The Electromagnetic Field Response of the Superatomic Cluster Doped with Transition Metal Atoms

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Previous research has highlighted that the majority of superatomic clusters are characterized by high symmetry point groups, such as I_h. However, in our current investigation, we have identified a superatomic cluster that possesses a stable geometric structure exhibiting relatively low symmetry. Utilizing the BPGA method, we conducted global optimization on isoelectric species of the Au-Pt nanoalloy. This process led to the discovery of two structures, Au_{13}^{5+} and $Au_9Pt_4^+$, each showcasing unique superatomic electronic properties. Spon-Orbit Coupling(SOC) effects are introduced within PBE0/sdd level, stem from SOC pseudopotential in sdd basis set, energy level splitting is discovered, showing the symmetry breaking in spin-orbit coupling. We calculated the modulus and phase of complex wave functions separately. Analogous to the equipotential surfaces of real wave functions, we plotted the isosurfaces of the modulus and used different colors on these isosurfaces to represent various phases.

To enhance the system's magnetic moment, we introduced transition metals into the structure. Calculations performed at the PBE0/sdd basis set level yielded the most stable distribution of electron spin. We discovered that doping V into the highly degenerate Au_{13}^{5+} increases its spin magnetic moment to 5μB. Subsequently, we assessed the nonlinear electric field response properties and induced current distribution, employing the SOS method and magnetic shielding tensor calculations via the GIAO method, respectively. A significant finding was the pronounced two-order electronic field response near the apex of the pyramidal-shaped $V@Au_9Pt_4^+$. This phenomenon is likely a consequence of the dense distribution of induced electrons around the cluster's tip.

Moreover, these transition metal-doped clusters exhibited strong aromaticity, compared with benzene and their corresponding undoped counterparts at the same level of theoretical analysis. Current integration through a designated plane revealed a considerable net induced current in $Au_9Pt_4^+$, which we attribute to the existence of disconnected paramagnetic regions. Further exploration revealed an antiaromaticity to aromaticity transition between $Au_9Pt_4^+$ and $V@Au_9Pt_4^+$. This transition is a result of highly delocalized electron orbitals within the pyramid's central region, underscoring the intricate relationship between structure and electronic properties in these superatomic clusters. The doping of V into the pyramid structure results in the center being filled with high-intensity diatropic currents. This connects the previously separated current

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loops in the Au_9Pt_4 cluster, bridging a huge connected diatropic current region. Additionally, the formation of current loops is illustrated, further elucidating the underlying reasons for this phenomenon.

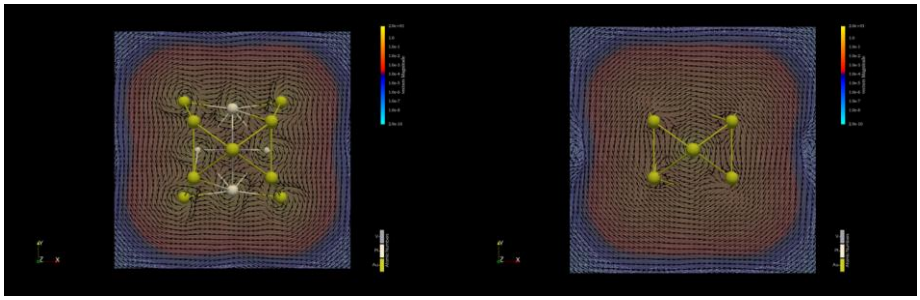

Figure 1. The induced current of $Au_9Pt_4^+$ under external magnetic field in *z*-axis.

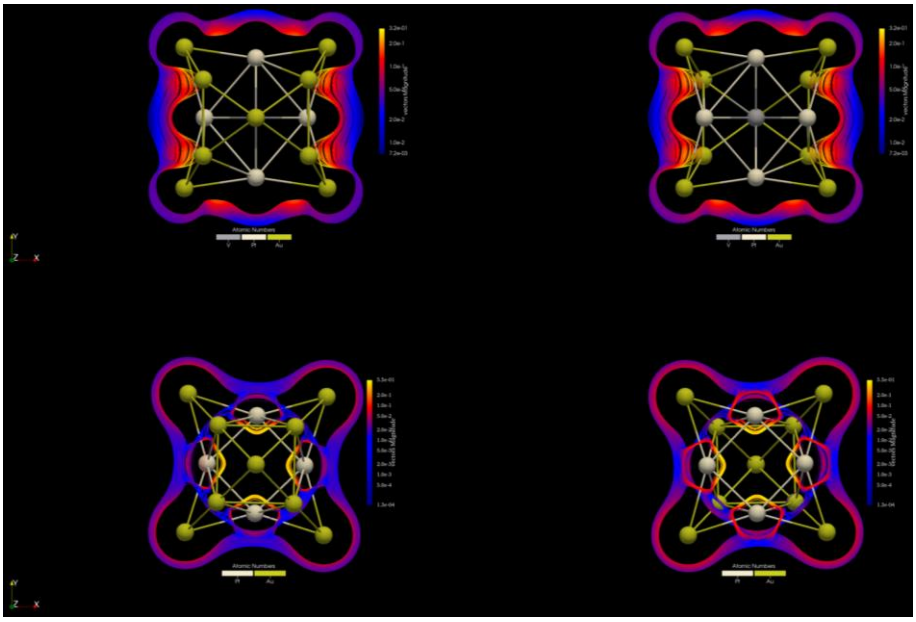

Figure 2. Induced current loop in x-y plane. The upper row is $V@Au_9Pt_4^+$, and the lower row is $Au_9Pt_4^+$, with each row' left and right columns representing view along z-axis and -z-axis, respectively.

Keywords： superatom; non-linear response; NMR; nanoalloy; genetic algorithm

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BIOGRAPHY

Guangyi Liang completed his bachelor degree in 2021 from SUN YET-SEN University and now is a PhD student in a joint program between USTC and CityU. His main research direction is nano cluster.