Theoretical Study of the Stability of $\text{Au}_n\text{Ge}_m$ Clusters

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Abstract. We investigate the properties of clusters formed from two connected $\text{Ge}_m$ cage-like clusters, such as experimentally synthesized $\text{Au}_3\text{Ge}_{18}^5$, using first-principles DFT methods. We focus particularly on $\text{Au}_n\text{Ge}_{12}^q$ formed from $\text{Ge}_6$, where $n = 0 - 3$ and $q = 0.2$. We examine the geometries, electronic structure, and thermal excitations of these clusters using the SIESTA code, where we test stability using short molecular dynamics simulations. Our examination of intercluster bridges between $\text{Ge}_m$, formed of either Ge-Ge or Au-Ge bonds, indicates that the overlap of interacting molecular orbitals of Ge$_m$ can either bind a cluster together or tear it apart depending on the orientation of the bridging atoms with respect to the cages. We characterize the properties of stable isomers of neutrally charged AuGe$_{12}$ and Au$_2$Ge$_{12}$, seeing that radially directed molecular orbitals stabilize AuGe$_{12}$ while a geometric asymmetry stabilizes Au$_2$Ge$_{12}$ and Au$_3$Ge$_{18}$. We examine a two-dimensional $\text{Au}_{2n}\text{Ge}_{2n}$ structure, finding it more stable than other periodic $\text{Au}_{n}\text{Ge}_{n}$ subunits. We observe no stable neutral isomers of Au$_3$Ge$_{12}$, but see that additional charge supports isomers of both Au$_2$Ge$_{12}$ and Au$_3$Ge$_{12}$.

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1 Introduction

Gold-Germanium alloys are important and interesting both from the perspective of basic science and technological application. The binary, eutectic Au-Ge system [1] displays bulk diffusion, phase separation, and subsequent crystallization of well separated Au and Ge [2,3]. Large spacing ions can stabilize crystalline solids such as ScAuGe and SrAu$_3$Ge which contain hexagonal planes of Au-Ge structure [4] and octahedra of Au$_3$Ge$_5$, respectively. Studies of Au atoms on Ge surfaces reveal a Luttinger-liquid like state [5] and Au is often used in catalyzing reactions in Ge. In nanoscale applications, the eutectic and catalytic behavior is less predictable, yet phase separation still drives interesting pattern formation such as Au-catalyzed Ge-nanowires [6,7,8,9,10,11]. Experimentalists and theorists alike have made significant progress in understanding the overall nanowire growth process, through the use of in-situ video rate TEM [12] and semi-empirical models [13,14]. Yet an atomic-scale description of Au-Ge bonds is essential for a broader physical understanding of these kinetic processes.

Compelling clusters of Au-Ge include AuGe$_{18}$ [15], Au$_3$Ge$_{18}^5$ [16], and Au$_5$Ge$_{25}^{18}$ [17] which are formed from linked Ge$_3^-$ clusters and stabilized with counterions. The building blocks Ge$_3^-$ are found experimentally as [Ge$_9$]$^{4-}$ Zintl ion clusters and within many Zintl solids including Cs$_4$Ge$_9$ [18]. Such Ge Zintl ions are stabilized by delocalized electrons, follow Wade’s Rules [19,20], and reveal bonding environments beyond the sp$^3$ bonds of bulk Ge structures [21]. Importantly, these Ge$_3^-$ clusters provide a method of synthesizing crystalline and micro-crystalline Ge solids [22,23,24] such as the synthesis of expanded phase Ge$_{136}$ by the oxidation of the Ge$_9^-$ Zintl anion by an ionic liquid [25].

While Ge$_3^-$ Zintl cages are widely studied, six-atom Ge clusters could provide an alternate pathway to growing Ge based materials. In this paper, we ask the following: Can Au link together other small Ge clusters? What does this teach us about Au-Ge bond lengths and angles? How does this depend on the electronic properties of the Ge cluster? Using density functional theory, our work examines cluster ions Ge$_3^-$ and Au$_5$Ge$_{18}^{18}$, which have been previously studied in experiment, and a theoretical series of Au$_n$Ge$_{3n}^{3n}$ clusters, where $n = 0 - 3$, that have a range of stability and electronic behavior which may indicate how stable Au-Ge bonds form.

We use the octahedral shaped Ge$_3^-$ as a model cluster, in part because its $O_h$ symmetry yields a significantly reduced set of possible Au-Ge bond angles to explore. Furthermore the $O_h$ symmetry follows Wade’s rules, which connect the overall shape of a cluster with $n$ vertices to its number of skeletal electron pairs, therefore a deformation away from octahedrality indicates whether excess charges have localized in the intercluster bridging struc-
ture or the Ge cage region of \( \text{Au}_6\text{Ge}_{12} \) clusters. Such Ge\( _6 \) cages have been experimentally synthesized in gas phase \([20]\) and solids \([27,28]\). Richards \textit{et al.} isolated the octahedral Ge\( _6 \) cluster, stabilized by organic groups, with reductive coupling \([29]\). Ge\( _6 \) cages have been studied computationally \([30-31]\) with a focus on the effects of ionic charge on cluster geometry; neutral Ge\( _6 \) flattens to a \( C_2v \) symmetry while ionic Ge\( _6^{2-} \) has octahedral \( O_h \) symmetry. The neutral Ge\( _6 \) geometry was also observed by Zhao \textit{et al.} in a computational study which focused primarily on fragmentation behavior in Ge\( _n \) clusters, and indicates Ge\( _6 \) as a common fragment of larger clusters \([32]\).

Au-Ge bonds lack a simple descriptive model that can simultaneously treat both the electron delocalization typical of metals and the localized bonds typical of semiconductors. Thus their treatment requires a first principals, or \textit{ab initio}, approach, that uses flexible basis sets to capture a variety of bond hybridizations. While \textit{ab initio} calculations are computationally expensive, alternative models that parameterize metal-semiconductor bonding with empirical potentials have not provided accurate descriptions of bond-angles in small clusters \([13,14]\). Thus we use first principles density functional theory (DFT) implemented with the SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) code \([33,34]\).

Previous Ge and Au-Ge cluster studies have focused on the configurational entropy of \( N \) atoms \([35,37,38,39]\), which is the essential concern of many DFT cluster studies. Such studies \([10,11]\) confirm that small gas phase Au-Ge clusters are amorphous, as observed experimentally \([42]\). Recent studies have focused on endohedral Ge clusters encapsulating a metal ion \([13,43]\). These previous studies examine electronic structure, vibrational frequencies, and cluster fragmentation properties, but molecular dynamics (MD) simulations at the DFT level are rare due to their computational expense.

In Sec. 2 we describe our computational methods in modeling neutral and charged clusters. Our general technique initializes the atomic positions in SIESTA with a hand-picked geometry and applies the Conjugate Gradient algorithm (CG) to relax the positions to a local minima. We focus on clusters similar to \( \text{Au}_3\text{Ge}_{18} \) which feature two well-separated Ge clusters connected with \( n = 0 \rightarrow 3 \) Au atoms. This requires an alternative to advanced sampling techniques such as metadynamics \([45]\) or a Genetic Algorithm \([39]\), which tend to calculate compact structures in their search for global energy minima. We consider the gas-phase (isolated) clusters with DFT, MD, and electronic structure studies, but acknowledge the necessity of counterions in experiment. As we predict new possible Au-Ge structures, these theoretical geometries may appear metastable, yet contain Au-Ge bonds that could be observed with ligand stabilization. We search for stabilizing trends in symmetric Au-Ge clusters, examining both internal bonds, which define an individual Ge\( _6 \) cage geometry, and external bonds, which describe how Ge\( _6 \) cages link to each other or with a bridge of Au atoms.

Our results, presented in Sec. 3, describe ground state cluster properties (geometry and electronic structure) and examine cluster stability with molecular dynamics at temperatures near the bulk eutectic temperature \( T_E = 361^\circ \text{C} \), where presumably small, unstable molecules will “melt” completely. The geometry analysis uses Wade’s Rules, examining the deviation of the cluster from perfect symmetry and its overall electron count, and reports typical bondlengths and angles. Our analysis of electronic states includes Molecular Orbitals (MO), Density of States (DOS), and an electronic partitioning method, Crystal Overlap Hamiltonian Population (COHP) \([46]\). In Sec. 3.1 we describe the electronic structure of Ge\( _n \), where \( m = 6, 9, 12 \), while comparing their geometries to both previous calculations and experimental measurements. We compare these to hypothetical Ge\( _{12} \) clusters composed of two Ge\( _6 \) cages in Sec. 3.2. After characterizing pure Ge clusters, in Sec. 3.3 we introduce Au-Ge clusters by describing calculated properties of the experimentally observed \( \text{Au}_3\text{Ge}_{18} \). In Sec. 3.4 we investigate ground-state properties of clusters with stoichiometry \( \text{Au}_n\text{Ge}_{12} \) composed of different configurations of two Ge\( _6 \) cages with \( n = 1 \rightarrow 3 \). In Sec. 3.5 we explore the stability of these configurations under molecular-dynamics simulations. We describe the effects of electronic charge on cluster properties in Sec. 3.6. Next we compare the electronic structures and stabilities of all clusters using the COHP in Sec. 3.7 to examine what constitutes a chemical bond. Finally in Sec. 3.8 we propose a new extended two-dimensional (2D) structure built upon Ge\( _6 \) cages. Our work uniquely examines the COHP properties of certain experimentally observed clusters, and extends the observations to examine the properties defining stability in Au-linked Ge clusters. We discuss our conclusions on electronic and geometric properties which lend overall stability to such clusters in Sec. 4.

## 2 Methods

We have carried out electronic structure calculations with the fully \textit{ab initio} DFT code SIESTA \([33,34]\) which uses Troullier-Martins norm-conserving pseudopotentials \([47]\) in the Kleinman-Bylander form \([48]\). The Kohn-Sham wave function was expanded with basis sets of the localized atomic orbitals (LCAO) of the method by Sankey and Niklewski \([50]\). The localization is a key advantage in studying charged states in molecular or nanosized systems. We use Double-Zeta Polarized (DZP) orbitals and the Generalized Gradient Approximation (GGA) of Perdew, Burke, and Ernzerhof \([51]\) for the exchange-correlation energy functional.

Our Ge basis set has cutoff radii for the 4s orbital of 7.12, 1.92 Bohr; 4p of 7.72, 4.92 Bohr; and a polarization orbital 4d with a cutoff of 7.79 Bohr \([52]\). The Au basis set has cutoff radii of 5d: 7.20, 5.57 Bohr; 6s: 6.50, 5.50 Bohr; and a polarization orbital 6p: 5.85 Bohr. We use soft-confinement potentials and an ionic core to create orbitals \([53]\). The Au pseudopotential includes the semicore 5d\(^{10}\) states \([54,55,56]\). Both Au and Ge use a partial-core correction to treat overlap between valence and core electrons.
The charge density was represented on a real-space grid with an energy cutoff of 100 Ry. A Monkhorst-Pack \textit{k}-point mesh of 10x10x10 ensured convergence. We used a Conjugate Gradient (CG) minimization with a maximum force tolerance of 0.04 eV/Å to reveal the local coordinate relaxations. For our molecular dynamics (MD) runs, we use the Nosé thermostat \textsuperscript{[57]} to simulate the canonical ensemble (NVT) with a Nosé mass of 200 Ry fs\textsuperscript{2}. We test the stability of our systems by subjecting them to a temperature of 600K during 1000 steps, each of 2 fs, as suggested by Ref. \textsuperscript{[55]}.

The COHP uses DFT matrix elements to separate electronic bonding states from antibonding states in the DOS. In both the DOS and COHP curves we use a small smearing value, \(s \approx 0.1\), and a high number of sampling points, \(n \approx 500\), to create smooth electronic structure curves. We treat neighbor interactions within 0.4 Å of the maximum considered “bond” lengths \textsuperscript{[58]}. In examining the electronic states, we focus on the hybridization of the levels presented as indicators of electron delocalization.

3 Results

3.1 Calibration of SIESTA with Ge Clusters

Ge is an example of a main-group element that participates in delocalized cage bonding. It can be analyzed in terms of Wade’s rules \textsuperscript{[19,20]}, which connect the shape of a cluster with \(n\) vertices to its number of skeletal electron pairs. The clusters \([\text{Ge}_6]\) and \([\text{Ge}_6]^2-\) have analogous shapes to BH\(_6\) and [BH\(_6\)]\(^2-\) clusters; where [Ge\(_6\)]\(^2-\) will form an octahedron (or \textit{closo} 6-vertex polyhedron). Similarly [Ge\(_6\)]\(^2-\) forms a \textit{closo} 9-vertex polyhedron, while Ge\(_{12}\) does not follow Wade’s Rules \textsuperscript{[59]}.

Using CG minimization in SIESTA, we initialize the geometries of \([\text{Ge}_6]\) and \([\text{Ge}_6]^2-\) clusters as octahedra with atomic coordinates \((\pm a, 0, 0), (0, \pm a, 0), (0, 0, \pm a)\) using \(a \approx 2.12\) Å, or initial Ge-Ge separations of 3.0 Å. In the relaxed clusters we find the same geometries as King \textit{et al.} \textsuperscript{[31]} where \([\text{Ge}_6]\) flattens to \(C_{2v}\) symmetry and ionic \([\text{Ge}_6]^2-\) has the expected octahedral \(O_h\) symmetry. Calculating a minimum and maximum relaxed Ge-Ge distance in \([\text{Ge}_6]\), we find respectively 2.53 Å and 2.85 Å, compared with previous calculations of 2.58 Å and 2.81 Å \textsuperscript{[31]} and 2.47 Å and 2.85 Å \textsuperscript{[29]}. Our calculated bond length, 2.68 Å, for octahedral [Ge\(_6\)]\(^2-\) compares favorably with that of 2.69 Å from Ref. \textsuperscript{[31]}, and has been measured to be 2.63 Å \textsuperscript{[29]} in a ligand stabilized system.

We characterize cluster symmetry using the deviation, \(\sigma_{dc}\), of the cluster from a perfect octahedron by averaging over the twelve skeletal Ge-Ge distances of a single cluster: \(d_G \pm \sigma_{dc}\). A perfect octahedral cluster is composed of twelve identical bonds with \(\sigma_{dc} = 0.0\) Å. Some deformation from \(O_h\) symmetry may occur while \(\sigma_{dc}\) remains zero; for instance we observe Ge\(_6\)\(^2-\) has nearly identical bondlengths such that \(\sigma_{dc} = 0.0\) Å yet it is slightly flattened. The neutral \([\text{Ge}_6]\) cluster with \(C_{2v}\) symmetry yields \(d_G = 2.68 \pm 0.20\) Å. In calculating \(\sigma_{dc}\) for our larger

![Fig. 1. Calculated densities of states (DOS) versus energy (eV) for (a) Ge\(_6\) and (b) [Ge\(_6\)]\(^2-\) where the total DOS is black, the 4s orbital is blue, 4p is green, and 4d is red. Contributions from other orbitals have not been treated.](image-url)
We briefly describe Ge$_9$ and Ge$_{12}$ to complete our calibration of the SIESTA code. We initialize the CG relaxation using previously reported geometries. Much like our detailed description of Ge$_6$, we observe very similar clusters to those previously calculated in Refs. [32, 59, 60, 61] both in geometry and electronic structure. Consistent with Wade’s rules, we observe the symmetry of Ge$_9$ increases to $D_{3h}$ with $q = 2$ and $C_{4h}$ with $q = 4$ as in Ref. [59]. As in Ref. [59], the low energy isomer of the Ge$_{12}$ cluster deviates from Wade’s Rules and resembles a tetracapped cube with $C_{2v}$ symmetry [Fig. 3(a)]. We see a qualitative agreement in the MOs, with the same symmetries and approximate energies levels as previously reported.

We conclude by calculating binding energies, $E_B$, and Fermi gaps, $E_{gap}$ (Table 1) of Ge$_m$ clusters. $E_B$ is calculated as:

$$E_B = \frac{E_T - (N_A E_A + N_G E_G)}{N_A + N_G}$$

where $N_A$ and $N_G$ are the total number of Au and Ge atoms, and $E_T$, $E_A$, and $E_G$ are the SIESTA calculated total energies for the cluster and isolated atoms, respectively. Our calculation shows systematically higher $E_B$ than previously reported for pure Ge clusters. The systematic difference in $E_B$ is consistent with cohesive energies calculated with SIESTA in Ref. [61] for bulk Si and elsewhere. While our values of $E_{gap}$ differ, given slight deformations in the geometries, and the known underestimates of $E_{gap}$ within GGA calculations, we consider our values reasonable comparisons to previous calculations.

### 3.2 Ge$_{12}$ Clusters: Relaxed Geometries and DOS

Next we examine isomers of Ge$_{12}$ formed by joining two Ge$_6$ together with one or two intercluster bonds. While these will not result in groundstate Ge$_{12}$ clusters, they provide a comparison to Au$_n$Ge$_{12}$ clusters examined in Sec. 3.1. We initialize each Ge$_6$ cluster as an octahedra, again with initial Ge-Ge separation of 3.0Å, and change their relative orientation. Here we present the initial configurations of three such Ge$_{n}$Ge$_m$ clusters and their CG-relaxed geometries. We describe three configurations in terms of two local Cartesian coordinate systems $(x, y, z)$ and $(x’, y’, z’)$ for each cluster. We present our clusters in order of highest to lowest binding energy (following CG relaxation), starting from $I_n$, where $n$ denotes the number of Au atoms. We will compare these clusters with the $C_{2v}$ symmetry Ge$_{12}$ cluster described in Sec. 3.1. We label the ground state as $Z_0$ since it is outside our schema of coupled Ge$_6$ clusters.

In configuration $I_0$, the axes $(x, y, z)$ and $(x’, y’, z’)$ differ by a linear translation so that all axes point respectively in the same directions and the atoms in the two equatorial planes $xy$ and $x’y’$ form two intercluster Ge-Ge links pointing locally along directions $\hat{x} + \hat{y}$ and $-\hat{x} - \hat{y}$. In configuration $I_0$, the two sets of axes again point in the same directions and a single intercluster link forms in the local directions $\hat{x}$ and $-\hat{x}$. In configuration $I_{10}$, the two octahedra are aligned so that two triangular faces of opposing octahedra are in parallel planes and three intercluster links form a prism.

We summarize our results for the CG-relaxed clusters Ge$_{12}$ in Table 2 and Fig. 3. The values of $E_B$ of all isomers are close to that of the ground state. $I_0$ and $I_{10}$ are nearly degenerate despite their different geometries. In Fig. 3 we show the CG-relaxed and MD “temperature shaken” geometries of each isomer, reserving description of the post-MD structures until Sec. 3.5, and proceed to describe the CG-relaxed configurations. The $Z_0$ tetracapped cube has a relatively compact structure including a short Ge-Ge bond of 1.90Å, and no octahedral structure (and thus we cannot measure $d_G = \sigma_{d_G}$ or $d_i$ in Table 2). The $I_0$ clusters remain similar to their input geometries by maintaining nearly octahedral Ge$_6$ cages and similar intercon-

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**Table 1.** Calculated $E_B$ and $E_{gap}$ (eV) of CG-relaxed clusters Ge$_6$, Ge$_9$, and Ge$_{12}$ ($Z_0$) from this work and those of Ref. [32] in parentheses.

|       | Ge$_6$ | Ge$_9$ | Ge$_{12}$ $Z_0$ |
|-------|--------|--------|-----------------|
| $E_B$ | 4.425  | 4.589  | 4.650 (3.270)   |
| $E_{gap}$ | 2.05  | 1.24   | 1.59 (2.003)    |

**Table 2.** Average skeletal distance $d_G$, deviation from octahedrality $\sigma_{d_G}$, range of bond lengths $\sigma_{d_G}$, intercluster distances $d$, (all distances inÅ), and binding energy per atom $E_B$ (eV) calculated for the CG-relaxed clusters Ge$_{12}$.

| Ge$_{12}$ | $d_G$ | $\sigma_{d_G}$ | $d_G$ | $d_i$ | $E_B$ |
|-----------|-------|----------------|-------|-------|-------|
| $Z_0$     | ——   | 1.90-2.80     | ——   | 4.527 |
| $I_0$     | 2.667| 0.104          | 2.55-2.80| 5.6   |
| $I_0$     | 2.683| 0.182          | 2.55-2.93| 5.6   |
| $I_{10}$  | 2.607| 0.064          | 2.57-2.77| 5.6   |

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Fig. 2. Molecular orbitals of (a) Ge$_9$ and (b) Ge$_9$°.
connections. II₀ has the most deformation with $\sigma = 0.182$ Å. I₀ maintains two intercluster bonds $d_i = 2.56$ Å and II₀ has one of length 2.68 Å, while III₀ deforms so that it has one strong intercluster bond of $d_i = 2.64$ Å and two elongated connections of $d_i = 2.80$ Å which are much longer than a typical bulk Ge-Ge bond, but not unusual within a nanocluster or cage geometry. Given that DFT cannot easily identify bonds, there is some question regarding the strength of the theses two elongated bonds in III₀. Since its energy is nearly that of II₀, these bonds appear weak, which is confirmed during MD simulation.

In Fig. 3 we present the DOS of the CG-relaxed Ge₁₂₂ structures. In (a) the DOS of Z₀ shows the 4s orbitals at $-6.0 < E - E_F < -4.0$ eV remain well separated with a similar magnitude as neutral Ge₀. The 4p states range over $-4.0 < E - E_F < 0.0$ eV, again of similar magnitude to Ge₀, but with a much broader range, indicating the many possible orientations of p orbitals in a tetracapped cube compared with an octahedron. The placement of the Fermi level at the center of the energy gap indicates this is a stable, insulating cluster. In (b) the DOS of I₀ we see a similar set of 4s and 4p states below $E_F$, with additional states at $E_F$ itself. These are likely due to the overlap of the two intercluster Ge-Ge bonds. The placement of $E_F$ indicates these states are metallic. Conversely in (c) the DOS of II₀ is similar to that of Ge₀ in Fig. 2(a). While the two highest 4s orbitals remain of similar magnitude to those of the other Ge₁₂ clusters, like Ge₀ they are located at $-4.5 < E - E_F < -3.0$ eV. There is greater symmetry indicated in this cluster, with the 4p orbitals in the range $-2.5 < E - E_F < 0.0$ eV, and higher/lower peaks than the other Ge₁₂ clusters, again much like an individual Ge₀ cluster. The II₀ cluster is insulating since $E_F$ is at the base of $E_{gap}$ like neutral Ge₀. The MD simulation will confirm that II₀ is readily broken into two separated Ge₀ clusters, so it is unsurprising that the overall DOS is qualitatively similar to neutral Ge₀. The additional peaks result from more available electronic states in Ge₁₂ than Ge₀, but we observe no states that may be clearly tied to the single intercluster bond. In (d) we show that III₀ is metallic with many states in $E_{gap}$. The DOS is similar to that of I₀, yet the 4s states at $-5.0 < E - E_F < -4.2$ eV are closer together, there are fewer peaks in the 4p orbitals, $-4.5 < E - E_F < -0.9$ eV, and there is a double peak at $E_F$. Again, the state is metallic, indicated the delocalized nature of the Ge-Ge connections in the intercluster bridging structure.

From the $E_R$ and DOS calculations, we confirm the Ge₁₂ Z₀ isomer is stable and conclude structures I₀ and III₀ have developed strong intercluster bonds while II₀ has not. While Z₀ has a large $E_{gap}$, I₀ and III₀ do not, and furthermore their $E_F$ values are placed at the top of a
seemingly large gap, probably due to their intercluster bridging structures. Conversely $I_0$ seems not to have formed a strong bridging structure, instead appearing as two closely spaced Ge$_6$ clusters. Our examination of $E_B$ and DOS for these Ge$_{12}$ clusters does not clearly identify whether these new isomers are stable, but do give some perspective on whether the isomer is composed of two interacting Ge$_6$ clusters or a more stable, bridged Ge$_{12}$ cluster. In latter sections, we will use MD and COHP analysis to evaluate stability in these isomers.

### 3.3 Au$_3$Ge$_{18}$ Clusters

Next we study CG-relaxed structures for [Au$_3$Ge$_{18}$]$^{3-}$ and its neutrally charged counterpart in vacuum to compare with the experimentally observed structure. As shown in Fig. 5, this structure consists of two deltahedron-shaped Ge$_6$ cages linked by three Au atoms. The three Au atoms bond to three Ge atoms in each cage, forming a prism-like interconnection. Since this figure highlights the interconnection, we mention the asymmetry of the clusters: the apex of one Ge$_6$ cage points along an apex of the prism while the opposing cage’s apex points in the opposite direction (see Ref. [17]).

In comparing the neutral prism while the opposing cage’s apex points in the opposite direction (see Ref. [17]). In comparing the neutral prism while the opposing cage’s apex points in the opposite direction (see Ref. [17]).

We calculated the binding energy $E_B$ for the neutral cluster as 4.427 eV, which compares well other calculations in this work. Our calculated $E_{\text{gap}}$ is considerably smaller than reported by Ref. [17]. Given the superiority of hybrid XC functionals for estimating optical gaps, this is unsurprising. However since our calculations show a stable cluster with a well-separated energy gap with the Fermi level at its base, which indicates overall cluster stability.

In Fig. 6 we present (a) the total DOS and species pDOS, (b) the Ge pDOS of orbitals 4s, 4p, and 4d, and (c) the Au pDOS of orbitals 5d, 6s, and 6p of the neutral cluster. The strongest Au-Ge mixing appears just below $E_F$ where the Au 5d states mix with the Ge 4p states. Below $E - E_F < -5.0$ eV the states are dominated by Ge 4s and between $-5.0 < E - E_F < -2.0$ eV they are dominated by Au 5d states. Here $E_F$ falls just below a larger gap, indicating a weakly conducting or insulating cluster. In (b) we observe similar Ge orbitals to those in the pure Ge$_{12}$ clusters with well separated 4s and 4p states. One sees these 4p orbitals have considerable hybridization and peak at $E - E_F \approx 1.5$ eV, much like the neutral Ge$_6$ cluster. In (c) one sees the 5d orbitals of Au in the region from $-4.5 < E - E_F < 0.5$ eV, which only strongly mix with the 6s orbital in the range $-1.5 < E - E_F < 0.5$ eV. The Fermi level is just below $E_{\text{gap}}$, indicating a weakly metallic nature in this cluster, and the highest occupied MO is of mainly 4p character, as shown in Fig. S1.

The electronic structure of Au$_3$Ge$_{18}$ is quite similar to the neutral cluster, however $E_F$ sits at the top of $E_{\text{gap}}$, which indicates it is unstable without external ligands. Indeed, we observe considerable rearrangement of both neutral and charged clusters under MD simulation, as shown in Sec. 3.5 which restores the electronic structure to a stable configuration.

### 3.4 Au$_6$Ge$_{12}$ Clusters: Geometry and DOS

Now we examine linked Ge$_6$Au$_n$Ge$_6$ configurations to compare with Au$_3$Ge$_{18}$. There are innumerable combinations of two octahedral Ge$_6$ cages connected to one or more Au atoms, so we focus on input geometries that were designed to test the linearity of Ge-Au-Ge links and accommodate the symmetries of the Ge$_6$ cages. We tried many such input geometries, but illustrate just a few of the most interesting cases which have similar initial Ge$_6$ orientations as

| $q$ | $d_G$ | $d_{AG}$ | $d_A$ | $\theta$ | Ref. |
|-----|--------|---------|-------|---------|------|
| 0   | 2.5-2.85 | 2.46-2.48 | 3.11-3.19 | 165°-174° |
| 5   | 2.56-2.86 | 2.53    | 3.03-3.34 | 165°-172° |
| 5   | 2.55-2.88 | 2.45-2.46 | 2.900-3.095 | 168°-174° | [16] |

Table 3. Ranges of calculated bond lengths (Å) found for Ge, Au-Ge, and Au-Au bonds for [Au$_3$Ge$_{18}$]$^{3-}$. Also shown, values for the angles $\theta$ connecting Au to the two cages.

Fig. 5. Au$_3$Ge$_{18}$ clusters with charge (a) $q = 0$ and (b) $q = 5$ Au atoms are gold and Ge atoms are gray.
those described in Section 3.2 now with intercluster Au atoms.

With just one Au atom, we examined orientations very similar to the CG structures I$_0$ and II$_0$ with an Au atom added. For both of these orientations, the axes of the octahedra are aligned with an Au atom at their midpoint. The input structure for I$_0$ produced I$_1$, where a total of four Au-Ge links could form in the equatorial planes of the two octahedra. Likewise II$_0$ and II$_1$ shared input structures where the added Au atom in in II$_1$ created two Au-Ge links in a line connecting the apices of the two octahedra. With two Au atoms, many possible interlinked combinations exist, but stable isomers resulted from placing both Au atoms in the common equatorial plane of the two octahedra, creating four Au-Ge links. With three Au atoms, we focused on canted octahedra, similar to structure III$_0$ [Fig. 3(c)], to create a nine-atom prism much like that in Au$_3$Ge$_{18}$.

Such initialization procedures require an exploration of geometry phase space to ensure our CG relaxations do not find highly metastable states. To ensure a more complete sampling of the possible configurations we use a “geometry sweep” much like the approach used to find the groundstate of crystal structures in DFT methods. In general, a sweep was generated by using as a variable the initial separation $d_{\text{init}}$ of Au from Ge atoms to which it was interconnected. For a given initial cluster orientation, independent CG relaxations of the cluster were run for a series of Au-Ge separations, yielding many isomers to compare, each with a relaxed geometry and binding energy. A single geometry sweep explored one input orientation with 15-20 different Au-Ge separations while setting initial Ge-Ge distances at 3.0 Å. The CG relaxations returned dense clusters with high binding energies for short Au-Ge distances and dissociated clusters with low binding energies at long Au-Ge distances. This paper focuses on the intermediate clusters which retained two Ge$_6$ cages connected by Au atoms. Generally within a broad range of $d_{\text{init}}$, these intermediate clusters are nearly identical after CG relaxation. From these intermediate isomers we present those with relatively high binding energies.

Figure 7 shows two geometry sweeps for AuGe$_{12}$, where each point represents a separate isomer. Each sweep produces compact clusters at $d_{\text{init}} < 2.5$ Å, intermediate clusters at $2.5 < d_{\text{init}} < 5.0$ Å, and dissociated clusters at higher separations. Sweep 1, with four Au-Ge interconnects, produces I$_1$ in the range $2.5 < d_{\text{init}} < 5.0$ Å, and yields low $E_B$ structure V$_1$ at $d_{\text{init}} = 2.5$ Å. Sweep 2, with two Au-Ge interconnects, produces many isomers: II$_1$-III$_1$ observed where $3.0 < d_{\text{init}} < 3.6$ Å, IV$_1$ in the range $3.8 < d_{\text{init}} < 4.8$ Å, and V$_1$ and VII$_1$ at $2.2 < d_{\text{init}} < 3.0$ Å. We show the geometries of I$_1$ and II$_1$ in Fig. 8 and III$_1$ - VII$_1$ in Fig. 8. We conclude that the geometry differences within a sweep are small and the overall range of $E_B/\text{atom}$ between isomers is less than 0.1 eV, indicating near degeneracy of the clusters. Interesting differences include those of II$_1$ and III$_1$, where III$_1$ is twisted about its long axis compared with II$_1$. V$_1$ is considerably more octahedral that I$_1$.

In each group Au$_n$Ge$_{12}$, $n = 1 - 3$, we identified a few highest binding energy structures for careful study and present geometry and energy data of their CG relaxations in Table 4. We examine clusters which maintain a recognizable pair of Ge$_6$ cages throughout a CG relaxation. Differences in energies between the highest and lowest in each group was small, typically less than 0.1 eV. There are no significant trends in the deviation from octahedrality $\sigma_{\text{dc}}$ with binding energy. Ge-Au-Ge angles $\theta$ vary from straight to bent (e.g., there is one structure, II$_3$, in the Au$_3$Ge$_{12}$ series that has a near tetrahedral angle). Due to the large number of CG-relaxed Au$_n$Ge$_{12}$ structures summarized in this table, we show only four representative structures in Fig. 8 which will be used to contrast properties of stability to those of instability in Sec. 3.5.
Table 4. Calculated average skeletal distances (Å) and deviations from octahedrality (Å) of the CG-relaxed clusters Au$_n$Ge$_m$ shown in Figs. 8 and S2. Also shown, ranges for bond lengths $d_G$, $d_{AG}$, $d_A$, and values for the angles $\theta$ connecting Au to the two cages and energy $E_B$ (eV).

| AuGe$_{12}$ | $\bar{d}_G$ | $\sigma_{d_G}$ | $d_{AG}$ | $d_G$ | $\theta$ | $E_B$  |
|-------------|-------------|----------------|---------|-----|--------|-------|
| I$_1$       | 2.731       | 0.242          | 2.66    | 2.58-3.29 | 104°  | 4.349 |
| II$_1$      | 2.663       | 0.127          | 2.46    | 2.53-2.86 | 180°  | 4.317 |
| III$_1$     | 2.664       | 0.127          | 2.465   | 2.51-2.88 | 180°  | 4.315 |
| IV$_1$      | 2.689       | 0.189          | 2.49    | 2.55-2.94 | 180°  | 4.284 |
| V$_1$       | 2.703       | 0.086          | 2.53    | 2.54-2.77 | 114°  | 4.270 |
| VI$_1$      | 2.673       | 0.124          | 2.49    | 2.57-2.83 | 180°  | 4.266 |
| VII$_1$     | 2.652       | 0.028          | 2.46    | 2.63-2.69 | 180°  | 4.247 |

| Au$_2$Ge$_{12}$ | $\bar{d}_G$ | $\sigma_{d_G}$ | $d_{AG}$ | $d_A$ | $d_G$ | $\theta$ | $E_B$  |
|----------------|-------------|----------------|---------|------|------|--------|-------|
| I$_1$          | 2.735       | 0.343          | 2.46-2.51 | 2.89 | 2.50-3.76 | 171.4°-176° | 4.292 |
| II$_1$         | 2.837       | 0.443          | 2.42-2.52 | 2.90 | 2.48-3.83 | 117-176° | 4.291 |
| III$_1$        | 2.709       | 0.232          | 2.52-2.64 | 2.81 | 2.52-3.14 | 172.5° | 4.256 |
| IV$_1$         | 2.654       | 0.063          | 2.46    | 4.09 | 2.57-2.72 | 148° | 4.241 |

| Au$_3$Ge$_{12}$ | $\bar{d}_G$ | $\sigma_{d_G}$ | $d_{AG}$ | $d_A$ | $d_G$ | $\theta$ | $E_B$  |
|----------------|-------------|----------------|---------|------|------|--------|-------|
| I$_1$          | 2.653       | 0.063          | 2.46-2.50 | 4.15 | 2.56-2.71 | 130-138° | 4.191 |
| II$_1$         | 2.661       | 0.048          | 2.49-2.81 | 3.45-3.59 | 2.58-2.73 | 109-175° | 4.187 |
| III$_1$        | 2.685       | 0.056          | 2.48-2.52 | 3.06 | 2.62-2.76 | 136-151° | 4.181 |
| IV$_1$         | 2.683       | 0.142          | 2.50-2.54 | 2.97 | 2.51-2.93 | 112-139° | 4.145 |
| V$_1$          | 2.760       | 0.356          | 2.51-2.69 | 2.78-2.94 | 2.52-3.74 | 174° | 4.135 |

The remainder of the structures listed in this table can be found in Fig. S2 We show $n = 3$ structures in Sec. 3.6 since we observe no stable neutral Au$_3$Ge$_{12}$ clusters, but see that additional charge supports a prism-like intercluster bridge.

Fig. 8(a) and (b) compares isomers I$_1$ and II$_1$, with four and two Ge-Au-Ge intercluster links. The octahedra of I$_1$ are more deformed than II$_1$, with $\sigma_{d_G}$ larger by 0.12Å, the Au-Ge bonds are longer in I$_1$ by 0.2Å, and $E_B$ is greater by approximately 0.03 eV. Likewise (c) and (d) compares isomers I$_2$ and III$_2$. Here I$_2$ is less symmetric than III$_2$ ($C_{2v}$ vs. $D_{2h}$) which coincides with reduced octahedrality in I$_2$ ($\sigma_{d_G} = 0.434Å$). I$_2$ (Fig. S2) is similar to I$_1$, with more exaggerated asymmetry ($\sigma_{d_G} = 0.443Å$), while IV$_2$ (Fig. S2) is similar to III$_2$ with a strongly bent Ge-Au-Ge link ($172.5°$ vs $148°$) and a widely separated Au-Au distance (4.09Å). The overall symmetry change between the isomers of Au$_2$Ge$_{12}$ appears to have direct consequences for the overall cluster stability.

The DOS of the Au$_n$Ge$_{12}$ clusters generally resembles that of Au$_3$Ge$_{18}$ where the Ge 4p orbitals dominate just below $E_F$ with some overlap with the Au 5d states. The Ge 4p and Au 5d states of I$_1$ have less overlap than II$_1$. The DOS of I$_2$ and III$_2$ are qualitatively similar, but the additional symmetry of III$_2$ promotes $E_F$ above the energy gap of I$_2$, indicating an electronic instability. However, it is not clear from DOS alone which clusters will be stable, but some additional insights are available with COHP analysis (Sec. 3.7). We see the most overlap between Ge and Au orbitals in Au$_3$Ge$_{12}$ due to the greater magnitude of the Au states, but it is clear from MD studies (Sec. 3.5) that this does not contribute to a stability of the Ge$_6$Au$_n$Ge$_6$.
erably in the cage environment supported with delocalized overall symmetry loss. Since Ge-Ge bonds elongate consider-ably in the post-MD structures are small deformations that lead to an average skeletal distances and deviations from octahedrality (Å) of the post-MD clusters Ge$_{12}$. 

| Cluster | $d_G$ | $\sigma_G$ | $d_G$ | $\sigma_G$ |
|---------|-------|------------|-------|------------|
| Ge$_6$  | 2.721 | 0.139      | 2.757 | 0.173      |
| Ge$_6^{2-}$ | 2.710 | 0.265      | 2.773 | 0.360      |
| Ge$_{12}$ | 2.767 | 0.292      | 2.732 | 0.278      |

Table 5. Calculated average skeletal distances and deviations from octahedrality (Å) of the post-MD clusters Ge$_{12}$.

In Ge$_{12}$ and Au$_n$Ge$_{12}$ stability is determined primarily on the formation/breaking of intercluster bonds and the preservation of octahedrality of the Ge$_6$ cages which may deform beyond recognition during the MD simulation. I$_0$ retains two intercluster bonds and measurably octahedral Ge$_6$ cages as shown in Fig. 3(b). II$_0$ breaks its intercluster bond but its Ge$_6$ clusters remain cage-shaped. With structure III$_0$, an intercluster bond breaks, and the relative tilting of the two cages has changed. In all cases, the deviation from octahedrality $\sigma_G$ is larger in the post-MD structures, the overall symmetry of the cluster is reduced, and the average skeletal Ge-Ge bond length has increased (as quantified in Table 5).

In Fig. 9 we compare the post-MD structures of Au$_n$Ge$_{12}$ to the previously described CG structures and describe the geometry differences in Table 6. In Fig. 8 we see I$_1$ (a) breaks an Au-Ge intercluster bond, while II$_1$ (b) maintains both: merely twisting about its Ge-Au-Ge intercluster link so $\theta_{Ge-Au-Ge}$ remains close to linear. When comparing the two predominant isomers of AuGe$_{12}$, the four Au-Ge intercluster bonds of I$_2$ are less stable than the two of II$_2$. We observe in $n = 2$ that stability under MD simulation appears to rely on more than number of intercluster links: the asymmetric I$_2$ and II$_2$ structures are stable under MD while the relatively symmetric III$_2$ and IV$_2$ structures are not although each have four linear Au-Ge intercluster links. This is consistent with the asymmetric coupling of the Ge$_9$ clusters in [Au$_4$Ge$_{18}$]$^{5-}$. We see that Au$_3$Ge$_{12}$ does not readily form linear stable Ge-Au-Ge links, whether the relative Ge$_9$ orientations are symmetric or asymmetric. However in the following section we discuss the additional stability of the Au$_3$Ge$_{12}$ cluster with an ionic charge.

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3.6 Stability of Charged Clusters

The influence of charge on cluster shape, dictated largely by Wade’s rules, is an essential consideration in Ge cluster studies. We briefly describe the effect of a charge $q = 2$ and $q = 4$ on some isomers of Au$_n$Ge$_{12}^{2-}$, with a focus on how the presence of additional charge stabilizes linear Ge-Au-Ge intercluster links in Au$_2$Ge$_{12}$ and Au$_3$Ge$_{12}$. To obtain these results, we ran identical geometry sweeps to our neutral charge calculations (Sec. 3.4), with charge $q = 2$ and $q = 4$ added to the cluster. Rather than present every new isomer observed, we show the CG-relaxed and post-MD geometries of Au$_3$Ge$_{12}^{2-}$ in Fig. 9 and that of Au$_3$Ge$_{12}^{4-}$ in Fig. 10, where the additional charge has stabilized structures not observed in neutral clusters. Properties of these isomers, including the combined octahedrality of the Ge$_9$ clusters, are summarized in Table 7.

Table 7 lists two stable isomers that were found for Au$_2$Ge$_{12}^{2-}$. The primary difference is in the linearity of...
Table 6. Results for the calculated average skeletal distances and deviations from octahedrality (Å) of the AuGe$_{12}$ clusters after MD runs, where a blank in a $\sigma_{dG}$ column indicates a complete disordering of the octahedra. Also shown, values for the angles $\theta$ connecting Au to the two cages and energy, $E_B$ (eV). Structures are shown in Figs. 8 and 52.

| AuGe$_{12}$ | $d_{AG}$ | $\theta$ | $(\sigma_{dG})_1$ | $(\sigma_{dG})_2$ | $d_G$ | $(\sigma_{dG})_1$ | $(\sigma_{dG})_2$ | $d_G$ |
|------------|---------|---------|-----------------|----------------|------|-----------------|----------------|------|
| I1         | 2.46    | 2.76    | 166$^\circ$     | 2.74           | 0.32 | 2.79           | 0.40           | 2.36-3.51 |
| II1        | 2.45    | 2.60    | 163$^\circ$     | 2.74           | 0.40 | 2.73           | 0.23           | 2.42-3.95 |

| Au$_2$Ge$_{12}$ | $d_A$ | $d_{AG}$ | $\theta$ | $(\sigma_{dG})_1$ | $(\sigma_{dG})_2$ | $d_G$ | $(\sigma_{dG})_1$ | $(\sigma_{dG})_2$ | $d_G$ |
|----------------|-------|---------|---------|-----------------|----------------|------|-----------------|----------------|------|
| I2            | 3.20  | 2.49    | 163$^\circ$, 177$^\circ$ | 2.779          | 0.379         | 2.743 | 0.309          | 2.53-3.73       |
| II2           | 3.03  | 2.47-2.73 | 173$^\circ$ | 2.774          | 0.318         | 2.812 | 0.409          | 2.43-3.87       |
| III2          | 3.42  | 2.41-2.84 | 102$^\circ$, 157$^\circ$ | 2.696          | 0.298 | —        | —              | 2.39-3.56       |
| IV2           | 3.27  | 2.38-2.73 | 125$^\circ$, 163$^\circ$ | 2.726          | 0.251 | —        | —              | 2.49-3.41       |

| Au$_3$Ge$_{12}$ | $d_A$ | $d_{AG}$ | $\theta$ | $(\sigma_{dG})_1$ | $(\sigma_{dG})_2$ | $d_G$ | $(\sigma_{dG})_1$ | $(\sigma_{dG})_2$ | $d_G$ |
|----------------|-------|---------|---------|-----------------|----------------|------|-----------------|----------------|------|
| I3            | 3.04  | 2.46-3.04 | 75$^\circ$, 169$^\circ$ | —              | —              | —    | —              | —              | 2.52-3.21       |
| II3           | 3.60-3.71 | 2.48-3.01 | 100$^\circ$, 175$^\circ$ | 2.68           | 0.11          | —    | —              | —              | 2.54-2.99       |
| III3          | 3.25-3.68 | 2.43-2.91 | 96$^\circ$, 165$^\circ$ | 2.81           | 0.28          | —    | —              | —              | 2.54-3.53       |
| IV3           | 2.75  | 2.45-2.89 | 127$^\circ$, 143$^\circ$ | 2.73           | 0.19          | —    | —              | —              | 2.37-3.29       |
| V3            | 2.77  | 2.48-2.84 | 150$^\circ$ | 2.81           | 0.37          | —    | —              | —              | 2.51-3.83       |

3.7 COHP Analysis of Bonding

By examining post-MD structures, we observe features of stable Au$_n$Ge$_m$ clusters which are not apparent merely from CG simulation. Given the computational expense of MD, it is desirable to have other methods to determine bond stability. Here we employ COHP electronic partitioning, as described in Sec. 3, to characterize stability in terms of electronic structure.

Figure 11 shows the COHP of the Ge-Ge bonds of the four CG-relaxed Ge$_{12}$ structures. The groundstate $Z_0$, Fig. 11(a), introduces the typical criterion of a stable cluster: the states switch from negative bonding to positive antibonding MOs at the Fermi level. In structure $I_0$, Fig. 11(b), the anti-bonding states first appears at $E_F$ at the top of the band gap. Given the overall stability of this cluster, this suggests the additional states introduced in the DOS (see Sec. 3.1) from the intercluster Ge$_0$-Ge$_0$ interaction are antibonding, and serve to keep the cluster as two separate, linked structures. Structure $II_0$, Fig. 11(c), has antibonding states below $E_F$ at the base of the energy gap, which can be correlated with the dissociation into two Ge$_0$ clusters in the post-MD structure. Cluster $III_0$, Fig. 11(d), appears metallic with the first antibonding state at $E_F$ (much like $I_0$) and a small energy gap. This is consistent with the post-MD rearrangements: the CG-relaxed structure of $III_0$ has three intercluster bonds and forms two during the MD run. We tentatively conclude that two intercluster Ge-Ge bonds provide a relatively stable connecting structure between Ge$_0$ octahedral cages.

We use the structures shown in Fig. 8 to compare the properties of stable CG-relaxed Au$_n$Ge$_{12}$ clusters: $II_1$ is compared to the less stable $I_1$ in AuGe$_{12}$ and $I_2$ to less stable $II_2$ Au$_2$Ge$_{12}$. We show their COHP interactions in three figures: Ge-Ge in Fig. 12, Au-Ge in Fig. 13 and Au-
Table 7. Calculated properties of the CG-relaxed clusters found in geometry sweeps for charged clusters Au$_n$Ge$_{12}$$^{n−}$. Also shown, the properties for these clusters post-MD.

| CG Properties | $d_z$ | $\sigma_{d_z}$ | $d_{Ag}$ | $d_A$ | $d_d$ | $\theta$ |
|---------------|-------|---------------|---------|-------|-------|---------|
| Au$_2$Ge$_{12}$ (1) | 2.66  | 0.05          | 2.49    | 3.92  | 2.56-2.73 | 148.5$^a$ |
| Au$_2$Ge$_{12}$ (2) | 2.70  | 0.15          | 2.53    | 2.84  | 2.53-2.95 | 178.5$^a$ |
| Au$_2$Ge$_{12}$ | 2.72  | 0.09          | 2.59    | 2.89  | 2.51-2.84 | 176$^a$ |
| Au$_3$Ge$_{12}$ | 2.67  | 0.06          | 2.58-2.75 | 3.14-4.0 | 2.51-2.84 | 140$^a$ − 149$^a$ |
| Au$_3$Ge$_{12}$ | 2.73  | 0.13          | 2.76    | 3.23-3.72 | 2.59-2.93 | 155$^a$ |

| MD Properties | $d_z$ | $\sigma_{d_z}$ | $d_{Ag}$ | $d_A$ | $d_d$ | $\theta$ |
|---------------|-------|---------------|---------|-------|-------|---------|
| Au$_2$Ge$_{12}$ (1) | 2.67  | 0.11          | 2.46-2.48 | 3.80  | 2.35-4.05 | 140$^a$,157$^a$ |
| Au$_2$Ge$_{12}$ (2) | 2.72  | 0.23          | 2.38-2.60 | 3.82  | 2.40-2.88 | 149$^a$,157$^a$ |
| Au$_2$Ge$_{12}$ | 2.79  | 0.17          | 2.62-2.70 | 2.76  | 2.51-3.26 | 161$^a$ − 164$^a$ |
| Au$_3$Ge$_{12}$ | 2.75  | 0.15          | 2.37-2.73 | 3.22-3.96 | 2.43-2.99 | 146$^a$ − 178$^a$ |
| Au$_3$Ge$_{12}$ | 2.82  | 0.24          | 2.58    | 2.93-4.16 | 2.58-3.39 | 135$^a$ − 171$^a$ |

**Fig. 11.** COHP analysis of Ge-Ge interactions Ge$_{12}$ after CG relaxation. Structures (a) Z$_0$, (b) I$_0$, (c) II$_0$, and (d) III$_0$.

Au in Fig. [13] Generally we see that the primary indicator of stability is that of the Au-Ge interaction.

In AuGe$_{12}$ the overall similarities of the Ge-Ge interaction of are apparent in Fig. [12](a-b) where a single, large bonding peak appears below $E_F$ at $E - E_F \approx -2.0$ eV. However I$_1$ shifts from Ge-Ge bonding to antibonding states at $E_F$ while II$_1$ has a small antibonding state in Ge-Ge at $E_F$. In the Au-Ge interaction [Fig. [13](a-b)], I$_1$ has antibonding states at $E_F$, while II$_1$ has no Au-Ge state at $E_F$. Instead $E_F$ is centered between occupied bonding and empty antibonding states. Given the lower stability of I$_1$, this indicates the Ge-Ge antibonding state arises from intercluster interaction, like that of I$_0$, but does not break the structure. The antibonding Au-Ge state at $E_F$ of I$_1$ is likely to cause the Au-Ge bond breaking observed in the post-MD cluster, whereas those in II$_1$ merely twist.

The Ge-Ge COHP curves of Au$_2$Ge$_{12}$ I$_2$ and II$_2$ are qualitatively similar [Figs. [12](c,d)]. Neither cluster has antibonding states below $E_F$, and the primary difference is the shift in the location of $E_F$ from I$_2$ to III$_2$. Significantly, while the Au-Ge interactions of I$_2$ have no antibonding character below $E_F$ [Fig. [13](c)], there is an antibonding interaction in III$_2$ [Fig. [13](d)], again confirming that antibonding states in Au-Ge below $E_F$ are correlated with cluster instability. In examining COHP curves of Au$_3$Ge$_{12}$, there are as many as three antibonding states below $E_F$ in Au-Ge interactions, thus it is unsurprising that no neutral stable clusters were observed.

We see no overall stability trends in the Au-Au COHP results. In Fig. [14] we show the Au-Au COHP results of (a) I$_2$ and (b) III$_2$. In both cases, there are significant anti-bonding MO’s below $E_F$. For comparison, we examine Au$_3$Ge$_{18}$, and present its COHP analysis in Fig. [15]. We note three features in this figure: in (a) the Au-Au interaction has strong antibonding states at $E_F$, in (b) Au-Ge has a weak antibonding state at $E_F$ (this disappears in the post-MD structure), and in (c) Ge-Ge is bonding up to $E_F$, whereas below $E_F$ indicating no intercluster antibonding states between Ge$_9$ clusters. In terms of antibonding states, the Au-Au COHP is consistent with that observed for Au$_2$Ge$_{12}$. This character remains in the COHP analysis of the the charged Au$_3$Ge$_{12}$.$^{5−}$. To further examine this antibonding state the electronic structure analysis should account for aurophilic Au-Au interactions as discussed in Refs. [17,35].

Generally the COHP of the charged systems are qualitatively similar to their neutral counterparts with $E_F$ moved beyond $E_{gap}$ into the antibonding states. It is clear
this is not a good predictor of the stability of charged states. This reflects the DFT treatment of charge rather than nature herself.

### 3.8 Extended $\infty^2[\text{Au}_2\text{Ge}_6]$ Structures

To extend our exploration of the ability of Ge$_6$ cages to bond with Au atoms, we consider crystalline Au-Ge structures built with this geometry. The precedent studies include Ref. [62], where 1D, 2D, and 3D structures formed of Ge$_6$ cages are examined. We show the hypothetical structure $\infty^2[\text{Au}_2\text{Ge}_6]$ in the inset of Fig. 15 which represents the isomer observed with binding energy maximum at $d_{\text{init}} = 2.6\text{Å}$. Here, Au atoms are placed in the positions of the radial non-bonding orbitals of isolated [Ge$_6$]$^{2-}$ clusters in the $xy$ plane. Following the techniques of Sec. 3.4 we vary the initial Au-Ge distance, perform CG minimization, and find the binding energy and relaxed geometry (Fig. 15). The relaxed structure features a subunit of a Ge$_6$ octahedron with four radial Au-Ge bonds. Each subunit is spaced closely to form a 2D crystal structure including Au-Au bonds. The binding energy has a peak at $d_{\text{init}} = 2.6\text{Å}$, where $d_{\text{init}}$ is the initial Au-Ge bond length. The average bond found in the Ge cages is $d_G = 2.72 \pm 0.06\text{Å}$, showing that the bonds are elongated compared to the isolated clusters, but the cages are close to octahedral. Ge-Ge bonds range from $d_G = 2.62 - 2.77\text{Å}$, which includes those in the two-dimensional plane forming a square with lengths of approximately 2.65Å and the out-of-plane bonds are 2.77Å. The Au-Ge bond lengths $d_A = 2.42\text{Å}$ are short compared with the clusters studied in Sec. 3.2 and the Au-Au bond is $d_A = 2.85\text{Å}$. The Ge-Au-Ge linking angle is 117°. We explored other stoichiometries, such as $\infty^1[\text{Au}_1\text{Ge}_6]$, $\infty^1[\text{Au}_2\text{Ge}_6]$, and $\infty^2[\text{Au}_4\text{Ge}_6]$, and observed considerably less smooth $E_B$ vs. $d_{\text{init}}$ curves, indicating these stoichiometries prefer dissociation or non-octahedral geometries in the input structures we examined. Again we see that a Au-Ge ratio of 1:6 seems to support greater overall stability in Au-Ge systems.

### 4 Discussion and Conclusions

Beyond its well known properties as a covalently bonded $sp^3$ semiconductor, the versatility in the Ge electronic structure allows it to form cage-like structures with extended bond lengths. Taken in isolation, cages Ge$_6$ and Ge$_9$ need additional electrons to stabilize their deltahedral shapes; two electrons being sufficient for the former,
and four for the latter, consistent with Wade’s Rules. By using DFT methods, we have examined the stability of combinations of octahedral Ge$_6$ cages in various forms. In examining linking structures between two such cages, we found that two bonds form and stabilize Ge$_{12}$, especially when the two clusters are aligned symmetrically with Ge-Ge bonds connecting the two equatorial planes of the octahedra. Other orientations are less stable, as can be seen using COHP analysis or by running brief MD simulations to examine how the cluster evolves. There are hints in these runs that 5-atom and 7-atom rings can form, similar to those found in clathrate and allo-Ge$^{\pm}$ systems. Our conclusion is that stable Au-Ge clusters or perhaps even extended structures are most likely to be found if 1-2 Au atoms are used to interconnect the equatorial planes of the octahedra, assuming external ligands or large spacing ions were employed to counterbalance ionicity. This suggests that geometry and charge state play a larger role in stable intercluster links than chemical species consistent with Wade’s rules.

We emphasize the importance of DFT to treat metal-semiconductor bonds in cage-like clusters, especially with the relativistic nature of valence electrons in Au. We recognize that the details of our results will be sensitive to the details of the DFT calculation. More over, there are fundamental problems with DFT methods, e.g., dispersion forces and their effects on MD results. In any DFT study, the selection of basis orbitals and the type of exchange-correlation functional may significantly alter some predictions. We have found SIESTA to have several positive virtues for this study, including its ability to partition electronic states and to study isolated multiply charged clusters.

As in many cluster studies, it is easy to get lost in the task of finding ground-state structures. We have been systematic in our choices of structures to study, and have found by CG minimization the usual large number of structures and their binding energies. While a more comprehensive sampling procedure would surely yield more information about definitive ground-state structures in vacuum, especially in Au$_{12}$Ge$_{12}$, this method revealed geometries that could be supported with external ligands. Importantly the observation of the same, or very similar, isomers over a range of initial Au-Ge separations is an assurance of cluster stability to small vibrations and perturbations.

A very helpful tool has been the use of COHP electronic partitioning to examine the stability of these clusters. Since COHP is calculated from orbital interactions that neglect exchange and correlation, it is an imperfect measure of bonding in DFT systems, yet we observe trends which suggest such analysis may be used to understand overall Au-Ge cluster stability. To test the COHP analysis, we have also used brief MD simulations to see whether a given structure is stable enough not to “shake apart” or have significant rearrangement of atoms during a run. Our work shows that strongly antibonding Au-Ge orbitals at $E_F$ will tear apart intercluster bonds. We expect experimental realizations of these systems to feature stronger Au-Au bonds as in Ref. [17] which notes the concept of aurophilicity, much like hydrogen bonds, that is not readily treated in DFT methods.

A question of this study was whether Au atoms would maintain much of their metallic bonding character in the compounds. And if Au connects two Ge cages, we observe that the bonding is more covalent, Au tending to be the
single interconnect between two Ge atoms. We have observed different behavior in more dense clusters, such as one Au bonding to multiple Ge atoms in a cluster, but our primary interest was in a direct analogy to the experimentally observed [Au₄Ge₁₈]⁵⁻.

Remaining still as a theoretical challenge are such problems as is the kinetic nature of Au’s role in crystallizing Ge or forming diamond-structure nanowires [11]. Recent work [64] in nanowire growth observes metastable crystalline AuGe catalysts which may further inform which geometries are favored in these nano-sized clusters. Our brief MD studies were not sufficient to make progress in this challenge. But perhaps understanding better Au-Ge bonds in existing compounds should be the center of future studies of this fascinating pair of elements.

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References

1. H. Okamoto and T. B. Massalski, Bull. Alloy Phase Diagrams 5 (1984) 601
2. R. M. Waghorne, V. G. Rivlin, and G. I. Williams, J. Phys. F: Met. Phys. 6 (1976) 147
3. Z. Tan, S. M. Heald, M. Rappooch, C. E. Bouldin, and J. C. Woicik, Phys. Rev. B 46 (1992) 9505
4. R. Pöttgen, H. Bornmann, C. Felser, O. Jepsen, R. Henn, R. K. Kremer, and A. Simon, J. Alloys Comp. 235 (1996) 170
5. Q. Lin and J. D. Corbett, J. Am. Chem. Soc. 134 (2012) 4877
6. C. Blumenstein, J. Schäfer, S. Mietke, S. Meyer, A. Dollinger, M. Lochner, X. Y. Cui, L. Patthey, R. Matzdorf, and R. Claessen, Nat. Phys. 4877 (2011) 776
7. J. Wu and J. L. Coffer, Adv. Mater. 20 (2008) 1571
8. S. Kodambaka, J. Tersoff, M. C. Reuter, and F. M. Ross, Science 316 (2007) 729
9. E. Sutter and P. Sutter, Nano Lett. 8 (2008) 411
10. S. A. Dayeh and S. T. Picraux, Nano Lett. 10 (2010) 4032
11. D. Wang and H. Dai, Angew. Chemie 114 (2002) 4977
12. A. D. Gamalski, C. Ducati, and S. Hofmann, J. Phys. Chem. C 115 (2011) 4413
13. S. Ryu, C. R. Weinberger, M. I. Baskes, and W. Cai, Model. Simul. Mater. Sci. Eng. 17 (2009) 075008
14. A. M. Dongare, M. Neurock, and L. V. Zhigilei, Phys. Rev. B 80 (2009) 184106
15. C. Schenk and A. Schnepf, Angew. Chemie Int. Ed. 46 (2007) 5314
16. A. Spieckermann, S. D. Hoffmann, F. Kraus, T. F. Füessler, Angew. Chem. Int. Ed. 46 (2007) 1638
17. A. Spieckermann, S. D. Hoffmann, T. F. Füessler, I. Krossing, and U. Preiss, Angew. Chem. Int. Ed. 46 (2007) 5310
18. S. C. Sevov, Intermetallic Compounds: Vol. 3. Principles and Practice, J. H. Westbrook and R. L. Fleischer (John Wiley & Sons, Ltd, Chichester, UK, 2002) 113
19. K. Wade, J. Chem. Soc. D Chem. Commun. 20 (1971) 792
20. A. J. Welch, Chem. Commun. 49 (2013) 3615
21. E. Zintl, Angew. Chemie 52 (1939) 1
22. G. S. Armatas and M. G. Kanatzidis, Nature 441 (2006) 1122
23. D. Sun, A. E. Riley, A. J. Cadby, E. K. Richman, S. D. Kolman, and S. H. Tolbert, Nature 441 (2006) 1126
24. A. Kiefer, A. J. Karttunen, M. Döblinger, and T. F. Füessler, Chem. Mater. 23 (2011) 4578
25. M. Gulyu, R. Ramlau, Z. Tang, W. Schnelle, M. Baitinger, and Y. Grin, Nature 443 (2006) 320.
26. T. F. Füessler, H.-J. Muhr, and M. Hunziker, Eur. J. Inorg. Chem. 1998 (1998) 1433
27. P. Kircher, G. Huttner, K. Heinze, and G. Renner, Angew. Chemie Int. Ed. 37 (1998) 1664
28. G. Renner, P. Kircher, G. Huttner, P. Rutsch, and K. Heinze, Eur. J. Inorg. Chem. 2000 (2000) 879
29. A. F. Richards, H. Hope, and P. P. Power, Angew. Chemie 42 (2003) 4071
30. S. Öğüt and J. R. Chelikowsky, Phys. Rev. B 55 (1997) R4914
31. R. B. King, I. Silaghi-Dumitrescu, and A. Kun, J. Chem. Soc. Dalt. Trans. 2002 (2002) 3999
32. L.-Z. Zhao, W.-C. Lu, W. Qin, Q.-J. Zang, C. Z. Wang, and K. M. Ho, Chem. Phys. Lett. 455 (2008) 225
33. D. Sánchez-Portal, P. Ordejón, E. Artacho, J. M. Soler, Int. J. Quantum Chem. 65 (1997) 453
34. J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys. Condens. Matter 14 (2002) 2745
35. H. Schmidbaur and A. Schier, Chem. Soc. Rev. 37 (2008) 1931
36. S.-D. Li, Z.-G. Zhao, H.-S. Wu, and Z.-H. Jin, J. Chem. Phys. 115 (2001) 9255
37. W. Xu, Y. Zhao, Q. Li, Qianshu, Y. Xie, Yaoming, and H. F. Schaefer III, Mol. Phys. 102 (2004) 579
38. S. Yoo and X. C. Zeng, J. Chem. Phys. 124 (2006)184309
39. W. Qin, W.-C. Lu, L.-Z. Zhao, Q.-J. Zang, G.-J. Chen, C. Z. Wang, and K. M. Ho, J. Chem. Phys. 131 (2009) 124507
40. X.-J. Li and K.-H. Su, Theor. Chem. Acc. 124 (2009) 345
41. X. Li, K. Su, X. Yang, L. Song, and L. Yang, Comput. Theor. Chem. 1010 (2013) 32
42. J. E. Kingcade Jr., U. V. Choudary, and K. A. Gingerich, Inorg. Chem. 18 (1979) 3094
43. N. Korber, Angew. Chem. Int. Ed. 48 (2009) 3216
44. B. T. Truong and M. T. Nguyen, J. Phys. Chem. A 115 (2011) 9993
45. D. Selli, I. A. Baburin, R. Martoňák, and S. Leoni, Sci. Rep. 3 (2013) 1466
46. R. Drongowski and P. E. Blöchl, J. Phys. Chem. 97 (1993) 8617
47. N. Troullier and J. Martins, Phys. Rev. B 43 (1991) 1993
48. L. Kleinman and D.M. Bylander, Phys. Rev. Lett. 48 (1982) 1425
49. W. Kohn and L. J. Sham, Phys. Rev. 140 (1965) A1133
50. G. Hutter, A. R. Winter, and K. H. Lischka, J. Phys. Rev. B 40 (1989) 3979
51. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865
52. E. Anglada, J. M. Soler, J. Junquera, and E. Artacho, Phys. Rev. B 66 (2002) 205101
Due to the computational expense of MD simulation, we limit the duration of our runs to 2 fs. While CG runs for clusters typically take on the order of 5 hrs on 8 cores, the MD simulations of the same cluster, as described in the methods section, take roughly 36 hrs on 8 cores with 2.4 GHz processors and 12 GB RAM.

In Fig. [S1] we show the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) for the CG-relaxed cluster Au$_3$Ge$_{18}$. These figures clearly show the asymmetry of the two Ge$_9$ cages. In the LUMO pictures, the right cage shows extended π-like hybridization connecting into triangle of Au atoms. The nodal structure of the orbitals for both cages changes from HOMO to LUMO. Note, COHP for the Au-Au bonds of this cluster is shown in Fig. [15].

In Tables 4 and 6, a number of clusters Au$_n$Ge$_{12}$, $n$ = 1, 2, 3, are listed and described. Four figures were picked as being representative examples for the main paper and are shown in Fig. 8 (specifically, I$_1$, II$_1$, I$_2$, and III$_2$). The remainder of those clusters are shown in Fig. S2. Clusters III$_1$ through VII$_1$ are shown only after CG minimization since the isomers have the same overall symmetry and number of bonds as I$_1$ and II$_1$, and thus exhibit similar behavior under MD simulation. The rest are shown after both CG minimization and MD simulation.

We show HOMO and LUMO states for five selected CG-relaxed clusters of Au$_n$Ge$_{12}$. COHP analysis is also shown for four of these five clusters in Sec. 3.7. In Fig. S3, we show two orientations each for AuGe$_{12}$, cluster I$_1$. Referring back to Fig. 8(a), we see that it is highly symmetric. An interesting feature is the spherical orbital centered on the Au atom, seen in (a) and (c), connecting only loosely to the extended π-like orbitals of the two cages. In the LUMO, (b) and (d), the center Au atom is not directly connected to the cages. As discussed in Sec. 3.7, this cluster is less stable than cluster II$_1$, we show the post-MD rearrangement and symmetry breaking of I$_1$ in Fig. 8(a).

In Fig. S4, we show the orbitals after CG minimization for the more stable $n$ = 1 cluster II$_1$. Cluster II$_1$ is again highly symmetric [Fig. 8(b)] but interestingly, the HOMO state is degenerate and shows very localized electronic density on the cages, with very minimal interaction with the central Au atom in this orbital. The LUMO state, Fig. S4(c), has electronic structure for the Au bridge site that is similar to that shown in Fig. S3(b), that is, an extended π-like orbital that does not include the central Au atom. The orientations of the cages relative to the bridging Au are different for I$_1$ and II$_1$, as seen when comparing Figs. S3 to S4 or comparing the CG picture for I$_1$ of Fig. 8(a) to the one for II$_1$ in Fig. 8(b).

As Figs. S3 and S4 corresponded to Figs. 8(a) and (b), in Figs. S5 and S6, we show the HOMO and LUMO states for $n$ = 2, which correspond to the images of CG-relaxed structures in Figs. 8(c) and (d). As discussed in Sec. 3.7, cluster I$_2$, Figs. S5 and 8(c), is more stable than cluster II$_2$, Figs. S6 and 8(d). The cage orbitals for the HOMO state for $n$ = 2 are less extended than for $n$ = 1. Because of the relative tilting of the two cages for I$_2$, the two Au atoms participate differently in the bonding in the HOMO, Fig. S5. In contrast, for II$_2$ shown in Fig. S6, both Au atoms are equally involved in bonding to each other in the HOMO, and not at all in the LUMO.
As seen in Fig. S2, all $n = 3$ clusters change significantly after a MD run. In Fig. S7, we show HOMO and LUMO for cluster I$_3$ to compare these with its CG-relaxed geometry [Fig. S2(h)]. The tilting of the two cages causes two of the three Au atoms to participate differently in the bonding in the HOMO and in the LUMO states. It is most interesting to compare this with the HOMO and LUMO states for Au$_3$Ge$_{18}$, Fig. S1. Here we see that the cage electrons in Au$_3$Ge$_{12}$ are much more localized than in Au$_3$Ge$_{18}$. 

**Fig. S1.** (a) HOMO and (b) LUMO of neutral [Au$_3$Ge$_{18}$] where the right column is a slice of the 3D orbitals shown on the left.
Fig. S2. Clusters of \(\text{Au}_{n}\text{Ge}_m\); (a)-(e), \(n = 1\), III\(_1\), IV\(_1\), V\(_1\), VI\(_1\), VII\(_1\); (f) and (g), \(n = 2\), II\(_2\) and (b) IV\(_2\); (h) - (l), \(n = 3\), I\(_3\), II\(_3\), III\(_3\), IV\(_3\), V\(_3\). For \(n = 1\), clusters are shown only for after CG minimization. Cluster IV\(_1\) only differs from VI\(_1\) due to a smaller horizontal cross section. For \(n = 2, 3\), clusters are shown after CG minimization and also after a MD run.
Fig. S3. (a,c) HOMO and (b,d) LUMO of neutral AuGe$_{12}$ I$_1$.

Fig. S4. (a,b) Degenerate HOMO and (c) LUMO of neutral AuGe$_{12}$ II$_1$.
Fig. S5. (a) HOMO states and (b) LUMO of neutral Au$_2$Ge$_{12}$ I$_2$.

Fig. S6. (a) HOMO and (b) LUMO of neutral Au$_2$Ge$_{12}$ III$_2$.

Fig. S7. (a) HOMO and (b) LUMO of neutral Au$_3$Ge$_{12}$ I$_3$. 