Ligand-protected gold nanoparticles (AuNPs) have attracted scientific interest ever since Michael Faraday synthesized and studied optical properties of gold colloids. The systems are widely used in sensing applications and represent examples in which electronic properties can be tuned by size and shape. For a long time, a detailed atomistic understanding of thiolate-protected AuNPs was missing due to experimental difficulties in synthesizing monodispersed AuNPs with high purity. However, following the complete determination of Au\textsubscript{102}(RS)\textsubscript{44} in 2007, a range of structures have been reported. A common motif in these geometries is a metal core protected by (RS)\textsubscript{m}Au\textsubscript{n} units. Interestingly, this is the same motif as for self-assembled monolayers of thiolates on Au (111), which have (RS)\textsubscript{2}Au\textsubscript{4} as protecting units.

In a recent communication, Gao and co-workers suggest a scheme to rationalize the structures of ligand-protected AuNP. The authors adopt the language of nuclear physics and postulate two types of elementary building blocks (particles), namely Au\textsuperscript{3} and Au\textsuperscript{4}. The trimer (equilateral triangle) and tetramer (tetrahedron) are both two-electron closed-shell systems and are in ref. associated with protons and tetraquarks, respectively.

Despite the fact that known ligand-protected AuNP can be decomposed according to the flexible scheme in ref. it is suggested that the stability of the metal core in ligand-protected AuNP should be related to the closed-shell character and stability of Au\textsuperscript{3} and Au\textsuperscript{4}. However, highly charged metal clusters are generally unstable with respect to fragmentation. This holds, e.g., for the low energy Au\textsuperscript{3} isomer discussed in ref. which is unstable with respect to fragmentation into two Au\textsuperscript{+} units by 1.4 eV. Moreover, Au\textsuperscript{2+} is unstable with respect to fragmentation into two Au\textsuperscript{+} units by 0.2 eV. The stability of ligand-protected AuNP is consequently difficult to rationalize using Au\textsuperscript{+} and Au\textsuperscript{2+} as building blocks and without considering the bonds to the ligands.

The underlying reason why some sizes of ligand-protected AuNP are possible to crystallize and structurally characterize, while other sizes are difficult to characterize in this way is not yet known. The crystallization is often sensitive to the experimental conditions, which stresses kinetic effects. The facile formation and enhanced stability of some sizes is presumably a balance between electronic and structural factors. Closed electronic shells result in enhanced stability but do not appear to be an absolute condition. Common for all ligand-protected AuNPs are, however, delocalized valence electrons that are confined by the potential generated by the metal cores of the particles. Models that aim to link stability with structure should preferably account for this fundamental property.

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**Fig. 1** Structural models and selected Kohn-Sham orbitals. 

a) Structural model of Au$_{315}(RS)_8$ with R being CH$_3$.  

b) The 1S orbital of Au$_{315}(RS)_8$. The protecting complexes are for clarity shown as lines.  

c) The structure and 1S orbital of Au$_{31}^+$.  

d) The structure and 1S orbital of Au$_{31}^{2+}$. Atomic color code: Au (orange), S (yellow), C (gray) and H (white).

**Methods**

Density functional theory is used in an implementation with local basis functions and the gradient corrected exchange-correlation functional according to Perdew, Burke, and Ernzerhof (PBE). The Kohn–Sham orbitals are expanded with atomic numerical basis functions that are stored on radial grids centered at the atoms. A double numerical basis set with polarization functions (dnp) is used for all atoms with a real-space cutoff of 5.0 Å. A semi-core pseudo potential with relativistic corrections is employed for Au to describe the interaction between the valence electrons (19 electrons) and the nuclei together with the inner-shell electrons. A double numerical basis set with polarization functions (dnp) is used for all atoms with a real-space cutoff of 5.0 Å. A semi-core pseudo potential with relativistic corrections is employed for Au to describe the interaction between the valence electrons (19 electrons) and the nuclei together with the inner-shell electrons.

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H.G. performed the research and wrote the paper.

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