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From isosuperatoms to isosupermolecules: new concepts in cluster science†

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As an extension of the superatom concept, a new concept "isosuperatom" is proposed, reflecting the physical phenomenon that a superatom cluster can take multiple geometrical structures with their electronic structures topologically invariant. The icosahedral and cuboctahedral Au_{13}^{5+} units in the $Au_{25}(SCH_2CH_2Ph)_{18}^-$, $Au_{23}(SC_6H_{11})_{16}^-$ and $Au_{24}(SAdm)_{16}$ nanoclusters are found to be examples of this concept. Furthermore, two isosuperatoms can combine to form a supermolecule. For example, the structure of the $\{Ag_{32}(DPPE)_5(SC_6H_4CF_3)_{24}\}^{2-}$ nanocluster can be understood well in terms of a Ag_{22}^{12+} supermolecule formed by two Ag_{13}^{8+} isosuperatoms. On the next level of complexity, various combinations of isosuperatoms can lead to supermolecules with different geometrical structures but similar electronic structures, *i.e.*, "isosupermolecules". We take two synthesized nanoclusters $Au_{20}(PPhpy_2)_{10}Cl_4^{2+}$ and $Au_{30}S(StBu)_{18}$ to illustrate two Au_{20}^{6+} isosupermolecules. The proposed concepts of isosuperatom and isosupermolecule significantly enrich the superatom concept, give a new framework for understanding a wide range of nanoclusters, and open a new door for designing assembled materials.

Introduction

Understanding the stability and structure of clusters is an interesting and challenging task, important on both experimental and theoretical sides. The early studies can date back to the 1980s, including the tensor surface harmonic model (TSHM),[1] the polyhedral skeletal electron pair theory (PSEPT)[2,3] and the jellium model.[4,5] Electronic shell closure based on the jellium model has successfully explained the observed experimental abundances of alkali-metal clusters in the gas phase.[6,7] In the 1990s, the superatom concept was introduced into cluster science, referring to clusters whose electronic and chemical properties are approximate to that of an atom.[8] The stability of superatoms may be understood within some known models,[9] in most cases the jellium model. To explain the stability of ligand protected nanoclusters (LPNCs), Häkkinen extended the superatom concept to treat Au-SR nanoparticles by accounting for ligand interactions with the nanoparticle core.[10] The superatom concept achieved great success in understanding the magic numbers in metal clusters and LPNCs.[10–23]

The superatom model has been extended theoretically in various directions. As a way to assemble superatoms, the super valence bond (SVB) model[24] points out that two superatoms can compose a supermolecule by sharing a certain number of atoms in addition to electrons. The SVB model was proposed to explain the electronic stability of some metal clusters with non-spherical shells, and also has been successfully used to understand the structures of some ligand-protected Au clusters.[25,26] Another extension of the superatom model is superatomic hybridization.[24,27,28] Analogous to the hybridization of atomic orbitals, certain molecular orbitals derived from the metallic core could mix and transform into several hybridized superatomic orbitals, and connect to ligands in the hybridization directions.

In all the previous studies, one superatom always has a unique geometric structure, usually of a quite high symmetry. Actually, this is not necessary. As a cluster, a superatom may have multiple isomers in principle. Nevertheless, different isomers could still have electronic structures similar to each other and to an atom, *i.e.*, correspond to the same superatom. Here we name these different isomers as "isosuperatoms". The isosuperatom concept introduces a new degree of freedom and leads to more choices for building blocks of assembled materials. According to the SVB method, isosuperatoms can combine to form supermolecules. Furthermore, various combinations of isosuperatoms may result in supermolecules which have different geometric structures but similar electronic properties, *i.e.*, "isosupermolecules". These two concepts would mark a major advancement in the superatom model.

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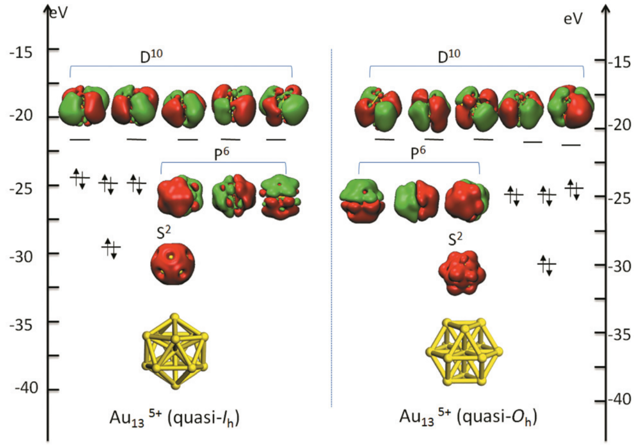

Fig. 1 Comparison of the Kohn–Sham MO diagrams between different Au_{13}^{5+} units. The quasi-I_h structure is obtained from ref. 12, and the quasi-O_h structure can be found in ref. 29 and 30.

Concepts

We will first illustrate the isosuperatom concept *via* the icosahedral (I_h) and cuboctahedral (O_h) Au_{13} units, both of which are widely found in LPNCs and attract intense interest. For example, $Au_{25}(SCH_2CH_2Ph)_{18}^-$ has a Au_{13} core with the quasi-I_h symmetry,[12] and quasi-O_h Au_{13} units are present in the $Au_{23}(SC_6H_{11})_{16}^-$ and $Au_{24}(SAdm)_{16}$ nanoclusters.[29,30] According to the electron count formula $n^* = N - M - z$ for $Au_N(SR)_M^z$, the Au_{13} units in these LPNCs have 8 valence electrons, and are identified as Au_{13}^{5+}.

Fig. 1 shows the canonical Kohn–Sham molecular orbital (MO) diagrams of the valence shells of the two Au_{13}^{5+} units.‡ Both the quasi-I_h and quasi-O_h Au_{13}^{5+} units have similar "superatomic orbitals", and their electronic configurations are both $|1S^2|1P^6|1D^0|$. Therefore, they are indeed isosuperatoms.

To give an alternative and vivid view on the chemical bonding of the clusters, we employ the adaptive natural density partitioning (AdNDP) method as a tool for analysis.[31,32] Based on the idea of electron pairs as the main elements of chemical bonding, AdNDP recovers both Lewis bonding elements (1c–2e and 2c–2e objects) and delocalized bonding elements (*n*c–2e).

Similar bonding patterns can also be seen in the AdNDP localized orbitals of the two Au_{13}^{5+} units (ESI, Fig. S1†), again confirming them to be isosuperatoms.

As the next step, isosuperatoms can be combined together to form a supermolecule. We take the ligand-protected silver cluster $[Ag_{32}(DPPE)_5(SC_6H_4CF_3)_{24}]^{2-}$ as an example, which was produced recently by Yang *et al.*[33] Based on the isosuperatom concept and the SVB model, we can give a new understanding on the structure rule of this nanocluster.

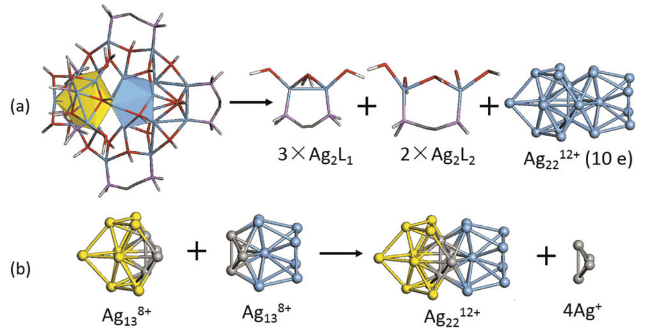

Fig. 2 (a) The $\{Ag_{32}(DPPE)_5(SC_6H_4CF_3)_{24}\}^{2-}$ compound, composed by three Ag_2L_1 units, two Ag_2L_2 oligomers, and a Ag_{22}^{12+} core. The phenyl groups are replaced by H atoms for simplicity and clarity. The Ag_2L_1 and Ag_2L_2 oligomers are shown as ball-and-stick models (Ag: blue; S: red; P: pink; C: grey; H: white). (b) Superatomic model of the Ag_{22}^{12+} core.

As Fig. 2b shows, the Ag_{22}^{12+} core of $\{Ag_{32}(DPPE)_5(SC_6H_4CF_3)_{24}\}^{2-}$ has 10 valence electrons, and is a supermolecule composed of two 13c–5e units (Ag_{13}^{8+}), sharing four nuclei. The two 13c–5e units are isosuperatoms (supernitrogen). They are both of the C_1 symmetry and have different structures.

According to the SVB model, Ag_{22}^{12+} is an analogue of N_2. To verify this point, Fig. 3 compares the MO diagrams of their valence shells. In the canonical MOs of N_2, the two s atomic orbitals (AOs) are split into two sets (σ_s and σ^*_s), the four p_x and p_y AOs are split into two doubly degenerate sets (π_{p_x,p_y} and $\pi^*_{p_x,p_y}$), and the p_z AOs are also split into two sets (σ_{p_z} and $\sigma^*_{p_z}$). The electronic configuration is $(\sigma_s)^2(\sigma^*_s)^2(\pi_{p_x,p_y})^4(\sigma_{p_z})^2$, where the $(\sigma_{p_z})^2$ MO consists of the N–N σ-bond and the HOMO–LUMO gap is (σ_{p_z})–$(\pi^*_{p_x,p_y})$. The canonical MO diagrams of Ag_{22}^{12+} are obviously analogous of those of N_2 in both MO shapes and orders.

In order to further illustrate how the two isosuperatoms form a supermolecule, Fig. S2† depicts a schematic representation of the MO/AO energy-level diagram for both the super-

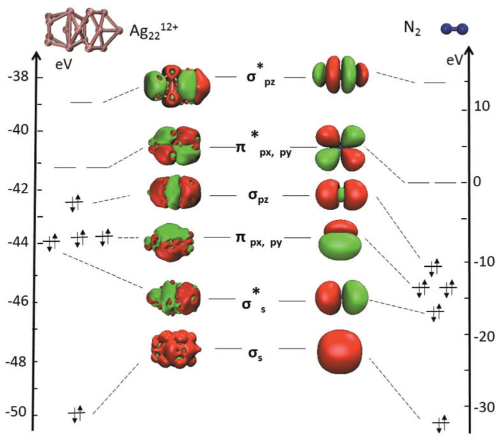

Fig. 3 Comparison of the Kohn–Sham MO diagrams between Ag_{22}^{12+} (left) and N_2 (right).

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‡ Computational details: the atomic coordinates of the crystallized clusters $Au_{25}(SCH_2CH_2Ph)_{18}^-$, $Au_{23}(SC_6H_{11})_{16}^-$, $Au_{24}(SAdm)_{16}$, $\{Ag_{32}(DPPE)_5(SC_6H_4CF_3)_{24}\}^{2-}$, $Au_{20}(PPhpy_2)_{10}Cl_4^{2+}$ and $Au_{30}S(StBu)_{18}$ are obtained from their single-crystal structure in ref. 12, 29, 30, 33, 34 and 35, respectively. Calculations are carried out using the Gaussian 09 package[47] at the B3LYP[47–51]/lanl2dz[52–54]/6-31G*[55,56] level. The Ag 4d and Au 5d orbitals are viewed as LPs with ON = 1.80–1.99|e|, which are excluded in analysis. Molecular orbital visualization is performed using VMD.[57]

atomic molecule (Ag_{22}^{12+}) and N_2, and there is indeed a one to one correspondence between them (ESI, Fig. S2†). AdNDP analysis reveals one 13c–2e super lone pair (LP) (super S) in each Ag_{13}^{8+} superatom, and one 22c–2e super σ-bond and two 22c–2e super π-bonds in the Ag_{22}^{12+} cluster (ESI, Fig. S3†). Such a bonding framework also shows that the Ag_{22}^{12+} cluster can be viewed as a supermolecule composed of two 13c–5e isosuperatoms sharing four nuclei.

Now we move onto the next level of conceptual complexity. As mentioned above, two isosuperatoms can form a supermolecule. Various combinations of the isosuperatoms will lead to different superatomic supermolecules, but in principle they could still have similar orbital patterns and electronic structures. If this happens, we will call them "isosupermolecules".

This kind of systems indeed exist. The Au_{20}^{6+} cores of the two nanoclusters $Au_{20}(PPhpy_2)_{10}Cl_4^{2+}$ and $Au_{30}S(StBu)_{18}$ [34,35] are found to be examples of this concept. The Au_{20}^{6+} core of $Au_{20}(PPhpy_2)_{10}Cl_4^{2+}$ has been identified as a supermolecule (super F_2)[25] composed of two identical superatoms of Au_{11}^{4+}. In the following section, we will show that the Au_{20}^{6+} core of $Au_{30}S(StBu)_{18}$ belongs to the same supermolecule, but is composed of two other different superatoms of Au_{11}^{4+}. Namely, the two cores in different clusters are isosupermolecules.

As Fig. 4 shows, both the Au_{20} cores are made up of two 11c–7e units by sharing two vertices. The two 11c–7e units (Au_{11}^{4+}) in Fig. 4b are identical and of quasi-C_{2v} symmetry, while the units in Fig. 4c are different and of C_1 symmetry.

We first make a comparison among the MOs of the valence shells of the two Au_{20}^{6+} cores and F_2 molecule, and the results are displayed in Fig. 5. The electronic configuration of the F_2 molecule is $(\sigma_s)^2(\sigma^*_s)^2(\sigma_{p_z})^2(\pi_{p_x,p_y})^4(\pi^*_{p_x,p_y})^4(\sigma^*_{p_z})^0$, and the electronic configuration of both Au_{20}^{6+} is $(\sigma_s)^2(\sigma^*_s)^2(\pi_{p_x})^2(\pi_{p_y})^2(\pi^*_{p_y})^2(\sigma_{p_z})^2(\pi^*_{p_x})^2(\delta_{d_{xy}})^0(\delta_{d_{x^2-y^2}})^0(\sigma^*_{p_z})^0$.

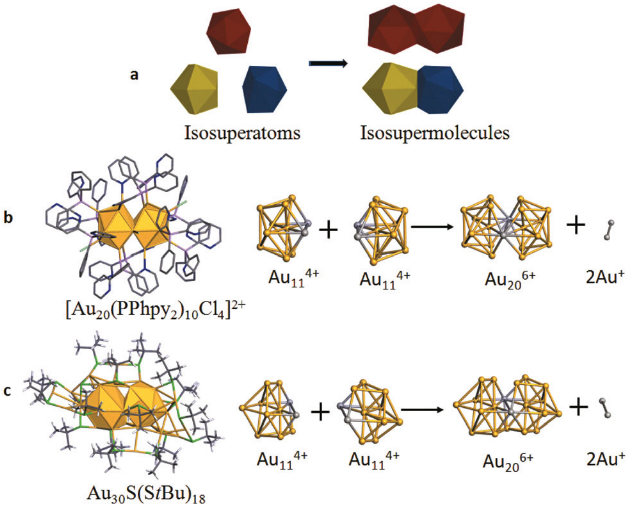

Fig. 4 (a) A schematic diagram of isosupermolecules formed by isosuperatoms; (b) superatomic model of the Au_{20}^{6+} core of $[Au_{20}(PPhpy_2)_{10}Cl_4]^{2+}$; (c) superatomic model of the Au_{20}^{6+} core of $Au_{30}S(StBu)_{18}$.

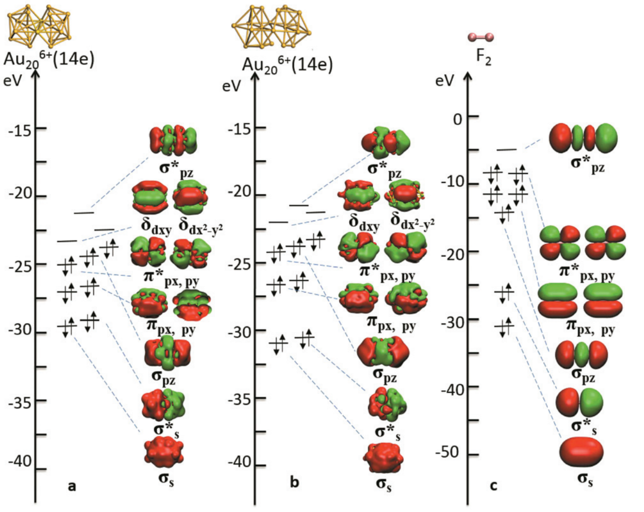

Fig. 5 Comparison of the Kohn–Sham MO diagrams between Au_{20}^{6+} cores and the F_2 molecule. Au_{20}^{6+} core of $[Au_{20}(PPhpy_2)_{10}Cl_4]^{2+}$ (a), Au_{20}^{6+} core of $Au_{30}S(StBu)_{18}$ (b) and F_2 (c).

Therefore, the two Au_{20}^{6+} cores are confirmed as isosupermolecules.

We also analyse the chemical bonding of the clusters by the AdNDP method (ESI, Fig. S4†). Each Au_{11}^{4+} superatom has three 11c–2e super lone pairs, and each Au_{20}^{6+} cluster has one 20c–2e super-σ-bond distributed in the whole cluster and three super LPs, which may be viewed as super S, P_x, and P_y, respectively.

All the systems studied above are isolated cores taken from LPNCs. Now we turn to the more realistic cases of cores embedded in LPNCs, *i.e.*, consider the ligand effects. We take

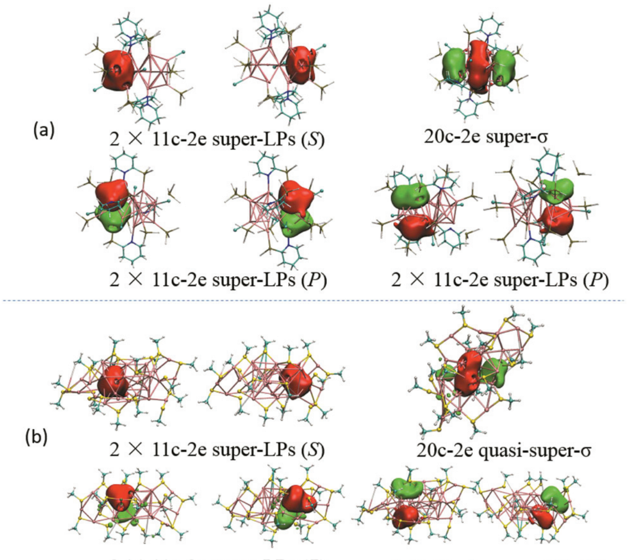

Fig. 6 AdNDP localized natural bonding orbitals of LPNCs. (a) $[Au_{20}(PPhpy_2)_{10}Cl_4]^{2+}$; (b) $Au_{30}S(StBu)_{18}$.

the above two clusters as examples, *i.e.*, $[Au_{20}(PPhpy_2)_{10}Cl_4]^{2+}$ and $Au_{30}S(StBu)_{18}$. With the ligand atoms, there are much more MOs in these systems, and in most MOs there are contributions both from the core atoms and from the ligand atoms, thus it becomes problematic to identify and analyze the orbitals of the core part. The AdNDP method is utilized to bypass this difficulty. Fig. 6 plots the bonding frameworks of the valence shells of both the LPNCs from AdNDP analyses. 14 electrons are delocalized in both the $Au_{20}{}^{6+}$ cores, including two s-type super-LPs, four p-type 11c–2e super-LPs, and one 20c–2e super-σ-bond. The localized orbitals of the two cores exhibit the same basic features, and are reminiscent of those for the cores without ligands shown in Fig. S4.† Therefore, the $Au_{20}{}^{6+}$ cores are still superatomic molecules under the influence of the ligands, and both the LPNCs share the same iso-supermolecule-core–shell growth mechanism. This is consistent with the traditional wisdom that the ligand effects usually do not change the superatomic molecular nature of the cores of LPNCs.[25,26]

Discussions

According to the above analyses and examples, it can be seen that the concepts of isosuperatom and isosupermolecule are natural and profound extensions of the superatom concept. These new concepts will be potentially very useful in areas such as LPNCs, metal/transition-metal clusters, magnetic clusters and cluster-assembled materials.

These concepts can shed light on not only the explanation of the structures of known compounds, but also the design and prediction of new compounds. For example, experimental and theoretical studies have revealed a variety of dimer and trimer structures of icosahedral $Au_{13}{}^{5+}$ *via* different bonding models (Fig. 7a).[36] Since the cuboctahedral $Au_{13}{}^{5+}$ unit is an isosuperatom of the icosahedral $Au_{13}{}^{5+}$ unit, we can propose a series of possible assemblies of the cuboctahedral $Au_{13}{}^{5+}$ units, as shown in Fig. 7b. Among these proposed structures, the structure with two cuboctahedral Au_{13} units sharing four atoms has been synthesized recently.[37]

The diversity of the symmetries of the building blocks is an important advantage with the new concepts. Traditionally, when we use the superatom concept, we usually focus on high symmetry clusters. This is a severe constraint to the problems to be investigated. After introducing these two concepts, many low symmetry clusters can be potentially treated based on the superatom idea. For example, the $Ag_{22}{}^{12+}$ and $Au_{20}{}^{6+}$ supermolecules shown in Fig. 2b and 4c are formed by isosuperatoms with the C_1 symmetry. Releasing the constraints of symmetry can provide many more choices for assembled materials. Similar observations were noted in the area of boron clusters, where most interest was concentrated on high symmetry structures like I_h B_{80}, until amorphous isomers were found to be more stable.[38–40]

In this work, the isosuperatoms or isosupermolecules are defined as having MO patterns similar to each other and to that of an atom or a molecule. They can be understood as cases of the isolobal principle.[41,42] Actually, they are somewhat stricter than normal usages of the isolobal principle, since they require a series of MOs similar to those of an atom or a molecule, while the usual examples of isolobality only involve the frontier orbitals.

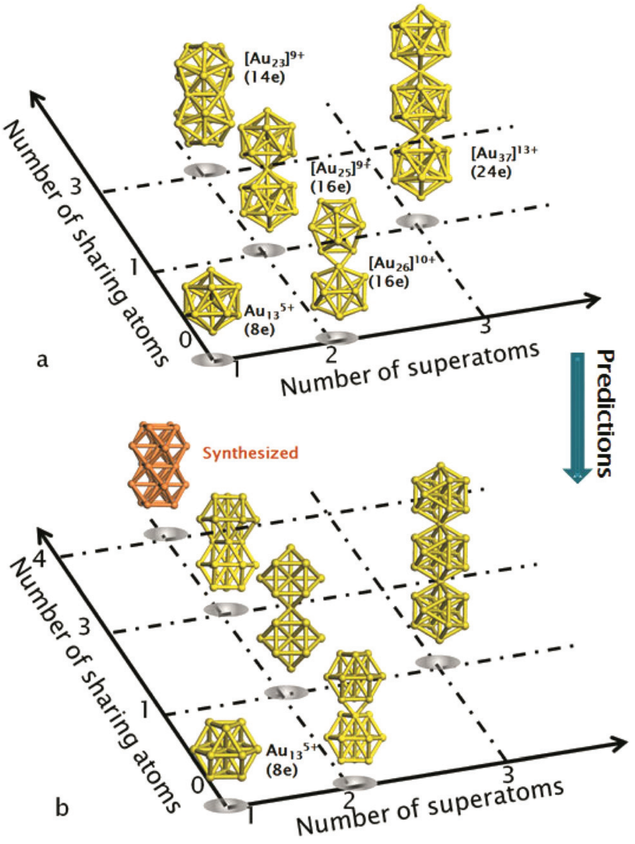

Fig. 7 (a) Dimer and trimer structures of icosahedral $Au_{13}{}^{5+}$ *via* different bonding models, for details see ref. 36. (b) Proposed structures of cuboctahedral $Au_{13}{}^{5+}$ isosuperatoms. The dimer formed by two superatoms sharing four atoms has been synthesized as shown in ref. 37.

In this work, the similarity of orbitals has been established by the naked eye. It would be interesting and beneficial to have a rigorous method to measure the "electronic similarity" of supermolecules. Here we propose such a mathematical method.

The key feature of the MOs of the isosuperatoms is that their angular distributions are similar to those of the AOs, *i.e.*, spherical harmonics. Therefore, if we construct a set of pseudo-AOs whose radial parts are tunable (characterized by a radius r_0), then at some suitable r_0, the overlap integral between a pseudo-AO and an isosuperatomic orbital should be rather significant, and the overlap integral between the pseudo-AO and any other mismatched isosuperatomic orbital should be rather small.

Herein, let us take the two isomers of $Au_{13}{}^{5+}$ in Fig. 1 as an example. We define the pseudo-AOs as hydrogen-like orbitals. Namely, the pseudo-s orbital is

$$\psi_S = \sqrt{\frac{1}{\pi r_0{}^3}} e^{-r/r_0},$$

Table 1 The overlap integrals between the pseudo-AOs and the isosuperatomic MOs and the r_0's of the pseudo-AOs

	φ_a (S)	φ_b (S)	φ_a (P_x)	φ_b (P_x)	φ_a (P_y)	φ_b (P_y)	φ_a (P_z)	φ_b (P_z)
ψ_S (r_0 = 4.0)	**0.51**	**0.40**	0.02	0.01	0.01	0.00	0.00	0.02
ψ_{P_x} (r_0 = 1.2)	0.00	0.01	**0.50**	**0.51**	0.13	0.06	0.08	0.08
ψ_{P_y} (r_0 = 1.2)	0.00	0.00	0.05	0.05	**0.49**	**0.61**	0.15	0.07
ψ_{P_z} (r_0 = 1.2)	0.01	0.02	0.04	0.07	0.07	0.04	**0.49**	**0.47**

and the pseudo-p orbitals are:

$$\psi_{P_x} = R_{21}(r) \times \sqrt{\frac{3}{4\pi}}\frac{x}{r};$$

$$\psi_{P_y} = R_{21}(r) \times \sqrt{\frac{3}{4\pi}}\frac{y}{r};$$

$$\psi_{P_z} = R_{21}(r) \times \sqrt{\frac{3}{4\pi}}\frac{z}{r};$$

where $R_{21}(r) = \left(\frac{1}{2r_0}\right)^{3/2}\frac{r}{\sqrt{3}r_0}\mathrm{e}^{-r/2r_0}$, $r = (x^2 + y^2 + z^2)^{1/2}$. These formulae are in the atomic units, so the unit of r_0 is Bohr, *i.e.*, 0.529 Å. We denote the wave functions of the quasi-I_h and quasi-O_h isomers as φ_a and φ_b, respectively. The overlap integrals are denoted as $C = \left|\int \psi(\vec{r})\varphi(\vec{r})\mathrm{d}\tau\right|$. The r_0 of a pseudo-AO is determined by the criterion that its overlap with the two corresponding isosuperatomic MOs takes maxima. The results of C and r_0 are shown in Table 1.

The overlaps between a pseudo-AO and its MO counterparts are typically around 0.5, while the other mismatched overlaps are close to zero. Therefore, this set of indices indeed work. Based on these computational results, we may propose some overlap threshold for two isomers being isosuperatoms, *e.g.*, 0.3.

Another measure which can be naturally proposed is the overlap integral between the corresponding MOs of two isosuperatoms. However, some of these overlaps are quite small. For example, the overlap between the S MOs of the quasi-I_h and quasi-O_h Au_{13}^{5+} is 0.07. This is because the radial parts of the two MOs are quite different, although their angular parts are both similar to those of AOs. In this sense, what matters is not to what extent the isosuperatoms are similar to each other, but to what extent they are both similar to the atom. Therefore, we turn to calculate the overlaps between the MOs and the pseudo-AOs, and get the above successful results.

When two (iso)superatom clusters combine in terms of the SVB model, a new cluster with a non-spherical shape is made. A traditional method to explain the stability of non-spherical clusters is the ellipsoidal shell model proposed by Clemenger.[43] By tuning the parameter δ to fit the energy levels of the clusters, the ellipsoidal shell model can work in many cases. On the other hand, the SVB model does provide more physical insight and can give better predictions without parameter fitting. Besides, based on localized interactions between (iso) superatoms, the SVB model can be easily extended to nanoclusters/crystals assembled from more than two clusters (*e.g.*, the tri-icosahedral ligand protected Au_{37},[44] ligand protected Au_{60}[45] nanoclusters and thiolated gold nanowires[46]), which is beyond the scope of the ellipsoidal shell model. Therefore, the isosuperatom/isosupermolecule concepts are general concepts, and not a rival to the ellipsoidal shell model.

Table 2 Comparison between atoms, superatoms, and isosuperatoms

	Atom	Superatom	Isosuperatom
Theoretical basis	Atomic physics	Jellium model	Jellium model Isolobal principle
Number	Single	Single	Multiple
Electron configuration	$1s^2 2s^2 2p^6$…	$\lvert 1S^2 \rvert 1P^6 \rvert 1D^{10} \rvert$…	$\lvert 1S^2 \rvert 1P^6 \rvert 1D^{10} \rvert$…
Symmetry	Spherical	High	Unlimited

Finally, in order to make the conceptual novelty clearer, a comparison between atoms, superatoms, and isosuperatoms is shown in Table 2.

Conclusions

Based on the physical phenomenon that a superatom cluster can take multiple structures with their electronic structures topologically constant, we propose two new concepts: "isosuperatom" and "isosupermolecule". Isosuperatoms can be used as building blocks to form supermolecules or even isosupermolecules. This proposal enriches the superatom concept, and opens a new door for building blocks of assembled materials. These concepts have the potential to be used to understand various kinds of nanoclusters, and guide the syntheses of new nanoclusters. By introducing these two concepts, we significantly expand the scope of phenomena in cluster science reachable by the superatom idea.

Acknowledgements

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