Systematic theoretical investigation of structure and electronic properties of pure copper and lithium doped copper clusters

Cheng-Gang Li\textsuperscript{a,b}, Hai-Jie Sun\textsuperscript{c}, Bao-Zeng Ren\textsuperscript{a}, Ya-Nan Tang\textsuperscript{b} and Meng Ju\textsuperscript{d}

\textsuperscript{a}School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou, China; \textsuperscript{b}School of Physics and Electronic Engineering, Quantum Materials Research Center, Zhengzhou Normal University, Zhengzhou, China; \textsuperscript{c}Department of Chemistry, Institute of Environmental and Catalytic Engineering, Zhengzhou Normal University, Zhengzhou, China; \textsuperscript{d}Institute of Atomic and Molecular Physics, Sichuan University, Chengdu, China

ABSTRACT
The pure copper and lithium-doped copper clusters are studied using the unbiased CALYPSO structure searching method and density function theory to understand the evolution of various structure and electronic properties. Theoretical results show the growth behaviours of doped clusters are organised as follows: Li capped \( \text{Cu}_n \) clusters or Li substituted \( \text{Cu}_{n+1} \) clusters as well as Cu capped \( \text{Cu}_{n-1} \) Li clusters. Moreover, the lowest energy structures of \( \text{Cu}_n \) Li favour planar structures for \( n \leq 3 \) and three-dimensional structures for \( n = 4-12 \). In addition, the calculated averaged binding energies, fragmentation energies and second-order difference of energies exhibit obvious odd–even alternations as cluster size increasing. At last, the highest occupied-lowest unoccupied molecular orbital gaps, molecular orbital energy, magnetic property, natural population analysis, natural electron configurations, electrostatic potential, electron density difference, Infrared and Raman spectra and density of states are also, respectively, operative for characterising and rationalising the electronic properties of doped clusters.

1. Introduction
In recent years, a considerable amount of effort has been focused on understanding the chemical and physical properties of molecules and solids. As a bridge between molecules and solids, cluster researches have been expanded into abundant aspects of metallurgy, microelectronics, catalysis, physical and chemical properties [1–5]. Cluster properties are sensitive to the number of atoms, which can change dramatically with the addition, substitution or removal of one atom from the clusters. So, we believe that the research for the evolution of structure can offer useful information for understanding the different physical and chemical properties of clusters.

In the light of the special sub-shell structure and valence electrons in lithium (1s\(^2\)2s\(^1\)) and copper (3s\(^2\)3p\(^6\)3d\(^{10}\)4s\(^1\)) atoms, investigations of the combination of copper and lithium atoms have been an active field to understand the structure and property in depth.
Experimentally, the bond length, frequency, binding energy, vertical ionisation potentials (VIP), vertical electron affinities (VEA), etc. are reported by many researchers for pure copper clusters and CuLi clusters [6–16]. In addition, with the development of rigorous calculation methods, numerous theoretical works have been performed by different programs, such as SIESTA, deMon-KS, ALLCHEM, Gaussian, etc. [17–24]. For example, density functional theory calculations of copper cluster \( \text{Cu}_n \) with \( n = 2-10 \) are analysed with respect to their molecular orbitals. It is shown that shell type orbitals of \( s, p, \) and \( d \) character govern the electronic structure growth and have an influence on the geometric structure [17]. The molecular structures, binding energy, structural and electronic properties of copper clusters are studied respectively by Jaque and Fernandez et al. [18,19]. Guzman-Ramirez and co-workers have studied minimum energy structures of copper clusters based on the genetic algorithm GEGA [20]. In addition, the static polarisabilities and polarisability anisotropies of copper and lithium clusters up to nine atoms are calculated in the framework of density function theory by Calaminici et al. [21]. The structural evolution of small copper clusters and the dissociative chemisorptions of \( \text{H}_2 \) on the minimum energy clusters are studied systemically by Guvelioglu et al. [22]. At last, the geometries, stabilities and electronic properties of \( \text{M}_m\text{Cu}_n \) (\( \text{M} = \text{Ge}, \text{Li} \)) and \( \text{Li}_n\text{Cu}_m \) (\( n, m \leq 4 \)) clusters are systemically investigated by Wang and Patricio et al. respectively [23,24]. For \( \text{Li}_n\text{Cu}_m \) clusters, the theoretical results show that the inclusion of lithium atoms on a bare copper cluster tends to break the Cu–Cu bond favouring the formation of polar Li–Cu bonds. Moreover, the electrons transfer from lithium to copper atoms. Although the \( \text{Li}_n\text{Cu}_m \) clusters have been observed, to our knowledge, there has been no report on \( \text{Li}_n\text{Cu}_m \) (\( n, m \geq 5 \)) clusters. And, a growing interest in theoretical modelling of bimetallic clusters has raised specific questions, such as: how does the evolution of ground structures change with increasing cluster size? How do the growth behaviours of doped clusters change as successive lithium atoms are added to make large species? Are their structures and properties greatly distinct from the pure copper clusters?

In order to further explore the structure and properties of doped clusters, in this letter, we investigate the evolution of structure and electronic properties of \( \text{Cu}_m\text{Li}_n \) clusters (\( n = 1–12 \)). Based on the CALYPSO (crystal structure analysis by particle swarm optimisation) method and the density function theory, we present extensive structure searches to explore the global minimum geometric structures. Our original motivation for this work is threefold. First, we hope that this work is to gain a fundamental understanding for the ground state structures. Second, our work is to re-examine a number of small doped clusters that have been reported previously by experimental or density function calculations. Finally, we expect that our research could be used a guide to explore the physical mechanism and provide relevant information for further theoretical and experimental studies.

In the following section (Section 2), we describe in brief the computational details. The ground state structure, growth behaviour and electronic properties are studied in Section 3. Finally, a summary is given in Section 4.

## 2. Computational details

Our approach involves global minimisation of energy surfaces, merging \textit{ab initio} total-energy calculation via CALYPSO cluster predication based on the particle swarm optimisation (PSO) algorithm in the CALYPSO code [25–27]. The significant feature of the method is the capability of predicting the stable structure with only the knowledge of the chemical composition at given external conditions. It has been successful in correctly predicting structures for various systems, including elements and binary and ternary compounds [25–32]. Structure predictions are, respectively, performed for copper and lithium-doped copper in current work. Each generation contains 30 structures, 70% of which are generated by PSO. The others are new and will be generated randomly. We followed 50 generations to achieve the converged structure.

The lowest energy candidate structures of the global minimum for each size are further to perform geometric optimisation using all electron density-function theory within generalised gradient approximation in the PW91 function, as implemented in the Gaussian 09 package [33]. For the noble copper metal, considering the all electron calculation is rather time consuming, so 19 electrons (3s\(^5\)3p\(^6\)3d\(^{10}\)4s\(^{1}\)) are considered, thus, replacing 10 core electrons with the effective core potential (ECP). Then, the basis sets-labelled GENECFP are the combinations of LanL2DZ and 6–311G(d) basis sets [34–38], which are implemented for the Cu and Li atoms, respectively. In order to determine an appropriate density functions, seven density functions (B3LYP, B3P86, B3PW91, BLYP, BP86, BPW91 and PW91) were performed in our calculations [39–45]. These density functions are commonly used in DFT calculations, and each has various degrees of success and merit. For a systematic comparison of all deviations from our calculations, the root-mean square (RMS) relative errors are calculated for each DFT functions. The parameter can be
Table 1. Calculated and experimental bond length (r), frequency (ω) and dissociation energy (D_e) for the Li_2, Cu_2 and CuLi clusters based on different sets and density functions, and root-mean square (RMS) relative errors in our calculation.

| Density function | Li_2  | Cu_2  | CuLi  |
|------------------|-------|-------|-------|
| r(Å)             | ω(cm^{-1}) | D_e(eV) | r(Å)     | ω(cm^{-1}) | D_e(eV) | r(Å)     | ω(cm^{-1}) | D_e(eV) | RMS |
| B3PW91           | 2.74  | 337.38| 0.81   | 2.25     | 260.07 | 1.92   | 2.29     | 381.78 | 1.70 | 0.117 |
| BPW91            | 2.75  | 328.51| 0.77   | 2.24     | 269.92 | 2.17   | 2.26     | 401.14 | 1.89 | 0.1059 |
| BP86             | 2.74  | 331.30| 0.89   | 2.23     | 274.57 | 2.32   | 2.25     | 406.22 | 2.08 | 0.0844 |
| BLYP             | 2.71  | 333.12| 0.89   | 2.25     | 264.16 | 2.28   | 2.24     | 408.69 | 2.09 | 0.0798 |
| B3LYP            | 2.70  | 343.25| 0.90   | 2.26     | 255.99 | 2.02   | 2.27     | 390.80 | 1.87 | 0.0763 |
| B3PW86           | 2.71  | 345.38| 0.89   | 2.24     | 267.53 | 2.07   | 2.27     | 392.80 | 1.87 | 0.0758 |
| PW91             | 2.73  | 331.84| 0.92   | 2.23     | 272.70 | 2.11   | 2.24     | 407.77 | 2.07 | 0.0672 |
| Exp [6-12]       | 2.673 | 351.4 | 1.056  | 2.22     | 265    | 2.08   | 2.26     | 465.9  | 1.95 |         |

expressed as:

\[
\chi_{exp} = \sqrt{\left( \frac{\chi_{exp} - \chi_{calc}}{\chi_{calc}} \right)^2_1 + \left( \frac{\chi_{exp} - \chi_{calc}}{\chi_{calc}} \right)^2_2 + \cdots + \left( \frac{\chi_{exp} - \chi_{calc}}{\chi_{calc}} \right)^2_n}
\]

where \( n \) is the number of experimental results for each parameter. In Table 1, we benchmark the performance of seven functions. Obviously, PW91 function gives the best performance. In addition, the effect of the spin multiplicity is performed in the geometric optimisation procedure, and a frequency analysis is carried to ensure the nature of the stationary points.

3. Results and discussions

3.1. Geometrical structures

3.1.1. Bare copper clusters \( \text{Cu}_n \) (\( n = 1-13 \))

To investigate the effect of impurity atoms on copper clusters, we performed firstly some optimisations and discussions on pure copper clusters by using an identical basis set and function. Based on the CALYPSO method, the lowest energy structures are optimised and shown in Figure 1 for copper clusters. Obviously, we can find that \( \text{Cu}_2 \) is a one-dimensional (1D) structure, \( \text{Cu}_3 \) to \( \text{Cu}_6 \) are two-dimensional (2D) systems, while \( \text{Cu}_7 \) to \( \text{Cu}_{13} \) are three-dimensional (3D) systems. Namely, \( \text{Cu}_7 \) cluster marks the transitional point for the structural changes from two to three dimensional. Furthermore, two growth patterns can be obtained here. The first is to remain essentially 2D and grow by forming successive triangle faces for \( n = 2-6 \). At \( n = 7 \), the growth pattern is abruptly interrupted, in which the cluster forms a pentagon bipyramid structure with the two capping atoms forming a bond (2.68Å). Attentionally, this geometric arrangement appears to be particularly stable and forms the basic structure on which larger copper clusters grow. Moreover, it becomes more closely packed with the increasing atomic number of clusters. Comparing with the previous theoretical research, we can find that the ground state structure in this work is in agreement with Ramirez and Jaque et al’s work [18,20].

3.1.2. Geometrical structures and growth behaviours

In a previous section, a detailed discussion of the growth behaviour was presented for \( \text{Cu}_n \) clusters. In the present section, the growth behaviour of \( \text{Cu}_n \) clusters will be discussed within the size range of \( n = 1-12 \). Optimisation with respect to spin has also been taken into account, finding that the lowest spin multiplicities are preferred, i.e. singlet for isomers with an even number of electrons and doublets for isomers with an odd number of electrons. Simultaneously, a harmonic frequency analysis was performed for all found structures to ensure they are the correct minima. In the view of space limitations, we merely list the lowest energy structure and a few low-lying isomers for each size in Figure 1.

For confirming the rationality of the basis sets and density functions, some experimental and calculated results are comprised. First, the ground state of \( \text{Cu}_3 \) has \( C_{2v} \) symmetry with a \( ^2\text{B}_2 \) state corresponding to a Jahn–Teller distortion of an equicrural triangle \( (R = 0.2307 \text{ Å}, \theta = 68.9479^\circ) \) in good agreement with the electron spin resonance spectrum studies [46]. In addition, VIP and VEA, the static mean polarisabilities \( \alpha \) and polarisability anisotropies \( |\Delta \alpha| \) are also presented in Figures 2 and 3 for \( \text{Cu}_n \) clusters, respectively. From Figures 2 and 3, we can see that our theoretical values are in good agreement with the previous and experimental results [13–16,21]. Second, the biatomic CuLi cluster with the electronic state is the ground-state structure; the calculated results about the bond length, dissociation energies and frequency are also in excellent agreement with available theoretical results [24,47,48]. In addition, the
Figure 1. Optimised structures of Cu$_n$ and Cu$_n$Li ($n = 1$–12) clusters, including their optimised energies and point group symmetries. The red (black) and purple balls represent copper and lithium atoms, respectively.
The calculated chemical potential ($\mu$) and hardness ($\eta$) for Cu$_n$Li ($n = 1, 3, 4$) clusters ($\mu$ = 3.68, 3.77, 3.71 eV, $\eta$ = 3.25, 2.91, 2.35 eV) are close to the previous theoretical values ($\mu$ = 3.18, 3.57, 3.29 eV, $\eta$ = 3.03, 2.73, 2.66 eV) [24]. Based on the above analysis, we can say that the agreement between the experimental data and calculated results is excellent. The reasonable agreement between the calculated and experimental values strengthens our choice of theoretical methods.

The first member of this series is the Cu–Li dimer. The optimised structure has a single spin state with $C_{\infty v}$ point group symmetry. The bond length is 2.24 Å and its frequency is 407.77 cm$^{-1}$. Adding a Cu atom to the optimised Cu–Li dimer with no symmetry constraints leads to Cu$_2$Li isomer. And, we can find that the lowest energy structure is an acute-angle triangular structure (2A) with $C_{2v}$ symmetry, a 60.79° angle, and 2.37 Å of Cu–Li bonds. The same structure also can be obtained by capping the Cu$_2$ dimer with a Li atom or by replacing a Cu atom in Cu$_3$ that is in a triangular geometry with a Li atom.

Two different geometries are optimised for the next cluster size, $n = 3$. The rhombus 3A isomer is optimised when a Cu atom is added to the 2A isomer or replaced a Cu atom in a planar Cu$_4$ rhombus structure with a Li. The other 3B isomer has a pyramid-like structure with electronic $^3A_1$ state and the energy of 3B isomer is 0.78 eV higher than that of the 3A structure.

With regard to the Cu$_n$Li clusters, the lowest energy structure show appearance of 3D geometries. 4A has $^2B_1$ electronic state, which is obtained by capping the planar Cu$_4$ rhombus with a Li atom (in the optimised structure, the planar rhombus is transformed into a bent rhombus structure). The planar fanlike structure (4C) can be obtained by capping the planar rhombus 3A in the same plane with a Cu atom on a Cu–Li arm. The trapezoid isomer 4B and 4D, which have identical $C_5$ symmetry, can be optimised after replacing one Cu atom at different sites for the ground state Cu$_5$ cluster.

When $n = 5$, the ground state (5A) shown in Figure 1 is obtained after one Cu adding on quadrangular pyramid structure (4A). The triangle 5B and 5C structures are similar and their energies are also very close to each other. These structures can be obtained by replacing a Cu atom by a Li from the top or edge of a triangular Cu$_6$ isomer. The next bipyramid structure 5D is energetically higher than the 5A, 5B and 5C isomer by 0.73, 0.36 and 0.30 eV, respectively.

Three different geometries were optimised for the next cluster size, Cu$_6$Li. First, from $n \geq 7$, the optimised Cu$_n$ structures begin to show appearance of 3D geometries. The first structure, 6A in Figure 1, is obtained by replacing a Cu atom in a top-capped Cu$_7$ cluster by a Li atom. Similarly, a new stable 6B structure can be born and is described as Li directly being replaced one Cu atom on the side of Cu$_7$ isomer. The difference between the optimised energies 6C and 6D is obvious. The optimised energy 6C is obtained when a Cu atom in the edge sites of 6A cluster is transferred to the bottom of 6A cluster. However, 6D can be obtained when a Cu atom is transferred to the top sites of 6A cluster. Among the stable isomers of Cu$_7$Li clusters, the ground-state 7A, with $C_6$ symmetry and electronic state of $^1A'$, can be yielded by replacing one Cu atom on the corner sites by impurity Li atom for Cu$_8$. However, one derived isomer (7B) can be optimised by replacing a Cu atom on the top sites by a Li atom. The higher symmetry isomer (7C or 7D) is described as on Cu atom added on isomer (6C or 6B), respectively. The total energy of the 7C and 7D clusters are higher than that of the 7A cluster by 0.11 and 0.16 eV.
Four different isomers were optimised for Cu₈Li clusters, the ground-state 8A can be obtained with an additional Cu cap on the other side of the 7D. The optimised structure of 8B is similar to that of 8C except in the position of the edge sites of Cu atom, and there is a minor difference in their optimised energies. The last isomer, 8D (C₂ᵥ point group symmetry), is a closed structure like a boat and has a total optimised energy close to that of the 8C isomer. When the size of CuₙLi clusters is up to 9, four kinds of structures can be verified to be the minima. Optimisation after adding a Li atom to different Cu–Cu side arm of the Cu₈ structure yield structure 9A, 9B or 9D. Isomer 9C is a modified bicapped pyramidal Cu₈Li (6A) structure with a boated base, where three additional Cu atoms have been added as side-capped elements. All of these structures have C₁ point group symmetry.

Following the growth pattern of the stable isomers in the CuₙLi series, four different stable isomers were optimised for Cu₁₀Li. Obviously, 10A and 10B structures are similar and their energies are very close to each other. These structures can be obtained by replacing a Cu atom by a Li from the top or edge of Cu₈Li isomer. 10C is obtained after adding a Li atom to one side of the Cu₁₀Li.

Four different isomers were optimised for Cu₆Li clusters, the first isomer, 11A, with C₃ᵥ point group symmetry, is an optimised structure with a modified 6A geometry capped by a Cu₅ quadrilateral on the open hexagonal face. Similarly, 11B can be obtained with a modified Cu₇ geometry capped by four Cu₄ and one Li atom. 11C is a combination of 6A and Cu₅ with an additional Cu atom at the edge position of Cu₇ isomer. In the isomer 11D, the optimised structure can be obtained by adding three Cu and one Li atom in the Cu₆Li isomer. All of these structures have C₁ point group symmetry.

The ground-state isomer 12A is obtained by adding one Cu atom to the 11C. The second structure 12B is optimised by transferring one Cu atom from the front of 12A to the behind of 12A. 12C is a combination of 6B and Cu₇ with two Cu atoms. For the fourth isomer, 12D can be optimised with a modified geometry by replacing a Cu atom by a Li atom.

Upon examining the growth pattern of CuₙLi clusters, it appears that CuLi is a 1D structure, Cu₂Li to Cu₃Li are ring structures, which is similar to the previous reported CuₙNa clusters [49]. When n ≥ 4, the ground-state structures exhibit a layer-like 3D configuration. Moreover, we also find that cluster growth can be classified into three different categories. The first is Li-capped structures where the Li atom is added to a smaller pure Cu cluster to form CuₙLi. Second, a Cu atom in Cuₙ₊₁ is replaced by a Li to form a CuₙLi cluster. Both of these categories are observed in the smaller cluster size range. Third, a Cu atom is added Cuₙ₋₁Li cluster to form CuₙLi. Furthermore, with an increase in size, we can find that Li directly substituted Cu atom of the Cuₙ₊₁ clusters and a Cu atom-added-Cuₙ₋₁Li clusters are dominant growth pattern.

### 3.2. Relative stabilities

The relative stabilities of CuₙLi clusters are discussed in this section on the basis of the various physical and chemical parameters – the averaged binding energies $E_b(n)$, fragmentation energies $\Delta_1E(n)$ and second-order difference of energies $\Delta_2E(n)$. For CuₙLi clusters, $E_b(n)$, $\Delta_1E(n)$ and $\Delta_2E(n)$ can be expressed as:

$$E_b(n) = \left[ n\left( E(Cu) + E(Li) - E(Cu_nLi) \right) \right] / (n + 1)$$

$$\Delta_1E(n) = E(Cu_{n-1}Li) + E(Cu) - E(Cu_nLi)$$

$$\Delta_2E(n) = E(Cu_{n-1}Li) + E(Cu_{n+1}Li) - 2E(Cu_nLi)$$

(2)

where $E(Cu_{n-1}Li)$, $E(Cu)$, $E(Cu_{n}Li)$ and $E(Cu_{n+1}Li)$ are the total energies of the corresponding clusters, respectively. For Cuₙ clusters, $E_b(n)$, $\Delta_1E(n)$ and $\Delta_2E(n)$ are defined as the follows:

$$E_b(n+1) = \left[ (n+1)E(Cu) - E(Cu_{n+1}) \right] / (n + 1)$$

$$\Delta_1E(n+1) = E(Cu_n) + E(Cu) - E(Cu_{n+1})$$

$$\Delta_2E(n+1) = E(Cu_n) + E(Cu_{n+2}) - 2E(Cu_{n+1})$$

(3)

where $E(Cu_{n-1})$, $E(Cu)$, $E(Cu_{n})$ and $E(Cu_{n+1})$ represent the total energy of the Cuₙ₋₁, Cu, Cuₙ and Cuₙ₊₁ clusters, respectively.

The calculated $E_b(n)$, $\Delta_1E(n)$ and $\Delta_2E(n)$ results of the lowest ground-state CuₙLi and Cuₙ₊₁ clusters ($n = 1-12$) clusters are plotted in Figure 4. Some primary features are concluded: (i) three conspicuous maxima are observed for the lowest ground state CuₙLi clusters at $n = 3, 7, 11$ on the size dependence of averaged binding energies, fragmentation energies, second-order difference of energies and highest occupied-lowest unoccupied molecular orbital energy gaps, implying that Cu₇Li, Cu₉Li and Cu₁₁Li clusters are magic clusters with relatively higher chemical stability. (ii) $E_b$ has an increasing tendency with the cluster size growing. And, the contributions to the $E_b$ are increase from Cu–Li (Cu–Cu) interaction. Simultaneously, $E_b$ curves of Cu₉Li and Cu₉₊₁ clusters increase noticeably from $n = 1$ to $n = 7$; then, the values show a smooth growing tendency in the clusters size range of $n = 8-12$. In addition, the $E_b$ values of Cu₉Li clusters are significantly lower than those of Cu₉₊₁ clusters, hinting that the impurities Li cannot improve the stabilities of copper clusters. Simultaneously, based on the dissociation energies of Cu₂, Li₂, and CuLi dimmers (2.08, 1.056 and 1.95 eV), these data adequately proved that the stability
is indeed decreased for Cu_nLi clusters. (iii) For the fragmentation energies $\Delta_1 E(n)$ and second-order difference of energies $\Delta_2 E(n)$, the positive values of $\Delta_2 E(n)$ mean that the clusters are particularly stable. Furthermore, we also find that the curves almost have the same tendency and exhibit obvious odd–even alternations, which may be due to the fact that both Li and Cu atoms possess an outermost $s$ valence electron. Finally, the Cu$_{11}$Li isomer corresponds to the local maxima of $\Delta_1 E(n)$, and the Cu$_7$Li isomer is a local peak of $\Delta_2 E(n)$. This is in accord with the above analysis based on $E_b(n)$ of Cu$_n$Li clusters.

In order to further investigate the stability of doped clusters and confirm the stability of the Cu$_n$Li clusters, the energy differences $E_{dis}(n)$ are also analysed for each size. The parameter are defined as follows:

$$E_{dis}(n) = E(Cu_n) + E(Li) - E(Cu_nLi)$$

$E(Cu_n)$, $E(Li)$ and $E(Cu_nLi)$ are the total energy of the ground state Cu$_n$, Li, and Cu$_n$Li clusters, respectively. Obviously, a local peak of $E_{dis}(n)$ is found in the Cu$_3$Li isomer in Figure 4. This also indicates that the Cu$_3$Li is relatively more stable than its neighbouring clusters.

3.3. The HOMO–LUMO gaps and molecular orbital energy

The highest occupied-lowest unoccupied molecular orbital (HOMO–LUMO) energy gaps have been proved to be a powerful tool to represent the ability of the molecule to participate in the chemical reaction in some degree. The larger results of HOMO–LUMO energy gaps correspond to a stronger chemical stability. For the lowest energy structures of Cu$_n$Li ($n = 1$–$12$) and Cu$_{n+1}$ clusters, the trends of HOMO–LUMO energy gaps with respect to cluster size are plotted in Figure 5. As shown in the figure, one can note that the HOMO–LUMO gaps present a similar odd–even oscillating behaviour as observed in $\Delta_1 E(n)$, $\Delta_2 E(n)$ and $E_{dis}(n)$. Moreover, the clusters with an even number of atoms have larger HOMO–LUMO gaps and are relatively weaker in chemical activity than those with odd number of atoms. As
already mentioned, the stability exhibited by even clusters is due to their closed shell states that always come along with an extra stability. This result agrees with the electronic shell jellium model [50,51], in which filled shell clusters are relatively stable. In addition, the local maximum values of HOMO–LUMO energy gaps are found at \( n = 3 \) for \( \text{Cu}_n\text{Li} \) clusters. This indicates that the magic cluster, \( \text{Cu}_3\text{Li} \) cluster, which has dramatically enhanced chemical stability, is in accord with the above analysis based on \( E_{\text{dis}}(n) \) of \( \text{Cu}_3\text{Li} \) clusters.

Figure 5. The HOMO–LUMO energy gaps for the lowest energy structure of \( \text{Cu}_{n+1}^+ \) and \( \text{Cu}_n\text{Li} \) \( (n = 1–12) \) clusters as a function of clusters size.

Figure 6 and Supporting Information show the molecular orbital energy levels together with their molecular orbital maps. It can be seen that \( \text{Cu}_3\text{Li} \) is characteristic of the degeneration of the molecular orbital energy level of HOMO, which probably leads to its largest value for the energy gap. Furthermore, the enhanced chemical stabilities can be also explained by the electron paired effect. The electron in a doubly occupied HOMO feels a stronger ECP since the electron screening is weaker for electrons in the same orbital than for inner shell electrons. Thus, the LUMO can hardly acquire an electron from the closed-shell HOMO of an even-number system than in the open-shell systems. Therefore, we can see that the clusters with even number of valence electrons are relatively stable.

3.4. Magnetic property

It is well known that the calculation of magnetic moments is foremost in elucidating how doped atoms are affected in impurity clusters. On the basis of the lowest ground states, the total magnetic moments of \( \text{Cu}_n\text{Li} \) and \( \text{Cu}_{n+1}^+ \), as well as the local magnetic moments of lithium and copper atoms, are presented in Table 2 and plotted in Figure 7, respectively. First, the total magnetic moments and local magnetic moments exhibit distinct odd–even oscillatory. More precisely, the clusters with odd-number valence electrons have a total magnetic moment of \( 1 \mu_B \). However, when the valence electrons are even, the cluster is a closed-shell system, whose \( \alpha \) and \( \beta \) spin orbitals are degenerating, so the corresponding magnetic moments are zero. Second, we can easily find that the local magnetic moments mainly come from Cu-4s orbital, while the 2p orbital bring the biggest effect for lithium atoms. So, the magnetic properties of clusters are related to a strong s–p orbital interaction.
For Cu$_3$Li cluster, the lithium atom-doped copper retains the planar structure and the system is non-magnetic. This can be understood as follows: the atomic configuration for a free lithium atom is 2s$^2$2p$^1$. When doped into Cu$_4$, the lithium atom undergoes s–p hybridisation. Due to the dopant, the Cu$_3$Li slightly distorts, such that the Cu–Li bond is 2.321 Å (the original Cu–Cu bond is 2.299 Å). There are no unpaired electrons or severe structural distortion, and thus no magnetism occurs at all.

### 3.5. Natural population analysis and natural electron configurations

To probe into the internal charge transfer, the natural population analysis (NPA) and the natural electron configurations (NECs) are summarised in Table 3. First, it is found that the Cu atom possess negative charges; the lithium atom has positive charges for Cu$_3$Li clusters. It means that the electrons transfer from Li atoms to Cu atoms. The results also coincide with the studied results of Patricio et al. [12]. Second, the values of 3d orbital reveal that the d orbital of the Cu atoms can be viewed as dominant core orbital in Cu$_n$Li clusters. With regard to lithium atom, 2p states make dominant contributions in Cu$_n$Li clusters. On the other hand, the valence electron configuration for free Cu and Li atoms is 3d$^{10}$4s$^2$ and 2s$^1$, respectively. When the Cu and Li atoms combine to form the Cu$_n$Li clusters, the configuration is 4s$^3$3d$^4$4p$^5$ for Cu atoms and 2s$^2$2p$^3$3p$^2$ for Li atoms, respectively. We can clearly see that the charge transfer happens between Cu 3d, 4s, 4p and Li 2s, 2p, 3p states. Therefore, we can conclude that there is spd hybridisation between Cu and Li atoms, and the electronic charge distributions of Cu$_n$Li clusters are primarily governed by d- and p-orbital interaction.

### 3.6. The electrostatic potential (ESP) and the electron density difference

To describe the potential energy associated with a charge distribution, the concept of electrostatic potential (ESP) is included. It may be employed to distinguish regions on the surface which are electron rich (subject to electrophilic attack) from those which are electron poor.

#### Table 2. Magnetic moment ($\mu_B$) of 2s, 2p and 3s states for Li atoms and 3d, 4s and 4p states for Cu atoms, respectively, as well as the local magnetic moment on Li and Cu atoms in the lowest energy Cu$_n$Li ($n = 1–12$) and Cu$_{n+1}$ clusters.

| Size | 3d/2s | 4s/2p | 4p/3s | Local | 3d | 4s | 4p | Local |
|------|-------|-------|-------|-------|----|----|----|-------|
| n = 1 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| n = 2 | 0.00/0.01 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| n = 3 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| n = 4 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| n = 5 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| n = 6 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| n = 7 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| n = 8 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| n = 9 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| n = 10 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| n = 11 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| n = 12 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00/0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

#### Table 3. The natural populations (NPA) and natural electron configuration (NEC) of the Cu and Li atoms for the lowest energy structures of Cu$_n$Li ($n = 1–12$) clusters.

| Clusters | Q (Cu) | Q (Li) | NEC (Cu) | NEC (Li) |
|----------|--------|--------|----------|----------|
| Cu$\text{ Li}$ | $-0.493$ | $0.493$ | $4s^{1.3}3d^{0.3}4p^{0.2}$ | $2s^{0.4}2p^{0.1}$ |
| Cu$_2$Li | $-0.536$ | $0.536$ | $4s^{0.9}3d^{1.0}4p^{0.2}$ | $2s^{0.4}2p^{0.1}$ |
| Cu$_3$Li | $-0.439$ | $0.439$ | $4s^{0.9}3d^{1.0}4p^{0.2}$ | $2s^{0.4}2p^{0.1}$ |
| Cu$_4$Li | $-0.317$ | $0.317$ | $4s^{0.9}3d^{1.0}4p^{0.2}$ | $2s^{0.4}2p^{0.1}$ |
| Cu$_5$Li | $-0.172$ | $0.172$ | $4s^{0.9}3d^{1.0}4p^{0.2}$ | $2s^{0.4}2p^{0.1}$ |
| Cu$_6$Li | $-0.029$ | $0.029$ | $4s^{0.9}3d^{1.0}4p^{0.2}$ | $2s^{0.4}2p^{0.1}$ |
| Cu$_7$Li | $-0.621$ | $0.621$ | $4s^{0.9}3d^{1.0}4p^{0.2}$ | $2s^{0.4}2p^{0.1}$ |
| Cu$_8$Li | $-0.585$ | $0.585$ | $4s^{0.9}3d^{1.0}4p^{0.2}$ | $2s^{0.4}2p^{0.1}$ |
| Cu$_9$Li | $-0.642$ | $0.642$ | $4s^{0.9}3d^{1.0}4p^{0.2}$ | $2s^{0.4}2p^{0.1}$ |
| Cu$_{10}$Li | $-0.294$ | $0.294$ | $4s^{0.9}3d^{1.0}4p^{0.2}$ | $2s^{0.4}2p^{0.1}$ |
| Cu$_{11}$Li | $-0.309$ | $0.309$ | $4s^{0.9}3d^{1.0}4p^{0.2}$ | $2s^{0.4}2p^{0.1}$ |
| Cu$_{12}$Li | $-0.435$ | $0.435$ | $4s^{0.9}3d^{1.0}4p^{0.2}$ | $2s^{0.4}2p^{0.1}$ |
Figure 8. Iso-electrostatic potential surfaces of the lowest energy structure of Cu$_n$Li ($n = 1–12$) clusters.

Figure 9. The electron density difference contour line map of Cu$_3$Li cluster in a two-dimensional plane.

Figure 10. The Gaussian broadened infrared intensities and Raman activities of Cu$_3$Li cluster. Insets show the frequency modes corresponding to the different intensity or activity.

(subject to nucleophilic attack) and has been found to be a very useful tool in investigation of correlation between molecular structure and the physiochemical property relationship of molecules. Therefore, based on the self-consistent-field molecular orbital methods, the ESP $V(\vec{r})$ evaluated at point specified by the position vector $\vec{r}$ is expressed as:

$$V(\vec{r}) = V_{nu}(\vec{r}) + V_{ele}(\vec{r}) = \sum_{A} \frac{Z_A}{|\vec{R}_A - \vec{r}|} - \int \frac{\rho(\vec{r}')}{|\vec{r}' - \vec{r}|} \, d\vec{r}'$$

(5)

where $Z_A$ and $\vec{R}_A$ stand for position vector and nuclear charge of atom $A$, respectively. If pseudopotential is used, then $Z$ is the number of explicitly expressed electrons. $\rho(\vec{r}')$ is the electron density as a function of the position vector $\vec{r}'$. Then, the isosurface of ESP of the lowest energy Cu$_n$Li species are displayed in Figure 8. Obviously, the colour of the transparent envelopes changes gradually from blue to red. The copper atoms reflect the most electronegative region and may show high electrophilic activity due to excess negative charge. Contrarily, the lithium atom show nucleophilic activity and reveal electronnegative region due to excess positive charge. Namely, the transparent envelopes close to the Li atom always show blue colour appearance means that the surrounding of Li atoms is positive potential. In other words, the charges
3.6. Electronic structure

Transfer of electron density from Li to Cu atom. This finding provides a support of our calculated results by aid of the NPA. It is well known that the electron density difference map can give a dynamic visualisation of electron redistribution upon molecule formation [52,53], which is defined as the difference between the total electron density and each constituent spherical atomic electron densities in molecular $\Delta \rho = \rho - \sum_i \rho_i$ ($i$ denotes the number of atom). Then, based on the Multiwn program [54], the 2D electron density difference map is performed in Figure 9. As observed in Figure 9, the solid lines indicate the regions in which the electron density difference has positive value ($\Delta \rho > 0$). That is to say, excess electron concentrate in this region, thus, the electron density difference will increase. The dashed lines show that the regions of the electron density difference are negative ($\Delta \rho < 0$), in which areas the electron is decreasing. In addition, we can see that the upward part of lithium atom is dashed lines, which means there is a large density flow from lithium to copper atom upon coordination. This is consistent to our expectation that the charges always transfer from Li atom to Cu atom due to larger electronegativity of the copper (1.90) than that of lithium (0.98). The result is in good agreement with the NPA and ESP.

3.7. Infrared and Raman spectra

In order to further check the structural feature and gain a deeper insight into the dynamical stabilities, the vibrational infrared (IR) and Raman spectra are calculated and displayed in Figure 10 for Cu3Li cluster. The insets show the direction vectors for the frequency with IR intensity or Raman activity. The two spectra can provide spectroscopic fingerprint to assist experimentalists to distinguish between different species and different isomers. From Figure 10, we can see that due to the high $C_{2v}$ symmetry, the Cu and Li contribute to the highest peaks of IR spectrum and Raman activity and the direction vectors are pointing to the outside in Figure 10. For the IR spectra, there are three conspicuous peaks. The highest intense peak of IR spectra is 103.4 km/mol at frequency 384.4 cm$^{-1}$. The second and third
degenerate IR intense peaks occur at frequencies 274.8 cm$^{-1}$ and 76.4 cm$^{-1}$. Raman activity mainly corresponds to the breathing modes, three strong vibration peaks are found. The highest Raman activity is 8.79 Å$^3$amu at frequency 384.4 cm$^{-1}$. Simultaneously, the topmost intensity is the breathing mode of the Cu atoms. And, we can find Cu and Li atoms move in the middle of clusters, and the other copper atoms remain static.

### 3.8. The density of states

Density of states (DOS) is an important concept in solid physics [55]. It indicates the number of states in unit energy interval. For isolated systems, the energy levels are discrete, and the concept of DOS is somewhat questionable. However, if the discrete energy levels are broadened to curves artificially, DOS graph becomes a valuable tool for visually characterising orbital composition [56–58]. In the present work, the total density of states (TDOS) and partial density of states (PDOS) from the contribution of different orbital components ($s$, $p$, $d$) are calculated for Cu$_3$Li and Cu$_4$ clusters in Figure 11. First, at around the Fermi level, the TDOS mainly originates from the states of Cu-$d$, Cu-$p$ and Li-$s$. By comparing the total and partial DOS, it is obviously found that the TDOS mainly generate the Cu-$d$ and Li-$p$ states. This result is in agreement with the above analysis based on the NECs. Second, the TDOS of Cu$_4$ and Cu$_5$Li at Fermi level are 4.603 and 6.087 eV, respectively. With the doped Li atom, the Fermi level gradually rises. In addition, the peak of TDOS is found at $-2.7005$ and $-2.8438$ eV for Cu$_3$Li and Cu$_4$ clusters, respectively. Then, we can say that impurities Li cannot improve the stabilities of copper clusters. This is in accord with the above analysis based on the averaged binding energies and HOMO–LUMO gaps.

### 4. Conclusions

We have report a detailed investigation on the structural evolution and electronic properties of Cu$_n$Li ($n = 1–12$) clusters using a combination of the unbiased CALYPSO structure searching method and density function theory. The results can be summarised as follows:

1. For Cu$_n$Li ($n = 1–12$) clusters, Li substituted Cu$_{n+1}$ clusters or Cu atom-capped Cu$_{n-1}$Li structures as well as Li-capped Cu$_n$ clusters are three kinds of dominating growth patterns. Based on optimised stable configurations, we observe that the ground-state structures are 2D structures very similar to those the pure copper cluster for $n = 1–3$ and 3D for $n = 4–12$ in Cu$_n$Li clusters.

2. The magic numbers of relative stabilities in terms of the calculated averaged binding energies, fragmentation energies, second-order difference of energies and HOMO–LUMO energy gaps are, respectively, 3, 7 and 11. Furthermore, the results also show that there exhibit a similar odd–even alternative phenomenon, indicating that the clusters with an odd number of copper atoms are more stable (or less reactive) than clusters with an even number of copper atom. In particular, we can conclude the clusters Cu$_3$Li and Cu$_5$Li have a dramatically enhanced chemical stability due to the larger HOMO–LUMO energy gaps of 2.49 and 2.06 eV, respectively. Furthermore, the atomic average binding energies of doped clusters are lower than those of pure clusters, indicating that the impurities lithium cannot improve the stabilities of copper clusters.

3. According to the electronic properties of doped clusters, we can see that the odd–even alternative behaviours are found in the magnetic moment (total or local), for which the clusters with odd-number valence electrons show relatively larger magnetic effects. Simultaneously, the magnetic properties of the clusters are related to a strong s–p orbital interaction. In addition, the electron transfer was discussed by the NPA, ESP and electron density difference. The results show that the electrons transfer from the Li atom to Cu$_n$ frames. The results of NECs manifest that there is spd hybridisation in Cu and Li atoms, and the electronic charge distributions of Cu$_n$Li clusters are primarily governed by d- and p-orbital interaction. At last, the calculated total density of states, as well as the partial density of states, clearly indicates that the TDOS mainly originates from the states of Cu-$d$, Cu-$p$ and Li-$s$ at around the Fermi level. Comparing with the peak of TDOS for Cu$_3$Li and Cu$_4$ clusters, we can find that the impurities Li cannot improve the stabilities of copper clusters.

### Disclosure statement

No potential conflict of interest was reported by the authors.

### Funding

National Natural Science Foundation of China [grant number 10974138], [grant number 11104190]; National Natural Science Foundation of China [grant number U1404109], [grant number 11504334].

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