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# Electronic Properties of Small Bimetallic $\text{Li}_n\text{Cu}_m$ ( $n, m \leq 4$ ) Clusters. A Comparison with $\text{Li}_n$ and $\text{Cu}_n$ Clusters

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**ABSTRACT:** The electronic structure and geometry of clusters of the type  $\text{Li}_n\text{Cu}_m$ ,  $\text{Li}_n\text{Cu}_m^{+1}$  ( $n, m \leq 4$ ),  $\text{Li}_n$ , and  $\text{Cu}_n$  ( $n \leq 8$ ) were theoretically investigated using density functional methods. The  $\text{Li}_n\text{Cu}_m$  bimetallic system is important to understand the promotion effects of the alkali atoms on the copper surface. Some clear trends have been found. The inclusion of lithium atoms on a bare copper cluster tends to break the Cu—Cu bond favoring the formation of polar Li—Cu bonds. In comparison with the bare  $\text{Li}_n$  and  $\text{Cu}_n$  clusters the geometrical shape and relative stability follow the same trend. However, the interatomic distances show strong variations. © 2005 Wiley Periodicals, Inc. *Int J Quantum Chem* 102: 498–505, 2005

**Key words:** copper; lithium; metal clusters; electronic structure

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## Introduction

The study of small metal clusters is an active area of research. Their properties may show both similarities to and differences from their bulk counterparts. Clusters containing from a few to several thousands of atoms have been investigated to study the evolution of properties of bulk matter

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from properties of atoms [1]. Most works have been done on homogeneous clusters. However, interesting questions pertain to the properties of impurity-induced defects. Therefore, bimetallic clusters have recently attracted the attention of chemists and physicists [2, 3]. Several experiments have addressed the question of presence or absence of electronic shells in bimetallic clusters by determining ionization potentials and reactivity [4–6]. Furthermore, bimetallic clusters may present better catalytic effects than simple metals [7, 8], and also in

some cases one expects the existence of a transition from a metallic to an insulator character, depending on the composition [9].

In this study, we focus on small  $\text{Li}_n\text{Cu}_m$  ( $n, m \leq 4$ ) clusters to understand their electronic properties as well as the geometrical structures. To our knowledge this is the first study of this family of clusters. They will be compared with the bare lithium and copper clusters. The former have been widely studied [10], whereas the latter are more complicated, from a theoretical point of view, and only few theoretical studies have been done [11]. The lithium clusters present a multicenter bond pattern with a marked s-p hybridization. On the other side, the copper clusters show little participation of the d-orbitals in the bonding but the s-p hybridization is not so favorable. However, both families of clusters present some similarities. The bare copper clusters are similar in structure to the lithium clusters, and both present a shell structure with the same magic numbers. Hence it is an interesting to know whether the mixed cluster preserves the same structures.

The bimetallic Li-Cu systems are important to understand the promotion effects of the alkali atoms on the copper surface [12]. Therefore, comparison of the bimetallic clusters with their pure metallic counterparts is important to understand the changes in electronic structure and in the chemical reactivity of the cluster.

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## Methodology and Computational Details

The electronic energy and properties were calculated by solving the Kohn-Sham equations in an atomic basis set formed by Gaussian functions. For the copper atoms the Stuttgart pseudopotential [13] with the corresponding basis set has been used. The pseudopotential replaces 10 core electrons, thus 19 valence electrons are considered. For the lithium atoms the D95 basis set [14] was used. Most of the calculations were done using the B3LYP [15] and the B3PW91 [15] exchange-correlation functionals. Because the results are generally very similar, only the B3LYP results have been incorporated into the tables. All the geometries were fully optimized without symmetry restrictions. The started geometries have been changed three or four times to have some confidence that the final geometry is the one

of lowest energy. All calculations were done using the GAUSSIAN98 program [16].

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## Results and Discussion

### GEOMETRIES

Figure 1 displays the geometrical structures of the three cluster families,  $\text{Li}_n$ ,  $\text{Cu}_n$ , and  $\text{Li}_n\text{Cu}_m$ . One can observe that the mixed clusters present a geometry similar to the corresponding bare clusters, with the exception of  $\text{Li}_3\text{Cu}_4$  where a pentagonal bipyramidal structure was not found. One possible explanation may be that the more symmetric tetrahedral structure with one vacancy presents Jahn-Teller distortion in the bare  $\text{Li}_7$  and  $\text{Cu}_7$  clusters. For the clusters with eight atoms, a tetrahedral structure has been predicted to be the one with lowest energy. It is important to consider that in many clusters various low-lying isomers can exist [10, 11] and, depending on the type of theoretical calculation, one can find one or another as the most stable one. Hence the comparison of calculated properties using a different methodology can be misleading. Figure 2 presents the geometrical structures of the positive charged  $\text{Li}_n\text{Cu}_m$  clusters. They are very similar to the structures of the neutral ones, with the exception of  $\text{LiCu}_4$ . In general, the clusters have similar structures: they are planar up to six atoms and then they are three-dimensional.

Now, we discuss the bond distance variations, for which the main information have been plotted in Figures 3–5. In Fig. 3, the shortest and average distances of the bare clusters  $\text{Li}_n$  and  $\text{Cu}_n$  are depicted. In both family of clusters the average distances approach smoothly the value of the bulk. The shortest distances show more variation, with a marked minimum for the clusters with four and eight atoms which may be due to the more compact structures and the shell effect. Figures 4 and 5 show the average and shortest distances for the mixed clusters, respectively. Three kinds of bond distances are shown, i.e., Cu—Cu, Li—Li, and Li—Cu. One can see that the Li—Cu distances in all cases are quite similar. They are approximately of the order of 2.4 Å. This indicates that in all mixed clusters Li—Cu bonds are formed. The Li—Li distances are in some cases even smaller than those in the bare lithium clusters. The Cu—Cu distances show a great variation among the studied clusters. They have marked maximum for the clusters with the same number of lithium and copper atoms, i.e.,

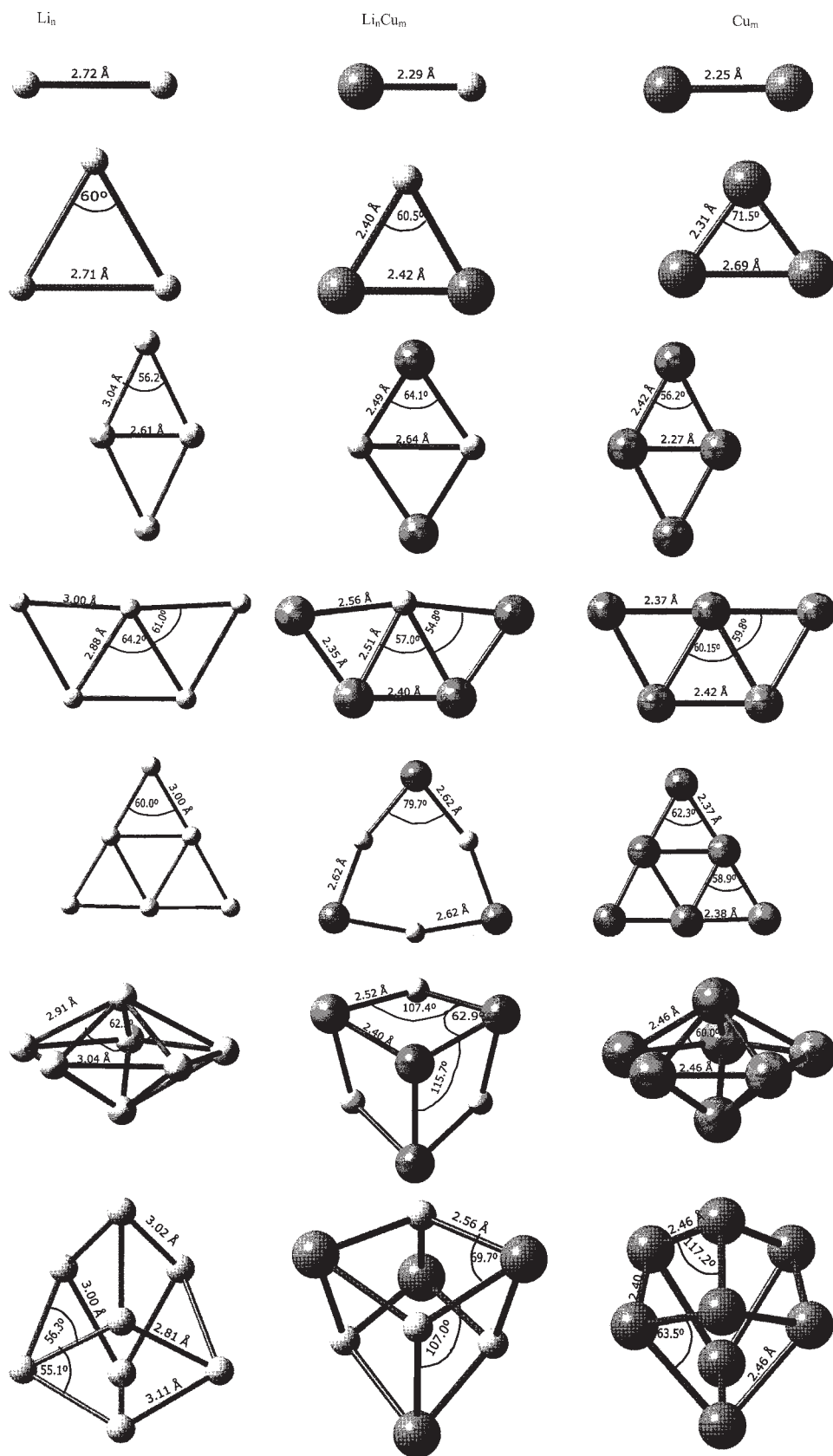


FIGURE 1. Geometrical structures of neutral  $\text{Li}_n$ ,  $\text{Cu}_n$ , and  $\text{Li}_n\text{Cu}_m$  clusters.

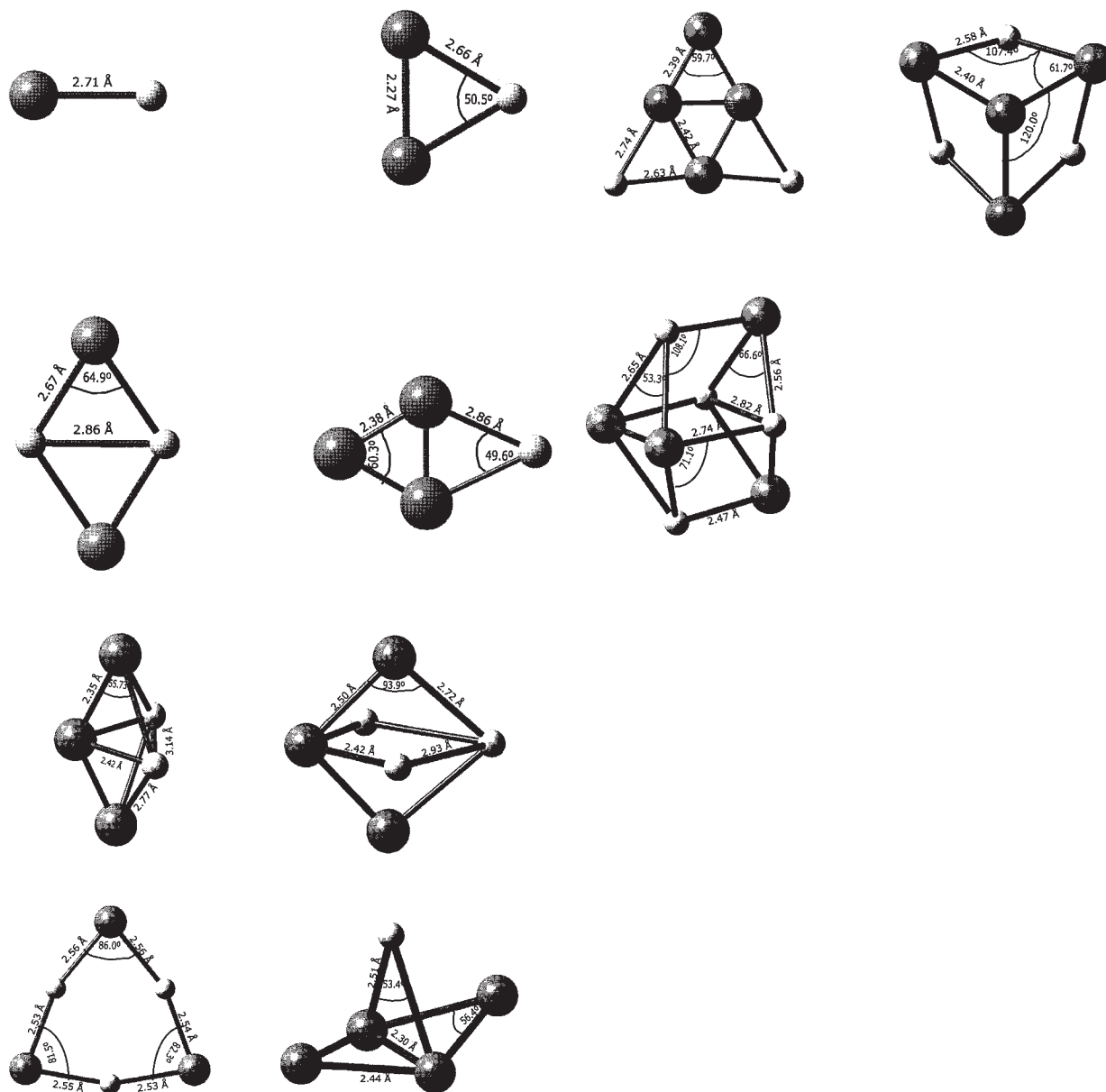


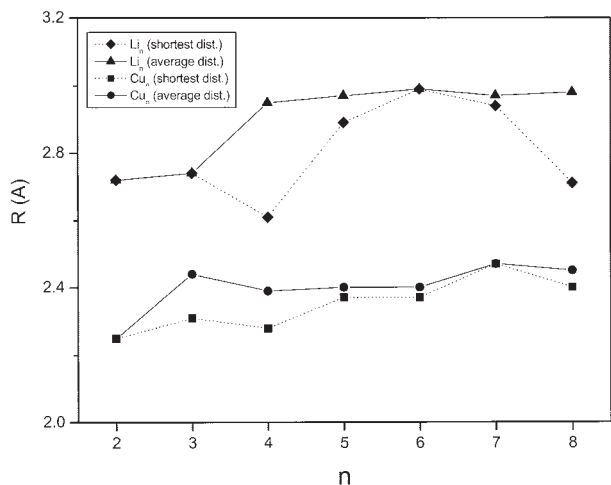
FIGURE 2. Geometrical structures of charged  $\text{Li}_n\text{Cu}_m$  clusters.

$\text{Li}_2\text{Cu}_2$ ,  $\text{Li}_3\text{Cu}_3$ , and  $\text{Li}_4\text{Cu}_4$ . In these cases, the shortest distances are greater than  $4.0 \text{ \AA}$ , indicating that there is not a Cu—Cu bond. It is clear that the inclusion of a lithium atom in a copper cluster breaks a bond between copper atoms and that the lithium atoms are located in the more coordinate center.

### ENERGIES

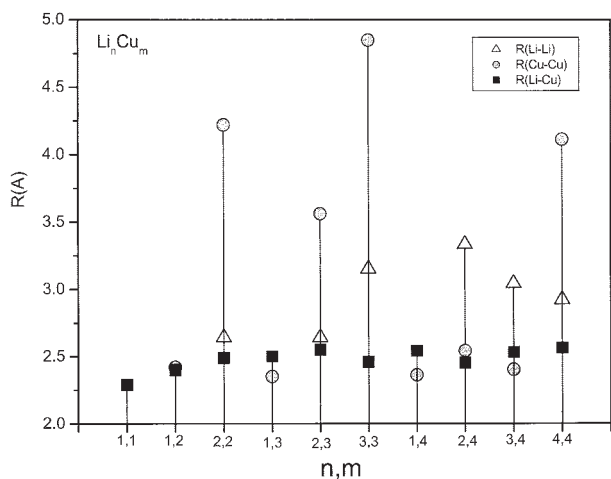
Now, we turn to the energetic characteristics of the studied clusters. For all the studied clusters, the

total energy, the binding energy per atom, and the vertical and adiabatic ionization potentials are collected in Table I. First, note [17] that the binding energy of the neutral  $\text{Li}_2$  is lower than that of charged  $\text{Li}_2^+$  which is against the most elemental molecular orbital model. Interestingly, the same is true for the other  $\text{Li}_n$  clusters as well as for the  $\text{Cu}_n$  clusters. However, the mixed clusters present the opposite, more normal, behavior. This indicates clearly that the nature of the bonds in the mixed cluster is different from the ones presented in the

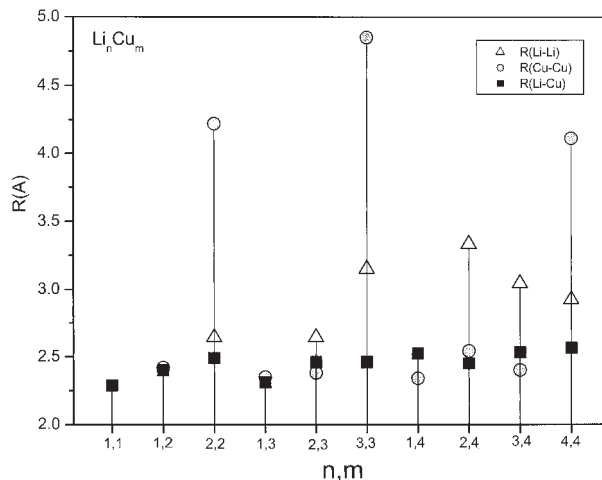


**FIGURE 3.** Shortest and average distances (in Å) for Li<sub>n</sub> and Cu<sub>n</sub> clusters.

bare clusters. The lithium clusters present binding energies much lower than the copper clusters, but the Li—Cu bond is almost as strong as the Cu—Cu bond, which is evident looking at the bond energies of Li<sub>2</sub>, Cu<sub>2</sub>, and LiCu. This explains the trend observed in Figure 6, where the bond energies per atom are displayed. The mixed clusters present bond energies very close to those of the copper clusters. In the last two columns of Table I one can observe the adiabatic and vertical ionization potentials. They present the known even–odd alterna-



**FIGURE 4.** Average distances (in Å) for Li<sub>n</sub>Cu<sub>m</sub> clusters.



**FIGURE 5.** Shortest distances (in Å) for Li<sub>n</sub>Cu<sub>m</sub> clusters.

tion, indicating clearly that the clusters with an even number of atoms are more stable.

Table II presents the chemical potential,  $\mu$ , and the hardness,  $\eta$ . Both quantities, defined in density functional theory [18], are commonly used to explain reactivity trends in molecules. The chemical potential is associated with the electronegativity concept and the hardness to the band gap of solids. Hence it is to expect that the hardness presents the same even–odd alternation encounter in the ionization potential. It is interesting to compare the hardness of the neutral clusters with the corresponding charged ones. The hardness is always higher in clusters with an even number of valence electrons, irrespective of the charge. In some cases, especially Li<sub>2</sub>Cu<sub>2</sub>, the charged cluster presents an extremely small hardness which could be indicative of an stable isomer of higher spin multiplicity. As a further test of the stability trends in the three family of clusters, the relative stability defined as

$$\Delta E = E(N + 1) + E(N - 1) - 2E(N) \quad (1)$$

is plotted in Figure 7.  $N$  refers to the total number of atoms. Of course, for the mixed clusters we have two different  $\Delta E$ . One relates to the gain or loss of a lithium atom and the other relates to the gain or lose of a copper atom. One can observe again the even–odd alternation being more stable in the clusters with an even number of atoms. The three families of clusters present the same trend, a clear sign

TABLE I

Total energies ( $E_{\text{tot}}$ ), binding energies ( $E_b$ ), and vertical ( $\text{IP}_v$ ) and adiabatic ( $\text{IP}_a$ ) ionization potentials for neutral and positive charged  $\text{Li}_n\text{Cu}_m$  clusters, with  $w = n + m$ .

	$E_{\text{tot}}$ (a.u.) neutral clusters	$E_{\text{tot}}$ (a.u.) charged clusters	$E_b/w$ (eV) neutral clusters	$E_b/w$ (eV) charged clusters	$\text{IP}_v$ (eV)	$\text{IP}_a$ (eV)
$\text{Li}_2$	-15.014719	-14.821946	0.44	0.62	5.34	5.25
$\text{Cu}_2$	-394.712081	-394.410231	0.94	0.97	8.28	8.21
$\text{LiCu}$	-204.879843	-204.628379	0.92	0.30	6.99	6.84
$\text{LiCu}_2$	-402.246756	-402.040259	1.02	1.02	5.80	5.62
$\text{Li}_2\text{Cu}_2$	-409.813897	-409.536745	1.28	0.80	6.76	7.54
$\text{Li}_3$	-22.502845	-22.370229	0.26	0.93	3.70	3.61
$\text{Cu}_3$	-592.065642	-591.844676	0.92	1.67	6.18	6.01
$\text{LiCu}_3$	-599.647781	-599.310950	1.31	1.04	6.76	6.70
$\text{Li}_2\text{Cu}_3$	-607.178528	-606.993011	1.26	1.37	6.04	5.05
$\text{Li}_3\text{Cu}_3(\text{I})$	-614.737384	-614.521147	1.36	1.31	6.47	5.88
$\text{Li}_3\text{Cu}_3(\text{II})$	-614.740740	-614.443900	1.37	0.96	7.07	8.08
$\text{Li}_4$	-30.055260	-29.888271	0.61	0.88	4.57	4.54
$\text{Cu}_4$	-789.464844	-789.162404	1.22	1.23	6.86	8.23
$\text{LiCu}_4$	-797.017615	-796.802037	1.31	1.26	6.25	5.87
$\text{Li}_2\text{Cu}_4$	-804.587236	-804.355078	1.45	1.33	6.49	6.32
$\text{Li}_3\text{Cu}_4$	-812.120916	-811.949703	1.41	1.54	5.13	4.66
$\text{Li}_4\text{Cu}_4$	-819.689060	-819.471869	1.49	1.45	6.86	5.91

that the relative stability of the clusters depends on the number of valence electrons irrespective of the kind of atom. This is, of course, a special case of the atoms with only one valence electron. Hence, the hardness, the relative stability as well as the binding energies point out that the shell effect is also present in the mixed clusters.

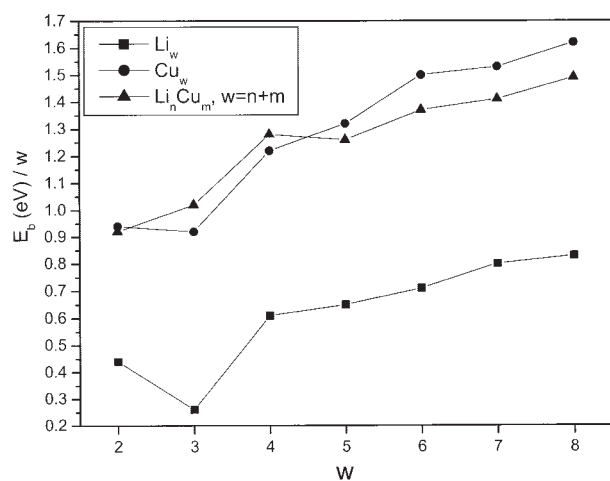


FIGURE 6. Binding energy per atom (in eV) for the three series of clusters.

Another way of looking at the electronic structure variations when a copper cluster is doped with lithium atoms is presented in Table III, which

TABLE II

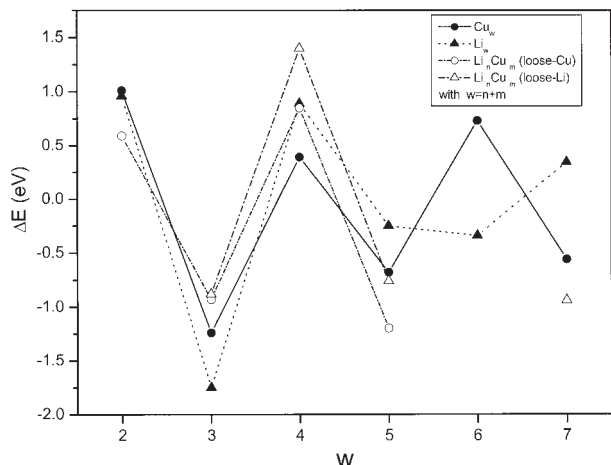
Chemical potential ( $\mu$ ) and hardness ( $\eta$ ) for  $\text{Li}_n\text{Cu}_m$  clusters.

	$\mu$ (eV) neutral	$\mu$ (eV) charged	$\eta$ (eV) neutral	$\eta$ (eV) charged
$\text{Li}_2$	2.54	7.76	2.19	2.58
$\text{Cu}_2$	4.26	11.59	3.33	2.08
$\text{LiCu}$	3.18	10.07	3.03	2.21
$\text{LiCu}_2$	3.08	9.33	1.59	3.94
$\text{Li}_2\text{Cu}_2$	3.28	9.36	3.29	0.04
$\text{Li}_3$	1.98	6.95	0.56	3.05
$\text{Cu}_3$	3.58	9.99	1.35	4.24
$\text{LiCu}_3$	3.57	8.36	2.73	3.30
$\text{Li}_2\text{Cu}_3$	3.49	7.93	1.55	2.86
$\text{Li}_3\text{Cu}_3(\text{I})$	3.36	7.75	2.71	1.41
$\text{Li}_3\text{Cu}_3(\text{II})$	3.57	9.78	3.75	0.06
$\text{Li}_4$	2.39	6.62	1.62	1.47
$\text{Cu}_4$	4.03	10.37	1.99	0.17
$\text{LiCu}_4$	3.29	8.55	2.66	2.07
$\text{Li}_2\text{Cu}_4$	3.55	7.10	2.47	2.76
$\text{Li}_3\text{Cu}_4$	3.00	7.28	1.34	3.43
$\text{Li}_4\text{Cu}_4$	3.52	7.70	3.68	1.58

shows the variations of the atomic binding energy per atom, the vertical ionization potential, and the hardness for the series  $\text{Cu}_4$ ,  $\text{Cu}_3\text{Li}$ ,  $\text{Cu}_2\text{Li}_2$ ,  $\text{CuLi}_3$ , and  $\text{Li}_4$ . As long as the clusters are dominated by Cu—Cu or Cu—Li bonds, which have similar bond energies, the atomic binding energies are similar, but already for  $\text{CuLi}_3$  the binding energy drops markedly. The same trend can be seen in the vertical ionization potentials. The variations in the hardness are interesting. Recall that the hardness represents the band gap of a solid; therefore, one expects a small hardness for metallic systems. This is the case in both extremes,  $\text{Cu}_4$  and  $\text{Li}_4$ . The clusters of  $\text{Cu}_3\text{Li}$  and  $\text{Cu}_2\text{Li}_2$  are governed by the formation of the polar Cu—Li bond which localize the electrons presenting higher values of hardness.

**CHARGES**

Table IV presents the calculated atomic charges in neutral clusters. Because the atomic charges are not physically observable, their definition is in some way arbitrary, and there are different forms to calculate them. Nevertheless, they are important in the study of trends among a family of systems. In this work, we compare the widely used Mulliken population analysis with the natural bond order (NBO) charges [19]. Table



**FIGURE 7.** Relative stability (in eV) of the three series of clusters. For the series  $\text{Li}_n\text{Cu}_m$ , a circle represents the lose of a copper atom and a triangle the lose of a lithium atom.

**TABLE III**  
Properties of a  $\text{Li}_x\text{Cu}_{n-x}$  family of clusters (in eV), with  $n = 4$  and  $x = 0-4$ .

	$\text{Cu}_4$	$\text{LiCu}_3$	$\text{Li}_2\text{Cu}_2$	$\text{Li}_3\text{Cu}$	$\text{Li}_4$
$E_b/n$	1.22	1.31	1.28	0.95	0.61
$\text{IP}_v$	6.86	6.76	6.76	5.38	4.57
$\eta$	1.99	2.73	3.29	2.15	1.62

IV depicts the results for the neutral clusters. Only the charges on the copper atoms are shown, and, whenever necessary, different values for the nonequivalent atoms are presented. The charges in the lithium atoms can be easily inferred from the neutrality condition. Note that the values refer to the number of electrons in excess at the respective atom. Because the important point is the study of trends along the series, in Columns 4 and 5 the results are normalized to the values obtained for  $\text{LiCu}$ . It is confirmed that both methodologies can give very different results in some cases. It is known that the Mulliken charges are not reliable, especially when the basis set contains diffuse functions [20]. Therefore, the use of the NBO methodology seems more appropriate. In all cases, the copper atoms take a fraction of electron charge from the lithium atoms, indicating the formation of a polar bond, and clusters with permanent dipole moment when the structure is not completely symmetric.

**Concluding Remarks**

The three families of clusters— $\text{Li}_n$ ,  $\text{Cu}_n$ , and  $\text{Li}_n\text{Cu}_m$ —were theoretically studied and their properties compared. We found that the lithium atoms donate charge to the copper atoms, breaking the Cu—Cu bonds. In comparison to the bare clusters, the mixed clusters present similar geometrical shapes and most of their properties follow the known even–odd alternation, depending more on the number of electrons than on the type of atom. The shell effect seems to be valid for the three families of clusters. However, the type of bond is different. The Li—Cu is a polar bond.

**TABLE IV**  
Mulliken and NBO charges on copper atoms.

	$q_{\text{Mu}}$ (Cu)	$q_{\text{NBO}}$ (Cu)	$q'_{\text{Mu}}$ <sup>a</sup>	$q'_{\text{NBO}}$ <sup>a</sup>
LiCu	-0.25	-0.57	1.00	1.00
LiCu <sub>2</sub>	-0.16	-0.36	0.64	0.63
Li <sub>2</sub> Cu <sub>2</sub>	-0.25	-0.63	1.00	1.11
LiCu <sub>3</sub>	-0.16, -0.05	-0.39, -0.04	0.64, 0.20	0.68, 0.07
Li <sub>2</sub> Cu <sub>3</sub>	-0.16, -0.17	-0.35, -0.59	0.64, 0.68	0.61, 1.04
Li <sub>3</sub> Cu <sub>3</sub> (I)	-0.15, -0.17	-0.61, -0.60	0.60, 0.68	1.07, 1.05
Li <sub>3</sub> Cu <sub>3</sub> (II)	-0.34	-0.57	1.36	1.00
LiCu <sub>4</sub>	-0.19, -0.03	-0.23, -0.08	0.76, 0.12	0.40, 0.14
Li <sub>2</sub> Cu <sub>4</sub>	-0.05	-0.41	0.20	0.72
Li <sub>3</sub> Cu <sub>4</sub>	-0.17, -0.1	-0.38, -0.15	0.68, 0.40	1.19, 0.70
Li <sub>4</sub> Cu <sub>4</sub>	-0.25	-0.55	1.00	0.96

<sup>a</sup> Charges normalized to the value on LiCu.

### ACKNOWLEDGMENTS

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