Geometries, stabilities, and electronic properties of Be-doped gold clusters: a density functional theory study*

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We have systematically investigated the geometrical structures, relative stabilities and electronic properties of small bimetallic Au_nBe ($n = 1, 2, \ldots, 8$) clusters using a density functional method at BP86 level. The optimized geometries reveal that the impurity beryllium atom dramatically affects the structures of the Au_n clusters. The averaged binding energies, fragmentation energies, second-order difference of energies, the highest occupied-lowest unoccupied molecular orbital energy gaps and chemical hardness are investigated. All of them exhibit a pronounced odd–even alternation, manifesting that the clusters with even number of gold atoms possess relatively higher stabilities. Especially, the linear Au_2Be cluster is magic cluster with the most stable chemical stability. According to the natural population analysis, it is found that charge-transferring direction between Au atom and Be atom changes at the size of $n = 4$.

Keywords: Au_nBe clusters, geometrical configuration, density functional method

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1. Introduction

Bimetallic clusters have been widely studied in recent years,[1−6] primarily because these clusters often exhibit more favourable physical and chemical properties than the corresponding pure metals.[7−9] Especially for doped gold bimetallic clusters, they have been extensively investigated due to their potential applications in materials science, microelectronics, biology, medicine and nanotechnology.[10−18]

In order to explore more properties, lots of studies on gold clusters doped with different atoms have been conducted by many groups. For instance, Torres *et al.*[19] studied the structures, electronics and magnetic properties of Au_nM^+ clusters (M=Sc, Ti, V, Cr, Mn, Fe, Au; $n \leq 9$) using density functional calculations in which the magnetic moment showed pronounced odd–even alternation phenomenon as a function of the cluster size. The stability of cationic clusters Au_nM^+, with M from Sc to Ni, were investigated by Neukermans and co-workers[20] using photofragmentation experiments. The electronic structures and magnetic properties of ring Au_6 cluster anions with doped metal atoms, MAu_6^- (M=Ti, V, Cr), were investigated by Li *et al.*[21] using combined photoelectron spectroscopy and density functional theory calculations. Graciani *et al.*[11] proved that the isolated V-doped Au_{12}^- clusters can bind a large number of oxygen molecules well above those in pure clusters and are deemed to be an improved novel catalyst for CO oxidation. Recently, we have studied the structures and electronic properties of Au_nFe (n = 1, 2, ..., 7) clusters[22] and copper-gold clusters.[23] We found that the lowest energy doped gold clusters are very similar to those of the ground-state gold clusters and all of them favour planar structures. For the copper-gold clusters, there is an interesting phenomenon that the charge-transferring direction between Cu and Au atoms changes as the cluster size increases. For beryllium-gold clusters, Balducci *et al.* reported the dissociation energy, vibration frequency and bond energy of bimetallic AuBe dimer by using mass spectrometry and density functional theory.[24] However, no systematic studies on beryllium-gold clusters have been further performed and reported. In this case, what geometrical structures and properties will appear when beryllium is doped into gold clusters?

In order to gain further insight on Au_nBe ($n = 1$, 2, ..., 8) clusters, we systematically study the geometrical structures, relative stabilities and electronic properties of gold clusters doped with beryllium atom using density functional method at the BP86 level.

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The calculated averaged binding energies, fragmentation energies, second-order difference of energies, the highest occupied–lowest unoccupied molecular orbital energy gaps and chemical hardness all exhibit a pronounced even–odd alternation phenomenon as a function of the cluster size. According to calculated results, the linear Au_2Be structure is proved to be the most stable isomer of Au_nBe (n = 1, 2, ..., 8) clusters. In addition, natural population analysis (NPA)[25,26] results show that charge-transferring direction between Be and Au atoms changes at the size of n=4. It is hoped that our theoretical study not only would be useful for deeply understanding the influence of local structure on material's properties, but also can provide powerful guidelines for the future experimental researches.

2. Computational methods

The structure optimizations, together with the frequency analysis of Au_nBe (n = 1, 2, ..., 8) clusters, have been performed using the density functional theory (DFT) method, as implemented in the GAUSSIAN 03 program.[27]

For the Au atom, the full electron calculation is rather time-consuming, so we adopt the relativistic effective core potentials to describe the inner-core electrons. Then, the basis sets labeled GENECP are the combinations of LANL2TZ (f)[28−30] and 6-311+G (d)[31,32] basis sets, which are adopted to describe the Au and Be atoms, respectively. Due to the spin polarizations, every initial structure is optimized at various possible spin multiplicities. It is worth while pointing out that all of the clusters are found to prefer the lowest spin state. The reliabilities of our computations have been tested by comparative calculations on AuBe and Au_2 dimers. The results including bond lengths, vibrational frequencies and dissociation energies are summarized in Table 1. It can be seen from Table 1 that the results based on BP86[33−36] method agree better with experimental values than others.

Table 1. The calculated bond lengths (r), dissociation energies (D_e), and frequencies (ω_e) for the AuBe and Au_2 clusters, 1 Å=0.1 nm.

	AuBe			Au_2		
Methods	r/Å)	D_e/eV	ω_e/cm^{-1}	r/Å	D_e/eV	ω_e/cm^{-1}
PW91	2.05	2.72	608.60	2.52	2.32	176.60
PW91P86	2.05	2.77	609.66	2.52	2.43	178.00
B3LYP	2.06	2.30	592.92	2.55	1.98	169.47
BP86	2.06	2.65	605.54	2.52	2.28	176.21
Experimental	2.06[a]	2.9[a]	607.68[a]	2.47[f]	2.30[f]	191.00[f]
		2.48[b]				
		3.28[c]				
		2.06[d]				
		2.425[e]				

[a]Ref. [37], [b]Ref. [38], [c]Ref. [39], [d]Ref. [40], [e]Ref. [24], [f]Ref. [41]

3. Results and discussion

3.1. Geometrical structures

In order to discuss the effects of impurity atom on the pure gold clusters, we first perform some calculations on Au_n (n = 2, 3, ..., 9) clusters. The lowest energy structures of Au_n clusters are displayed in Fig. 1. For Au_nBe clusters at each size, although we obtain lots of stable structures, we only show a number of optimized low-lying isomers in Fig. 1. According to the energies from low to high, these isomers are designated by na, nb, nc and nd, where n represents the number of Au atoms in the Au_nBe (n = 1, 2, ..., 8) clusters.

All the ground-state structures of Au_n (n = 2, 3, ..., 9) clusters favour the planar structures and no three-dimensional (3D) isomers are obtained. For the Be-doped gold clusters, due to the influence of the Be atom, it is worth while pointing out that the ground-state geometries of Au_nBe clusters for n = 2, 6, 7, and 8, are different from those of pure Au_{n+1} clusters. The bond length of AuBe dimer is 2.06 Å, which is shorter than that of Au–Au (2.52 Å). There may be two reasons: one is the smaller Be atom radius than that of Au atom; the other is the ionicity and covalence effects of Be–Au bond. For Au_3 clusters, the $^2E'$ state with

D_{3h} symmetry undergoes pseudo-Jahn–Teller distortion. It is distorted from D_{3h} to C_{2v} structures which are respectively the ground-state $^2B_2$ and excited state $^2A_1$. The optimized results of Au_2Be clusters illustrate that the linear isomer 2a, with $D_{\infty h}$ symmetry, is the most stable structure. Another linear structure 2b with Be atom at one end is the next isomer with 2.09 eV higher in energy than the 2a isomer. The trigonal structure 2c is the second metastable structure, with a distance 2.18 Å and angle 76.0° between Be–Au. The most stable configurations of Au_3Be and Au_4Be clusters have structures similar to the ground-state of pure gold clusters. The Y-shaped isomer 3a with C_{2v} symmetry can be obtained by replacing the central Au atom in the ground-state of Au_4 cluster. The most stable structure of Au_4Be clusters is a distorted trapezoid, in which the Be atom moves on the centre location of the Au_5 frame due to the stronger interaction of Be–Au bond. In the case of Au_5Be clusters, the lowest energy structure (5a) and other three low-lying isomers (5b, 5c, 5d) are obtained in energy range 0.79 eV. When the fifth Au atoms cap on different sites of 4a structure, two planar structures 5a and 5b are generated. With regard to the Au_6Be clusters, four isomers are shown in Fig. 1. The ground-state structure 6a with C_{2v} symmetry is found to be the most stable structure among all isomers. The planar isomer 6c, with a central Be atom surrounded by six Au atoms, is a high-symmetry (D_{2h}) structure, which is expected to be the lowest energy structure. However, its energy is higher by 0.12 eV than that of 6a isomer. As for Au_7Be clusters, the optimized structures are displayed in Fig. 1. The most stable structure of Au_7Be clusters is the planar 7a isomer with C_{2v} symmetry, which can be viewed as Au atom capping on isomer 6a. The geometry of 7b isomer is similar to the 7c isomer, but the energy of 7b is lower by 0.02 eV than that of the 7c. According to our calculations, the lowest energy structure (8a) of Au_8Be is also a planar configuration. We find three other structures (8b, 8c, 8d) within 0.31 eV of the lowest energy. Closest in energy the isomer (8b), which is the most stable 3D structure with D_{3h} symmetry, is still less stable than 8a isomer by 0.27 eV.

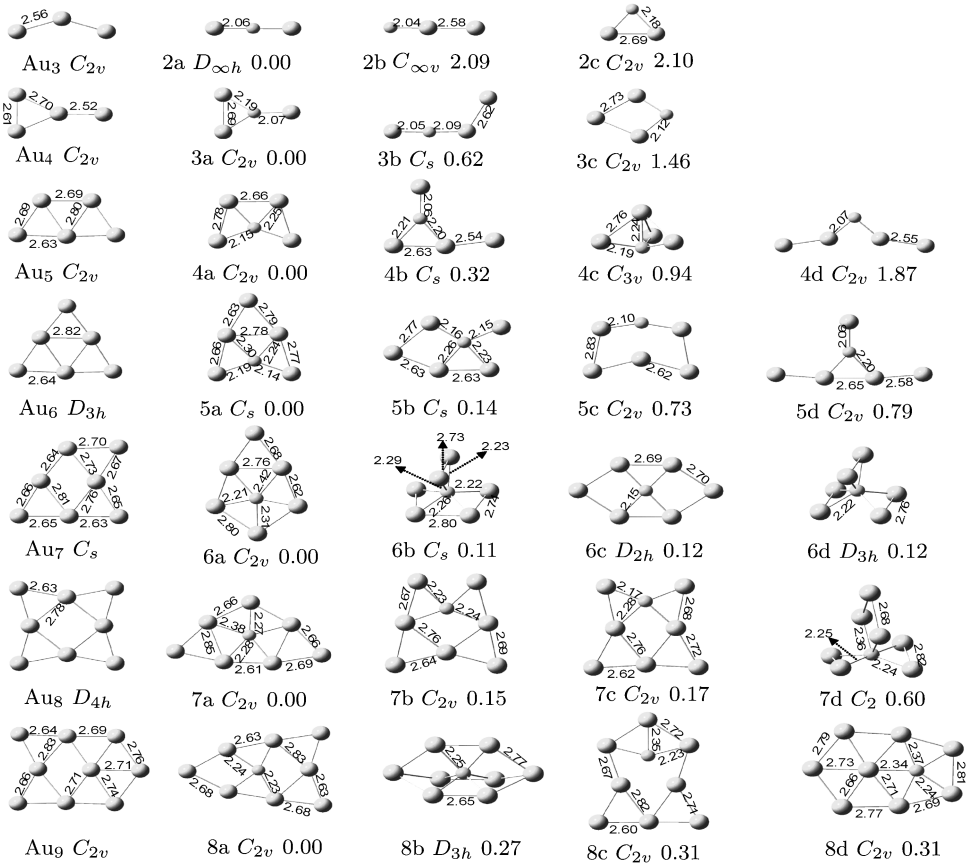


Fig. 1. The lowest energy structures and low-lying isomers for Au_nBe ($n = 2, 3, \ldots, 8$) clusters and the ground-state structures of pure gold clusters Au_{n+1} ($n = 2, 3, \ldots, 8$) have been listed on the left. The corresponding point-group symmetries and bond lengths (Å) along with relative stabilities (eV) are presented by the BP86 calculations.

3.2. Relative stabilities

In this subsection, the relative stabilities of Au_nBe (n = 1, 2, ..., 8) clusters are analysed based on the averaged binding energies, fragmentation energies and second-order difference of energies. Considering the influence of the impurity atom on the pure gold clusters, we compared all the following calculations with the Au_{n+1} clusters.

The averaged binding energies for Au_nBe and Au_{n+1} clusters can be defined as the following formula:[42]

$$E_b[Au_nBe] = (nE[Au] + E[Be] - E[Au_nBe])/(n+1), \quad (1)$$

$$E_b[Au_{n+1}] = \{(n+1)E[Au] - E[Au_{n+1}]\}/(n+1), \quad (2)$$

where E[Au], E[Be], E[Au_n Be], and E[Au_{n+1}], represent the total energies of the most stable Au atom, Be atom, Au_nBe cluster and the Au_{n+1} cluster, respectively. The relationships of E_b for the lowest energy Au_{n+1} and Au_nBe clusters versus n are plotted in Fig. 2(a). In Fig. 2(a), it is found that the averaged binding energies of Au_{n+1} clusters have a gradually increasing tendency with increasing clusters size, which is in accord with the results of previous work.[43] For Au_nBe clusters, the averaged binding energies display odd–even oscillatory behaviour. Namely, the clusters with even number of Au atoms have a higher relative stability compared to their neighbours. Particularly, a visible peak occurs at n=2 in the curve, which hints that Au_2Be isomer is relatively more stable than its neighbouring clusters. In addition, the averaged binding energies of Au_nBe clusters are significantly higher than those of Au_{n+1} clusters. This character illustrates the impurity beryllium atom can enhance the stability of gold clusters for n = 1, 2, ..., 8.

To further investigate the stability of the Au_nBe clusters with the size-dependent behaviour, the fragmentation energies ΔE is introduced, which can be defined as

$$\Delta E[Au_nBe] = E[Au_{n-1}Be] + E[Au] - E[Au_nBe], \quad (3)$$

$$\Delta E[Au_{n+1}] = E[Au_n] + E[Au] - E[Au_{n+1}], \quad (4)$$

where E represents the energy of the ground-state cluster or atom. The relationships between ΔE and clusters size[44] are plotted in Fig. 2(b). As shown in Fig. 2(b), the fragmentation energies of the Au_nBe and Au_{n+1} clusters all exhibit pronounced odd–even alternations. However, it is clearly found that the doped impurity atom makes the stable pattern of the host cluster contrary. In Fig. 2(b), particularly prominent maxima are found at n = 2, 4, 6, for Au_nBe cluster. This indicates that the clusters containing even number gold atoms have a higher relative stability as compared with their neighbours.

The second-order difference of energies ($\Delta^2 E$), another useful quantity for determining the stability of clusters, is often compared directly with the relative abundances determined in mass spectroscopy experiments.[44] For the ground-state Au_nBe and Au_{n+1} clusters, it can be defined as

$$\Delta^2 E[Au_nBe] = E[Au_{n+1}Be] + E[Au_{n-1}Be] - 2E[Au_nBe], \quad (5)$$

$$\Delta^2 E[Au_n] = E[Au_{n+1}] + E[Au_{n-1}] - 2E[Au_n], \quad (6)$$

where E is the energy of the ground-state clusters. The relationships between the second-order difference of energies and the cluster size for the most stable Au_nBe and Au_{n+1} clusters are displayed in Fig. 2(c), in which the curves of $\Delta^2 E$[Au_nBe] and $\Delta^2 E$[Au_n] both show obvious odd–even oscillation. This is consistent with the results based on the fragmentation energies.

3.3. Electronic properties

The electronic properties of Au_nBe (n = 1, 2, ..., 8) clusters are investigated in terms of the energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The HOMO–LUMO energy gap reflects the ability for electrons to jump from occupied molecular orbital to unoccupied molecular orbital, which represents the ability of molecule to participate in chemical reaction to some degree. For the ground-state of Au_nBe (n = 1, 2, ..., 8) clusters, the HOMO–LUMO energy gaps ranging from 0.25 eV to 3.36 eV can be obtained and the size dependence of the HOMO–LUMO energy gaps for the lowest energy isomers is plotted in Fig. 2(d). As seen in Fig. 2(d), the HOMO–LUMO energy gaps for Au_nBe and Au_{n+1} clusters also show a visible odd–even oscillation and the energy gaps of Au_nBe clusters are distinctly higher than those of Au_{n+1} clusters for even n. Especially for Au_2Be cluster, it has a particularly large value (3.36 eV). Based on the above analysis, the Au_2Be cluster can be viewed as the building block of the novel material due to its large relative stability and strong chemical stability.

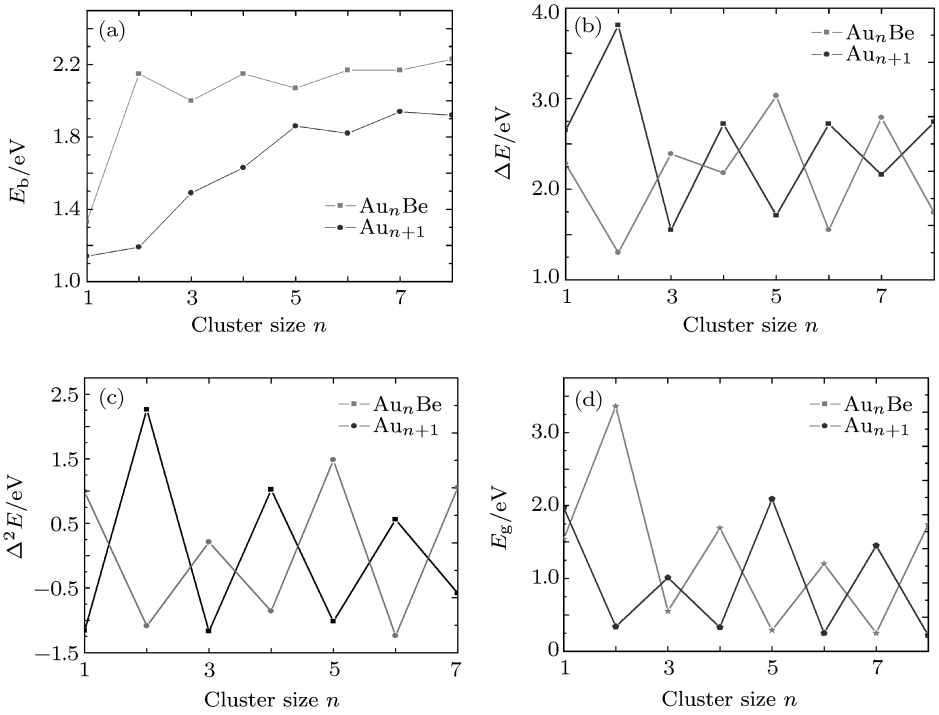


Fig. 2. (a) Size dependence of the averaged binding energies, (b) fragmentation energies, (c) second-order difference of energies, and (d) the HOMO–LUMO energy gaps for the ground-state Au_nBe and Au_{n+1} clusters.

Previous investigations suggested that charge-transferring direction may be changed when the size of the TM-doped Si_n clusters (TM=Ni, Ta and Zr) increases.[45–47] However, according to the natural population analysis of Au_nBe clusters, we also discovered this interesting phenomenon. From Table 2, it can be clearly seen that the beryllium atom possesses charges ranging from $-0.381e$ to $0.403e$ and the charge-transferring direction between Au atom and Be atom changes at $n = 4$. In other words, the charges in the small-sized cluster ($n \leq 3$) transfer from Be atom to Au atoms. On the contrary, the charges in the middle-sized clusters ($4 \leq n \leq 8$) transfer from Au atoms to Be atom.

Table 2. Natural charge populations of the lowest-energy Au_nBe ($n = 1, 2, \ldots, 8$) clusters.

	Be	Au-1	Au-2	Au-3	Au-4	Au-5	Au-6	Au-7	Au-8
AuBe	0.361	–0.361							
Au_2Be	0.403	–0.201	–0.201						
Au_3Be	0.035	0.044	0.044	–0.123					
Au_4Be	–0.381	0.064	0.127	0.127	0.064				
Au_5Be	–0.231	–0.058	0.150	0.070	0.049	0.019			
Au_6Be	–0.373	–0.060	0.038	0.188	0.038	–0.018	0.188		
Au_7Be	–0.162	–0.009	–0.022	0.192	0.016	0.016	–0.022	–0.009	
Au_8Be	–0.036	0.027	0.066	–0.151	0.014	0.066	0.014	0.027	–0.027

3.4. Hardness

As an electronic property, chemical hardness has been used to characterize the relative stability of molecules. In a finite-difference approximation, the hardness can be defined as

$$\eta = V_{\mathrm{IP}} - V_{\mathrm{EA}}, \tag{7}$$

where V_{IP} and V_{EA} represent the vertical ionization potential and vertical electron affinity, respectively, which can be calculated by employing the following formulas:

$$V_{\rm IP} = E_{(\text{cation at optimized neutral geometry})} - E_{(\text{optimized neutral})}$$

and

$$V_{\rm EA} = E_{(\text{optimized neutral})} - E_{(\text{anion at optimized neutral geometry})}.$$

For the doped gold clusters Au_nBe (n = 2, 3, ..., 8), the values of chemical hardness, $V_{\rm IP}$ and $V_{\rm EA}$ are listed in Table 3, and the corresponding changes of η, $V_{\rm IP}$ and $V_{\rm EA}$ versus n are shown in Fig. 3.

Table 3. The calculated chemical hardness (η), vertical ionization potential ($V_{\rm IP}$) and vertical electron affinity ($V_{\rm EA}$) for Au_nBe (n = 2, 3, ..., 8) clusters.

n	η	$V_{\rm IP}$	$V_{\rm EA}$
2	8.02	9.02	1.00
3	5.03	7.72	2.69
4	5.93	8.04	2.11
5	4.26	6.62	2.36
6	5.01	7.51	2.50
7	3.93	7.21	3.27
8	5.62	8.37	2.75

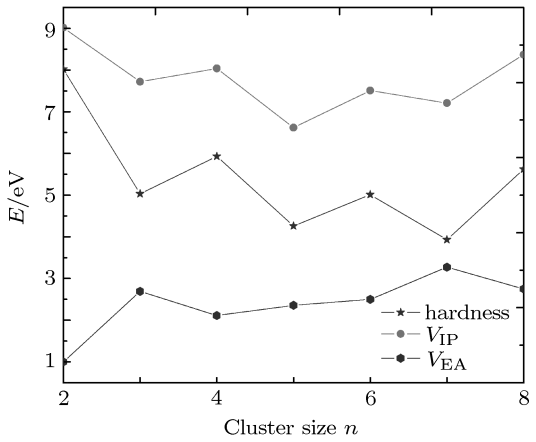


Fig. 3. Hardness, $V_{\rm IP}$ and $V_{\rm EA}$ in eV calculated at the BP86/genecp level for Au_nBe (n = 2, 3, ..., 8) clusters.

As seen in Fig. 3, the chemical hardness presents an obvious oscillating behaviour as the cluster size increases. It indicates that the clusters containing an even number of Au atoms possess a higher hardness, namely, they are more stable than their neighbouring ones. Particularly, the maximum occurs at n = 2, which hints that Au_2Be can be considered as the building block of the novel material for its large chemical hardness. Besides, the $V_{\rm IP}$ is one of the most important characteristics reflecting the size-dependent relationship of electronic structures in cluster physics. The trend of $V_{\rm IP}$ versus n shows the same oscillating behaviour as the corresponding chemical hardness, which implies that the clusters with even number of Au atoms have higher $V_{\rm IP}$ than those with odd number of Au atoms. Similar to the $V_{\rm IP}$, the vertical electron affinities also show a remarkable oscillation phenomenon, whereas the alternation pattern is opposite to that of $V_{\rm IP}$.

4. Conclusions

The geometrical structures, relative stabilities and electronic properties of the Au_nBe (n = 1, 2, ..., 8) clusters have been studied by density functional calculations at BP86 (LANL2TZ (f) for Au atom and 6-311+G (d) for Be atom) level. We find several interesting results, which are summarized as follows:

(i) The equilibrium geometries of Au_nBe (n = 1, 2, ..., 8) clusters are optimized. The results show that all the ground-state structures prefer the lowest spin multiplicity and the lowest energy configurations of Be-doped clusters are different from those of pure Au_{n+1} clusters.

(ii) The calculated fragmentation energies, second-order difference of energies, the HOMO–LOMO gaps and chemical hardness of Au_nBe clusters show that the clusters with even number of Au atoms are more stable than those with odd number of Au atoms. Particularly, the linear Au_2Be structure have the most stable chemical stability and can be viewed as the building block of the novel material for its large relative stability and strong chemical stability.

(iii) According to natural population analysis (NPA), we find that charge-transferr direction between Au and Be atoms changes at the size n = 4. When the size of Au_nBe is less than 4, charge transfers from Be atom to Au atom, whereas charge transfers from Au atom to Be atom when $n > 4$. This indicates that the charge distribution around Be atom appears clearly metallic in character for small-sized clusters and covalent in character for the middle-sized clusters. In addition, we also find the chemical hardness, $V_{\rm IP}$ and $V_{\rm EA}$ display odd–even oscillatory behaviour.

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