus, in this work we also select lithium cluster to verify the concept of superatomic molecule. Geometries of small Li clusters have been subsequently studied by various density functional theory (DFT) and *ab initio* methods.^{13–18} The energy landscape of Li clusters is rather smooth, so we revisit the global minimum (GM) structures of Li_N clusters with $N = 2–26$ by unbiased global search of the DFT landscape using the genetic algorithm implemented in our group. There are certainly gaps in relative energies of different isomers between different theoretical methods. However, this work focuses only on the most stable isomers where different methods should get consistent results, so we just simply choose the famous hybrid B3LYP functional with the all-electron 6-311+G* basis set. All DFT calculations are carried out on GAUSSIAN 09 package,¹⁹ and molecular visualization is performed using MOLEKEL 5.4.²⁰

The energies of the resulting putative GMs of Li_N clusters at B3LYP/6-311+G* with $N = 2–26$ are depicted in Fig. 1 in a manner that emphasizes particular stable minima or “magic numbers” simulating the experimental mass spectra. Our simulated mass spectra are in good agreement with

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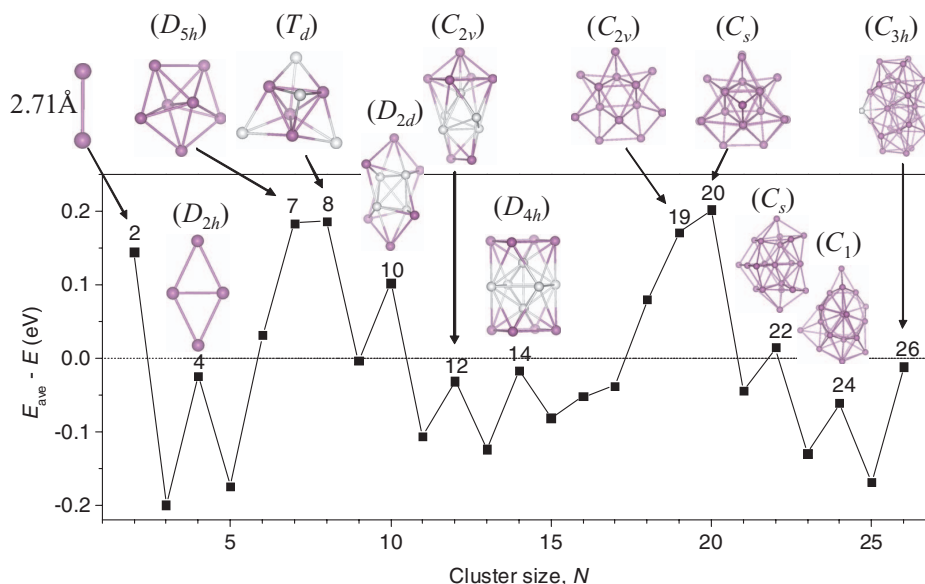


FIG. 1. Energies of the GMs of Li_N clusters at B3LYP/6-311+G* relative to E_{ave} , a fit to the energies of the GMs at size ratio $2 \leq N \leq 26$ using the form $a + bN^{1/3} + cN^{2/3} + dN$, which represents the average energy of the GMs. Upward peaks, as labeled, represent particular stable minima or “magic numbers” relative to the “average energy” of the GMs. The structures and point groups of the upward peaks are labeled in the figure, where Li atoms may be given in different colors for better viewing.

the experimental spectra¹ at both large ($N = 8, 20$) and small ($N = 10, 12, 14$) peaks at $N \leq 20$ indicating high reliability. Li_4 (D_{2h}) is a planar motif in all-metal σ -antiaromaticity;²¹ Li_7 is a ideal tetrahedron in D_{5h} symmetry; Li_8 (T_d) is a tetrahedron with all four faces capped; Li_{10} (D_{2d}) is a prolate body-fused bi-tetrahedron sharing four nuclei; Li_{12} (C_{2v}) and Li_{14} (D_{4h}) are both prolate clusters; Li_{19} (C_{2v}) and Li_{20} (C_s) are in same packing style (all in Fig. 1). Stability of small Li clusters is mainly determined by the electronic shells (e.g., Li_8 and Li_{20}), and contributions of the atomic shells (e.g., Li_7 and Li_{19}) are also very clear. The filled electronic shells of Li_{20} have been fully discussed using the Jellium model,¹⁻³ and we will tell a new story about the geometric and electronic structures of Li_8 , Li_{10} , Li_{12} , and Li_{14} .

First, we focus on the prolate double-core Li_{14} . Based on our concept of superatomic molecule, the prolate cluster can be seen as a union of two ten-center seven-electron (10c-7e) spherical superatoms sharing a six-nucleus octahedron (see Fig. 2(a)). The 10c-7e superatom mimics the behavior of F atom in valence shells (s^2p^5), and can be seen as a super F atom. The canonical Kohn-Shan molecular orbital (MO) diagrams (Fig. 3(a)) reveal clearly that Li_{14} mimics the behavior of F_2 in electronic structures.²² The first two valence MOs (HOMO-4 and HOMO-3) of Li_{14} are super σ_s and σ_s^* ; HOMO-2 is a doubly degenerate π -bond MOs (π_{px} and π_{py}); HOMO-1 is a super σ_{pz} ; HOMO is a doubly degenerate π -antibond MOs (π_{px}^* and π_{py}^*); LUMO+3 is a super σ_{pz}^* . Two δ -type MOs (LUMO and LUMO+1) and a σ_{2s} -type MO (LUMO+2) are lower than the σ_{pz}^* MO. The reason may be that the shoulder-by-shoulder MOs (π and δ) are favored more at a shorter atom-atom/superatom-superatom distance, which is also the reason for the difference of the orders of $\pi_{px,py}$ and σ_{pz} between Li_{14} and F_2 .

The canonical MO pictures reveal that Li_{14} is an analogue of F_2 based on the MO theory. Next, we will compare the

bonding pictures based on the VB theory. To give a straightforward view of superatom-superatom bond, we selected the Adaptive Natural Density Partitioning (AdNDP) method as a tool for chemical bonding analysis. This method was recently developed by Zubarev and Boldyrev²³ and successfully used to analyze chemical bonding in organic molecules and clusters.²³⁻²⁸ AdNDP recovers both Lewis bonding elements and delocalized bonding elements (nc -2e), which is a method of description of the chemical bonding combining the compactness and intuitive simplicity of Lewis theory with the flexibility and generality of canonical MO theory. As shown in Fig. 3(b), AdNDP analysis reveals three 10c-2e super lone-pairs (LPs) in each superatom with occupancy number ON = 1.99–2.00 lel in Li_{14} (s , p_x , and p_y), and one 14c-2e super

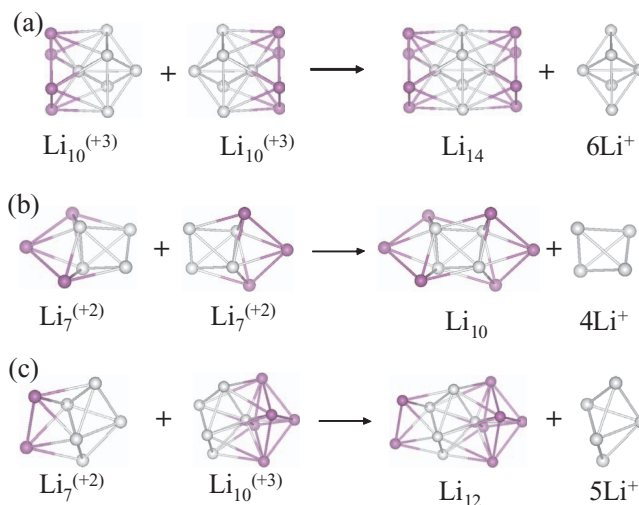


FIG. 2. Di-superatomic model for the prolate (a) Li_{14} , (b) Li_{10} , and (c) Li_{12} clusters.

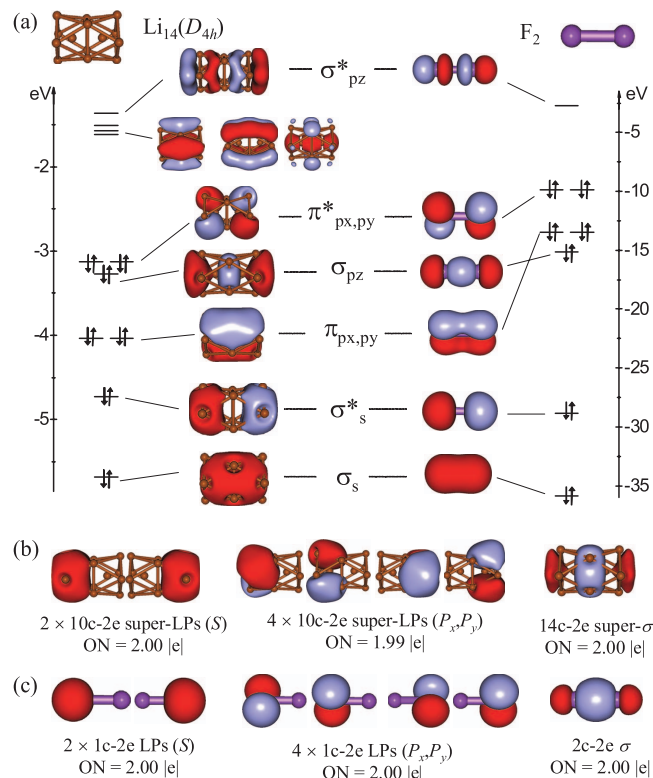


FIG. 3. (a) Comparison of the geometries and Kohn-Sham MO diagrams of Li_{14} cluster and F_2 molecules. (b) AdNDP localized natural bonding orbitals of Li_{14} cluster. (c) AdNDP localized natural bonding orbitals of F_2 molecule. The isosurface values for Li clusters and F_2 molecule are 0.10 and 0.02, respectively.

σ -bond ($ON = 2.00$ |e|). The bonding framework of Li_{14} is an analogue of that of F_2 (Fig. 3(c)) based on the VB theory.

Second, we investigate the chemical bonding of Li_{10} . Similarly, the prolate cluster can be seen as a union of two $7c-5e$ spherical superatoms (super N), in which a four-nucleus tetrahedron and three covalent pairs (triple bond) are shared by the two super N (see Fig. 2(b)). The canonical MO diagrams (Fig. 4(a)) reveal that Li_{10} is a complete analogue of N_2 in both MO shapes and orders, except for a σ_{2s} -type MO below σ_{pz}^* MO. AdNDP analysis reveals one $5c-2e$ super s -type LP ($ON = 1.96$ |e|) in each superatom, one $10c-2e$ super σ -bond ($ON = 2.00$ |e|), and two $10c-2e$ super π -bonds ($ON = 2.00$ |e|) in Li_{10} (Fig. 4(b)), which is same with N_2 (Fig. 4(c)) in bonding framework.

The situation in Li_{12} is also similar. As shown in Fig. 2(c), the prolate cluster can be seen as a union of a $7c-5e$ spherical superatom (super N) and a $10c-7e$ spherical superatom (super F), in which a five-nucleus bi-tetrahedron and two covalent pairs (one σ and one π , double bond) is shared by this two superatoms. Thus, Li_{12} is an analogue of NF molecule.

Finally, we tell a new story of Li_8 other than the spherical Jellium model. It is found that the peak at $N = 8$ is much smaller than the peak at $N = 20$ in the experimental spectra. Moreover, the tetrahedral Li_8 is far from spherical. Thus, we think Li_8 is also a superatomic molecule instead of super Ne atom due to the size effect in atomic shells. After comparisons of geometries, canonical MO diagrams, and chemical bonding framework of AdNDP localization between Li_8 and CH_4 , we

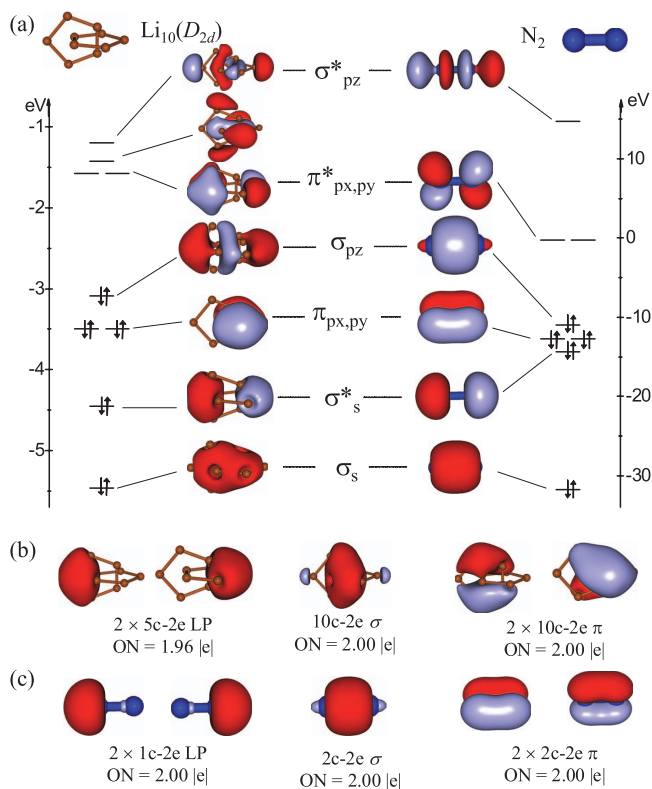


FIG. 4. (a) Comparison of the geometries and Kohn-Sham MO diagrams of Li_{10} cluster and N_2 molecules. (b) AdNDP localized natural bonding orbitals of Li_{10} cluster. (c) AdNDP localized natural bonding orbitals of N_2 molecule.

conclude that Li_8 is a super CH_4 molecule (see Fig. 5). The central tetrahedron is a $4c-4e$ super C and the four capped tetrahedra are $4c-1e$ super H. A three-nucleus triangle and one covalent pair are shared by the super σ -CH bond.

It should be pointed out subtle difference exists between MOs of covalent molecules and supermolecular clusters. The former can be well described by linear combination of atomic orbitals. However, the valence MOs of Li clusters are really

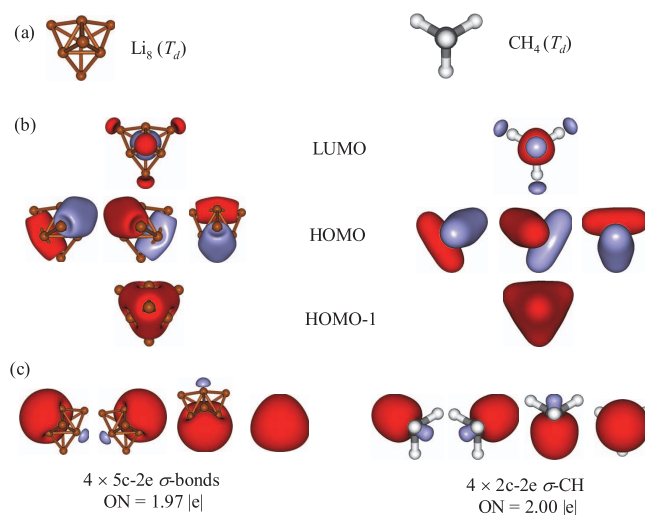


FIG. 5. Comparison of the (a) geometries, (b) Kohn-Sham MO diagrams, and (c) AdNDP localized natural bonding orbitals of Li_8 cluster and CH_4 molecule.

delocalized. This difference is caused by the fact that both valence pairs and nuclei are shared for shell closure of Li clusters. Due to the same reason, complicated concepts such as charge-shift bonding given by Shaik and Hiberty,^{29,30} cannot be directly applied to Li clusters.

After the good analogy of Li clusters with simple molecules in both electronic state and chemical bonding, now we can give our conclusions: (i) metal clusters can mimic the behavior of simple molecules in electronic shells in both MO diagrams and bonding patterns; (ii) following the definition of superatom of Jellium model and the VB theory, we propose the super valence bond (SVB) model to explain such a superatom-superatom bonding pattern; (iii) borders between bonded superatoms are not so clear as between atoms, in which nuclei at the borders may be shared by several superatoms; (iv) the criterion for singling out the correct building blocks in specific cases superatom based on the Jellium model is “spherical” and “geometric shell closure,” of which both nuclei and electrons are shared and the superatoms can be seen as in charge neutrality.

Actually, chemical bonding is just a definition of certain behavior of electrons, however, has achieved great success in explanation and prediction for the properties and structures of molecules and materials. Perhaps, the SVB model is telling the same story with Clemenger’s ellipsoidal shell model¹² in different ways for the prolate cases. However, the SVB model gives a direct physical insight of electronic shell closure, but the ellipsoidal shell model is parameter-based giving no direct physical picture. Moreover, stability of the tetrahedral Li₈ cannot be understood by Clemenger’s ellipsoidal shell model.¹² Assembling crystals from clusters has long been an issue in literatures,^{31,32} of which interactions between superatoms and superatoms/atoms are based on localized bond, ionic bond, or van der Waals interactions. Although there is no unfathomable theory, the SVB model gives pictures of materials and clusters packed by superatoms weldlessly, and will be potentially very useful in the areas of metal clusters, nanoalloys, and materials, where super bonding may also exist.

Chemical and mechanical properties of pure metals are often not so good. However, alloys with certain composition may have excellent properties. It can be expected that, based on the SVB model, the properties of bulk alloys can also be determined by the electronic shell closure as in metal clusters. That is, bulk alloys can be seen as superatomic crystal (analogues of atomic crystals, such as diamond). Moreover, based on the SVB model, novel cluster-assembling materials may be designed, such as the colloidal nanocrystal architectures.³³ In short, superatom theory has extended the periodic table to three dimensions, and the SVB model will open a new door in the area of clusters and cluster-assembling materials.

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