Evidence for the Superatom—Superatom Bonding from Bond Energies

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ABSTRACT: Metal clusters with specific number of valence electrons are described as superatoms. Super valence bond (SVB) model points out that superatoms could form the superatomic molecules through SVBs by sharing nucleus and electrons. The existence of superatom—superatom bonding was verified by the shape of their orbitals in former studies. In this paper, another important evidence—bond energy is studied as the criterion for the SVBs using the density functional theory method. In order to get the reliable values of bond energies, the series of Zn–Cu and Mg–Li superatomic molecules composed of two tetrahedral superatoms which do not share their nucleus are designed. Considering the number of the valence electrons in one tetrahedral superatomic unit, (ZnCu)2/(MgLi)2, (ZnCu)2/(MgLi)2, (ZnCu)2/(MgLi)2, and (ZnCu)2/(MgLi)2 clusters are 8e, 7e, 6e, and 5e binary superatomic molecules with super nonbond, single bond, double bond, and triple bond, respectively, which are verified by chemical bonding analysis depending on the SVB model. Further calculations reveal that the bond energies increase and the bond lengths decrease along with the bond orders in Zn–Cu and Mg–Li systems which is in accordance with the classical nonbond, single bond, double bond, and triple bond in C–H systems. Thus, these values of bond energies confirm the existence of the SVBs. Moreover, electron localization function analysis is also carried on to describe the similarity between the superatomic bonds and atomic bonds in simple molecules directly. This study reveals the new evidence for the existence of the superatom—superatom bonding depending on the bond energies, which gives the new insight for the further investigation of the superatomic clusters.

1. INTRODUCTION

The metal clusters with specific valence electrons could be described by a nearly confined free electron gas in a spherically symmetric potential which is defined as the spherical shell. Jellium model, and these novel clusters are named as the superatoms. The electronic states in superatoms are proposed to bunch into several superatomic orbitals of 1s21p62s22p63s23p64s24p65s25p66s26p67s27p68s28p69s29p610s210p611s211p612s212p613s213p614s214p615s215p616s216p617s217p618s218p619s219p620s220p6, where the resulting magic numbers are 2, 8, 18, 20, 34, 40, 58, 68, and 90. This theory of superatom has achieved great success in standing the electronic structures of variety superatomic clusters, especially in some nonspherical clusters. For example, the prolate double-core Li14 could be viewed as the union of two 10e–7e (ten-center seven-electron) spherical superatoms sharing a six-nucleus octahedron, which is the analogues of F2 with the single covalent bond. Another example is Li12Mg8 (26 super valance electrons), it is formed by two 13c–13e (thirteen-center thirteen-electron) superatoms and has the similar electronic structure as V2, where the super quintuple bonding exists. In addition to the super covalent bonds between superatoms, the superatomic orbitals could also

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hybridize to form the super hybrid bonds in the ligand field.\textsuperscript{34,42,43} The super orbitals of the Au\textsubscript{6} core in the ligand-protected gold clusters could compose the sp\textsuperscript{3}, sp\textsuperscript{2} and, sp\textsuperscript{1} hybrid to interact with the peripheral atoms to form the super hybrid bonds, which are similar as CH\textsubscript{4}, NH\textsubscript{3}, and H\textsubscript{2}O molecules with tetrahedral, trigonal pyramidal, and angular shapes.\textsuperscript{44,45} Moreover, the sp\textsuperscript{2} Au\textsubscript{6} superatomic unit could compose the Au\textsubscript{6}2\- cluster with \( \pi \) aromaticity.\textsuperscript{46} Another example is the Au\textsubscript{20} cluster, in which the superatomic orbital of the truncated tetrahedron Au\textsubscript{16} core undergo the \( d^3 \) hybridization to interact with the four apical Au atoms.\textsuperscript{47–51}

A recent study reveals the 8e ligand-protected [Au\textsubscript{12}(SR)\textsubscript{6}]\textsuperscript{2−} cluster with the sp\textsuperscript{3} core, which exhibits the special bonding and optical properties.\textsuperscript{52}

The SVB model reveals various bonding patterns between superatoms depending on the shape of orbitals. However, bond energy corresponding to the bond order is another key parameter for chemical bonding which has not been discussed for superatomic molecules before. In this paper, bond energies between superatoms are calculated and compared with the atomic bonds to verify the existence of SVBs. As the bond energies between superatoms sharing nucleus are hard to evaluate in the superatomic molecule, we design a series of Zn–Cu and Mg–Li metal clusters composed of two tetrahedral superatoms in which superatoms are just sharing electrons to form the SVB for our study. AdNDP (adaptive natural density partitioning) chemical bondings are investigated to reveal the superatomic bonding patterns in these superatomic molecules. The calculated bond energies of the superatomic bonds are compared with the nonbond, single bond, double bond, and triple bond between simple atoms. Further electron localization function (ELF) analysis is carried out to ensure the existence of these kind of SVBs from the strength of the electronic interaction.

2. RESULTS AND DISCUSSION

2.1. Geometric Modeling. The superatoms with the tetrahedral structure are popular in ligand-protected metal clusters,\textsuperscript{48–50} such as (Au\textsubscript{6}) the core of [Au\textsubscript{6}(Ni\textsubscript{3}(CO)\textsubscript{6})\textsubscript{4}]\textsuperscript{2−} cluster,\textsuperscript{49} and (Ag\textsubscript{4}) core in Ag\textsubscript{4}X\textsubscript{4} (X = H, Li, Na, K, Cu, Ag, Au, and F, Cl, Br) clusters.\textsuperscript{51}

Therefore, two tetrahedral 8e superatoms Zn\textsubscript{4} and Mg\textsubscript{4} with the electronic shell filled as 1s\textsuperscript{2} 1p\textsuperscript{6} are chosen as the objects in our study. Take the Zn\textsubscript{4} cluster as the example, two Zn\textsubscript{4} superatom compose the prolate (Zn\textsubscript{4})\textsubscript{2} superatomic molecule, then Zn atoms in contraposition of two separate units are gradually replaced by Cu atoms with one less valence electron and the similar electronegativity, in order to obtain the superatomic molecules of (Zn\textsubscript{3}Cu)\textsubscript{2}, (Zn\textsubscript{2}Cu\textsubscript{2})\textsubscript{2}, and (ZnCu\textsubscript{3})\textsubscript{2} with the differe
cent valence electrons. All the structures are optimized at the PBE0/def2-tzvp level of theory, and the optimized structures are plotted in Figure 1a−c. As shown in Figure 1a, Zn\textsubscript{4} is a T\textsubscript{d} superatom with the large highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) energy gap of 4.12 eV. The (Zn\textsubscript{3}Cu)\textsubscript{2} cluster composed of two Zn\textsubscript{4} units in Figure 2b has the D\textsubscript{4d} symmetry and the HOMO–LUMO gap of 2.96 eV. In Figure 1c, two vertex atoms of the (Zn\textsubscript{4})\textsubscript{2} cluster are replaced by Cu to form the D\textsubscript{4d} (Zn\textsubscript{2}Cu\textsubscript{3})\textsubscript{2} cluster in order to ensure that the electronic density is more concentrated in the waist of the cluster which indicates a strong interaction. This cluster has a more compact structure compared to (Zn\textsubscript{4})\textsubscript{2} and the large HOMO–LUMO gap of 2.65 eV. When another two Zn atoms in contraposition of the cluster are replaced by Cu, the (Zn\textsubscript{3}Cu\textsubscript{3})\textsubscript{2} cluster gets a better symmetry of C\textsubscript{3v} and the HOMO–LUMO gap of 2.00 eV, of which the triplet state is more stable. Finally, the (ZnCu\textsubscript{3})\textsubscript{2} cluster is obtained by replacing the other two Zn atoms by Cu. This cluster has the C\textsubscript{2v} symmetry with HOMO–LUMO gap of 2.35 eV. Moreover, the bond lengths and the distances between the centers (labeled green) in back faces of two tetrahedral units in Angstrom (Å) are labeled.

2.2. Chemical Bonding Analysis. As mentioned above, Zn\textsubscript{4} cluster could be viewed as the superatom of the 8e close shell electronic structure. Thus, it could be inferred that (Zn\textsubscript{4})\textsubscript{2} is composed of two Zn\textsubscript{4} superatoms through the 8e–8e super nonbond. As the Cu atom has one less valence electron than
Zn, \((\text{Zn}_{3}\text{Cu})\) unit could be viewed as a 7e superatom, which would form the single SVB when composing the \((\text{Zn}_{3}\text{Cu})_{2}\) cluster. Similarly, \((\text{Zn}_{2}\text{Cu}_{2})_{2}\) is composed of two 6e \((\text{Zn}_{2}\text{Cu}_{2})\) units through the double SVB, and \((\text{ZnCu}_{3})_{2}\) is formed by two
5e (ZnCu) units through the triple SVB. The Mg–Li binary clusters would follow the similar rule in their chemical bonding systems. In order to verify our inference, electronic characters of these clusters are discussed depending on the SVB model using the AdNDP method. This method was developed by Zubarev and Boldyrev and wildly used to analyze the multicenter bonding systems in carbon, boron, and metal clusters.

As shown in Figure 3, AdNDP analysis reveals that there are four 4c–2e super lone pairs (LPs) in each tetrahedral Zn4/Mg4 unit with ON (occupied number) = 2.00 lel (s), 1.92 lel (p), 1.84 lel (p) in (Zn4)1, and 2.00 lel (s), 1.96 lel (p) in (Mg4)2. Therefore, the Zn4/Mg4 unit could be viewed as the 4c–8e superatomic molecule through the 8e–8e super bond just as two inert gas atoms or two CH4 molecules.

In Figure 4a, (ZnCu)2 could be viewed as the union of two 4c–7e (ZnCu) superatoms. AdNDP analysis reveals that there are three 4c–2e super LPs in each (ZnCu) unit with ON = 1.97 lel (s), 1.83 lel (p) and one 8c–2e p−p σ bond between two (ZnCu) units (ON = 2.00 lel). The (MgCu)2 also has three LPs at each side of the superatomic molecule (ON = 2.00 lel (s), 1.95 lel for p) and one 8c–2e p−p σ bonds (ON = 2.00 lel), as shown in Figure 4b. These clusters have the similar bonding pattern as F2 and CH3=CH2 molecules, which could be viewed as the super single bond.

As shown in Figure 5a, (ZnCu)2 could be viewed as the union of two 4c–2e (ZnCu) superatoms. AdNDP analysis reveals that there are four 4c–2e super LPs (s, p) in each (ZnCu) unit with ON = 1.98 lel, 1.83 lel, respectively. Moreover, the other p orbitals of two (ZnCu) units form the 8c–2e p p σ bond and p p π bond with ON = 2.00 lel. Similarly, the (MgCu)2 also has two LPs at each side of the superatomic molecule (ON = 2.00 lel (s), 1.94 lel for p) and two 8c–2e bonds (p p, p p, p p) (ON = 2.00 lel), as shown in Figure 5b. These clusters have the similar bonding pattern as O2 and CH3=CH2 molecules, which could be viewed as the super double bond.

As shown in Figure 6a, there is one 4c–2e LP (s) in each (ZnCu) unit with ON = 1.96 lel. The p orbitals in two (ZnCu) units of the (ZnCu)2 cluster form one 8c–2e p p σ bond and two 8c–2e π bonds (p p, p p) with ON = 2.00 lel. (LiMg)2 also has one LPs at each side of the superatomic molecule (ON = 1.99 lel) and three 8c–2e bonds (σ, 2π) (ON = 2.00 lel), as shown in Figure 6b. These clusters have the similar bonding pattern as N2 and CH=CH molecules, which could be viewed as the super triple bond.

2.3. Comparison of Bond Energies. AdNDP chemical bonding analysis verifies that non bond, single bond, double bond and triple bond have also existed in the superatomic molecules depending on the SVB model. Furthermore, bond energy is another key parameter for chemical bonding. Thus, the bond energies of these super non bond, single bond, double bond and triple bond are calculated and compared with the corresponding atomic bonds in the following part.

As these superatomic molecules are formed by the two tetrahedral superatomic units which do not share the atomic nucleus, their bond energy is defined as Efi (superatomic molecule) = Ei (superatomic molecule) − 2Efi (superatomic) in our discussions, such as Efi (Zn4)2 = (Ei (Zn4)2) − 2Efi (Zn4). The bond energies for Zn−Cu, and Mg−Li systems with different superatomic bond orders and their variation trend are obtained in Figure 7. Moreover, the bond energies of the classical nonbond, single bond, double bond, and triple bond in C−H, Zn−Cu, and Mg−Li systems.

![Figure 7. Bond energies vs bond orders in C−H, Zn−Cu, and Mg−Li systems.](image-url)
bond, the variation trends of bond energies versus the face-face distance between two tetrahedral units in Zn–Cu and Mg–Li systems with different bond orders are calculated respectively. The lowest point in the energy curve represents the equilibrium structure of the cluster, of which the corresponding R (face-face distance) is the bond length. The result in Figure 8 indicates that the bond lengths decrease and the bond energies increases along with the bond orders, which is in accordance with the classical atomic non bond, single bond, double bond, and triple bond.

2.4. Electron Localization Functions. Electron localization functions (ELFs) are studied in this part to further reveal the electronic characters for the superatomic bondings discussed above. ELF results indicate electronic density distribution in the cross section of the clusters in color and shape. It is the relative value within the range of (0, 1), in which highest value of 1.0 with red color represents the full delocalization of strong interaction, whereas smallest values of 0.0 with blue color represents no delocalization of the weak interaction.

In order to make the results of ELFs comparable, all Zn clusters \((\text{Zn}_4)_2^{n+}\) with different valence electronic numbers \(n\) are chosen as the objects in our study to represent the superatomic bonding systems with different bond orders, and their structures are built without optimization to keep the same geometry (the distance between the centers in back faces of two tetrahedral units is 3.18 Å). Specifically, beside \((\text{Zn}_4)_2\) with super non bond, \((\text{Zn}_4)_2^{2+}\), \((\text{Zn}_4)_2^{4+}\) (singlet and triplet), \((\text{Zn}_4)_2^{6+}\) are isoelectronic cluster of \((\text{Zn}_4\text{Cu})_2\), \((\text{Zn}_2\text{Cu}_2)_2\) and \((\text{ZnCu}_2)_2\) which contain the super single, double, and triple bond, respectively.

The ELF scan is carried on the middle cross section of these clusters as shown in Figure 9. Moreover, the \(\text{Ne}_2\) with nonbond, \(\text{F}_2\) with a single bond, \(\text{O}_2\) (singlet and triplet) with a double bond and \(\text{N}_2\) with a triple bond are also investigated for comparison. The shape and color of the ELF results indicate the similarity between the simple bonds and the corresponding superatomic bonds with the same bond order. In general, the ELF values increase and the color gradually becomes vivid along with the bond orders, which indicates that the strength of interactions increases. It is worth noting that the shape of the super double bond in singlet and triplet \((\text{Zn}_4)_2^{4+}\) has the similar electronic characters as \(\text{O}_2\). The singlet state is composed of one \(\sigma\) bond and one \(\pi\) bond, whereas the circular triplet pattern contains one \(\sigma\) and two 1/2 three-electron \(\pi\) bond exhibiting a magnetic property, of which the latter pattern is more stable. Moreover, the singlet-triplet energy gap of \((\text{Cu}_2\text{Zn}_2)_2\) is 0.46 eV at PBE0/def2-tzvp level of calculation, and bond energies of singlet and triplet \(\text{Cu}_2\text{Zn}_2\)–\(\text{Cu}_2\text{Zn}_2\) cluster are 80.89 and 106.66 kcal/mol, respectively. This result of ELFs confirms the superatomic bonding characters existed in superatomic molecules.

3. CONCLUSIONS

In summary, series of Zn–Cu and Mg–Li superatomic molecules with double tetrahedral structures are designed and their bond energies are discussed by density functional
theory (DFT) calculation. Depending on the SVB model, AdNDP analysis reveals that there are super nonbond in 8e−8e (Zn4Cu2)2/(Mg2Li2)2 single bond in 7e−7e (ZnCu2Cu2/MgLi2Li2)2 double bond (ZnCu2Cu2/MgLi2Li2)2 and triple bond in 6e−6e (ZnCu2Cu2/MgLi2Li2)2, which have the similar characters as the corresponding atomic chemical bonds. Moreover, bond energies are calculated as the key evidence to confirm the bonding characters of these SVBs. The results indicate that the bond energies increase and the bond lengths decrease along with the bond orders in Zn−Cu and Mg−Li systems which is in accordance with the classical nonbond, single bond, double bond, and triple bond in C−H systems. Finally, ELF analysis is carried on to give the direct description for the strength of the superatomic interaction to reveal the similarity between the superatomic bonds and the atomic bonds in simple molecules with different bond orders, which confirms the existence of the superatom–superatom bonding systems.

Our study gives the new evidence for the existence of the superatom–superatom bonding depending on bond energies, which would give reference for the further study and design of superatomic clusters.

4. COMPUTATIONAL DETAILS

Geometry optimizations and subsequent calculations are performed using DFT methods with PBE0/def2-tzvp level theory. AdNDP chemical bonding62−65 and ELF69−71 analysis is carried on for the optimized geometries to reveal the shape of their chemical bonds at the same level. All the calculations are carried out in the Gaussian 09 package,72 and the MO visualization is performed using Molekel 5.4.73

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