

Physical and chemical characterization of Pt_{12-n}Cu_n clusters via *ab initio* calculations

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The physical, structural, and chemical properties of bimetallic Pt_{12-n}Cu_n clusters, where n goes from 0 to 12, have been investigated within density functional theory. We find that the electronic and magnetic properties depend a lot on the atomic fraction of Cu atoms, mainly as the number of Cu atoms changes from even to odd. The chemical potential increases monotonically as a function of the Cu concentration, whereas other chemical properties such as electrophilicity depend on local changes and decreases monotonically, as well as the ionization potential. The hardness has an oscillatory behavior, which depends on the total number of electrons. The reactivity has been spatially analyzed by studying the highest occupied molecular orbital and lowest unoccupied molecular orbital. Charge delocalization is largely increased by the number of copper atoms, whereas for largely Pt concentrations, the charge is more atomiclike. That charge dependence gives another cluster outside view, which shows a rich spatial reactivity. The magnetic dependence of the cluster on the Cu atom concentration opens the door to potential chemistry applications on bimetallic magnetic nanostructures in the field of spintronics. © 2009 American Institute of Physics. [DOI: 10.1063/1.3187031]

I. INTRODUCTION

Alloys are among the material systems which have attracted a lot of attention due to large chemistry diversity when different atomic compositions are considered.¹ One of the fields, which has received a large momentum by these materials, is catalysis. Basically, assorted type of alloys gives a diversity on geometrical motifs and electronic properties, which leads to different surfaces reactivities, different interactions with molecular structures, and add new degrees of freedom in the case of interfaces. Those effects are embodied in what is called the ligand potential.² Between the different alloys scientists that have been working on, we consider the particular case of Pt–Cu.

Copper has been used as a second metal to improve the catalytic behavior in systems such as Ni–Cu, Ru–Cu, Os–Cu, and Rh–Cu.^{3–10} For example, by using these catalysts, the hydrocracking reactions, favored on the base metal, are strongly inhibited when copper is added. On the other hand, the important role played by Pt in chemical industry and in electrocatalysis points out that it is not surprising that alloys with this metal are still deeply studied. In the case of Pt–Cu alloys, there are several efforts to produce and characterize them by using different methodologies.^{11–13} On the other hand, Pt–Cu alloys have been investigated to elucidate the alloying effects in adsorption and catalysis of many different compounds.^{14–19} The dilution of Pt with Cu was found to be the main reason of the changes in catalytic activity and selectivity in reactions such as hydrogenation,²⁰ isomerization,²¹ hydrocracking,^{22–25} CO oxidation,^{26,27} and NO_x storage/reduction.^{28,29} For example, He *et al.*³⁰ and Liu

*et al.*³¹ reported the catalytic activity of oxygen electroreduction in several alloys and they found that, between others, Pt–Cu did show a large activity. On the other hand, Shek *et al.*³² showed the dependence of desorption of CO as function of the Cu doping concentrations on Pt and found interesting changes as the atomic composition is varied. Even though the Pt–Cu catalytic converter has a good performance advantage, platinum replacement by copper has another important attractive: Copper is one of the most abundant metals on the Earth's surface. Therefore, this bimetallic material is cheaper than pure Pt.

Bulk alloys are of great interest in many different fields, but more recently, scientists have started to look at the catalytic activities of alloy nanoparticles (see the nice review of Ferrando *et al.*³³ and the paper of Bönnemann and Richards³⁴ and references therein) mainly due to the changes in the chemical activity as well as optical properties with respect to the cluster size. Cluster can be obtained by many different means such as laser ablation or grinding, and they can be deposited on different types of surfaces to also modify the electronic properties. In general, current advances in nanofabrication techniques allow the preparation of catalytic nanoparticles with an improved potential performance. This is mainly because, at that scale, the catalytic activity depends on their structure, the surface/volume ratio, and the possibility of reaching alternative reactions paths that cannot be achieved with microscopic catalyst. Even though alloying is a pretty well known phenomenon, little is assessed when the alloy is persistent at a nanoscale. Therefore a valid question is how the activity is related to the alloy and how the structure is affected when alloy plays a role. Therefore, in this field of nanoscience, the understanding of the structural,

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electronic, and chemical properties of the ground state isomers of bimetallic atom clusters represents an important key issue.

With respect to Pt–Cu bimetallic clusters, there are only few reports in literature. Anguiano *et al.*³⁵ studied the interaction between a pyramidal Pt₃Cu cluster and a H₂ molecule by means of a Hartree–Fock self-consistent field. They found similar capture and activation energies of H₂ as well as depth of energy wells, barriers, adsorption distances, and H–H bond relaxation when Pt₃Cu–H₂ and Pt₄–H₂, with the same geometry, were considered. This means that there is no loss of the H₂ activity compared to pure metal cluster. Avdeev *et al.*³⁶ studied the adsorption of ethylene on Cu₁₂Pt₂ clusters. Their calculations show that the stability of the active site is determined by the local structure of the surface around the Pt atoms. Due to the fact that the difference in electron valence number (Cu has [Ar]3d¹⁰4s¹ and Pt has [Xe]4f¹⁴5d⁹6s¹) is expected, minimal geometry will be a competition between surface effects and packing.³⁷ Besides, Cu and Pt have fcc structures in the bulk.

The primary objective of this study is to understand the influence of the relative concentrations of Pt and Cu atoms on the geometrical, electronic, and chemical properties of a 12 atom Pt–Cu cluster. The stability analysis is carried out from the atomization energy and first order energy difference, whereas the electronic properties are obtained from the energy gap between the highest occupied and lowest unoccupied energy levels, the different molecular orbitals and, in particular, those ones close to the electronic gap, the hardness, and the electrophilicity. As explained below, in order to improve our predictions in relation to the calculated chemical parameters, we use the difference in energies between cationic and anionic clusters with respect to the neutral cluster to embody the reactivity. We also recognize that some of the minimal structures happen to be magnetic and we introduce, in the search for the minimal structure, the total magnetization as another degree of freedom.

Section II describes the theory and level of approximations used in our calculations. Section III describes the obtained minimal energy structures and the rationalization on the performed search, whereas Sec. IV is a summary of the functional dependence of electronic properties with respect to the relative Pt–Cu concentration. In particular, Sec. V presents a summary of our findings and a perspective of the use of these types of alloyed nanoclusters.

II. THEORY AND COMPUTATIONAL DETAILS

The electronic structure of our system has been obtained using the SIESTA code,³⁸ which performs a fully self-consistent density functional calculation to solve the Kohn–Sham equations.^{39,40} We have employed the local-density approximation (LDA) approximation for the exchange–correlation energy. The Ceperley–Alder form was adopted for the exchange and correlation energy functional.

The ionic pseudopotentials⁴¹ were generated from the atomic configurations 4s¹4p⁰3d¹⁰ for Cu and 6s¹6p⁰5d⁹ for Pt, with the corresponding cut-off radii of 1.98, 2.30, and 1.98 for Cu and 2.24, 2.84, and 1.93 for Pt. The core correc-

tions are included with core radii of 3.43 and 1.70 a.u. for Cu and Pt, respectively. Valence states have been described using double- ζ basis sets with two orbitals having different radial forms. We consider 400 Ry for the energy cutoff used to define the real space grid for numerical calculations involving the electron density.

The structural optimization to obtain the minimal energy configuration has been carried out by molecular dynamics using the conjugate gradient algorithm. The positions of all atoms were relaxed without any symmetry constraint until the forces on them were less than 0.02 eV/Å. In those cases, where magnetic configurations were considered, the extension of the LDA has been used, as it is also called local spin density approximation. Instead of using the multiplicity as a criterion for the search, we have used the magnetization mainly because it is a more general constrain on magnetic systems.

To obtain the minimal energy configurations for a specific Pt_{12-n}Cu_n alloy, we build different potential clusters coming from different criteria.

- All possible different combinations for the atomic positions coming from a structure with a D_{2d} point symmetry group. A structure found in some monometallic clusters as in Au (Ref. 42) and which also happens to be our minimal structure for the Pt₁₂.
- All possible different combinations now coming from a cluster with a point symmetry, such as C_{5v} , which corresponds to a well packed structure. This symmetry occurs for a 12 atom cluster when described by a Lennard-Jones potential.
- Minimal cluster structure obtained from a genetic algorithm (GA) as described in Ref. 43 for that particular alloy. The classical interaction potential used corresponds to the modified Gupta potential (see Ref. 44 for details). The binary interaction was assumed to be as in the same publication.

For the first two cases, atoms were replaced by running over all combinatorial positions for the species with the smaller number and keeping the original group symmetry fixed. Of course, it did produce different symmetry groups after the replacement was performed. For the last case, only the lowest energy structure was used as it came from the stochastic search performed within the GA and under the phenomenological interaction potential. After the structures were defined, first principles calculations were performed for nonpolarized or polarized solutions. In the case of polarized calculations, we have also changed the magnetization on the cluster to search all possible potential magnetic configurations. After the total energy minimal structures were identified, they were characterized by studying their electronic and magnetic properties under the view of different chemical descriptors, as we now discuss briefly.

As it is well known, the ground state density functional theory fundamental expression for the change in energy due to the electron particle number operator or changes in the external potential is given by

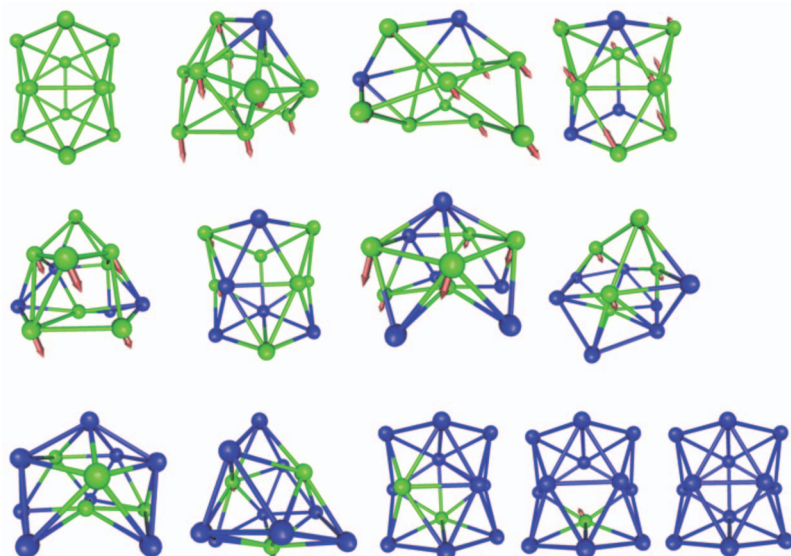


FIG. 1. Total energy minimal structures for bimetallic clusters of Pt_{12-n}Cu_n composition, where green corresponds to Pt and blue corresponds to Cu. Arrows denote the magnetic moment per atom.

$$dE = \mu dN + \int \rho(r) \delta V(r) dr, \quad (1)$$

where μ , $\rho(r)$, N , and $V(r)$ are the chemical potential, the electron density, the total number of electrons, and the external potential of the system, respectively. Hence, both μ and $\rho(r)$ can be considered as a response function to perturbations on N and $V(r)$. From Eq. (1), the chemical potential is given by

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{V(r)}, \quad (2)$$

and it can be proven that the first partial derivative of μ with respect to N is the global hardness η ,⁴⁵

$$2\eta = \left[\frac{\partial \mu}{\partial N} \right]_{V(r)} = \left[\frac{\partial^2 E}{\partial N^2} \right]_{V(r)}. \quad (3)$$

Therefore, every chemical descriptor^{46,47} such as the electronic gap and the chemical hardness can be calculated from the finite different expression obtained from Eqs. (2) and (3). An additional descriptor comes from a ratio of the intensity of hardness and the electronic gap and it is called electrophilicity, which is a measure of the electronic flow disponibility of a given compound.⁴⁸ In what follows, all our results have been obtained by using the path previously described. After the minimal energy structure is identified, the total energy, for the corresponding anion and cation, was calculated. With all those energy values, the predefined descriptors were calculated.

We have also used the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) to rationalize some of the observations and to identify the spatial locations with higher reactivity and sensitivity to electrophilic or nucleophilic attack. This has been performed also for the magnetic clusters, where the HOMO and LUMO could correspond to a specific spin state. We did perform a similar analysis by using the cation and anion cluster but with the same conclusions than using the HOMO and LUMO of the neutral structure.⁴⁹

III. MINIMAL ENERGY GEOMETRIES AND MAGNETISM

The lowest energy configurations of Pt_{12-n}Cu_n ($n = 0-12$) are reported in Fig. 1 and Table I. We start with the monatomic clusters, where the D_{2d} point group symmetry was obtained as the more stable structure for both atomic cases. Our results differ from those published in Ref. 44 for Cu and Ref. 50 for Pt, where a fragment of an icosahedron was reported in both cases. We should point out that in those references classical phenomenological potentials were used. In order to check our differences, we have performed a global optimization of the same cluster symmetry as the one reported in those references. After a total minimization was performed, we found that the initial symmetry was kept but they happen to be higher in energy than the ones we have obtained. In particular, we found an energy difference of 1.580 eV for Pt and 0.426 eV for Cu. We should also point out that the same references have reported that the minimal structure for Cu₁₃ and Pt₁₃ is an icosahedral, which is not in agreement with *ab initio* calculations, where a cuboctahedral has been obtained.⁵¹ This would be expected mainly because the classical potentials used to generate those clusters have been parametrized with respect to the bulk properties and it is not expected that as we change the atomic neighborhood and decrease dimensionality, the classical potential would remain, capturing the chemical description.

The average binding distances for Pt and Cu clusters are found to be smaller than the first neighbor distance in the bulk by 9% and 6%, respectively, as seen in Fig. 2. This is expected because as we increase the number of surface atoms, there is a bond contraction related to the decrease in neighboring atoms.

Now, going on from pure metal clusters to the bimetallic nanoalloys, the number of possible structures increases by a large factor. From the different compositions we have considered, we see that the optimization takes the initial D_{2d} point group type symmetry and usually leads the cluster to a different symmetry group and, in some cases, to a disorderedlike state, where no symmetry is present. In the case of

TABLE I. Binding energy, relative energy to the theoretically computed minimum energy state ($\Delta E = E - E_{\min}$), magnetic moment, binding average distances, and IPs.

Cluster symmetry		E_b (eV/atom)	Magnetic moment (μ_B)	$d_{\text{Pt-Pt}}$ (Å)	$d_{\text{Pt-Cu}}$ (Å)	$d_{\text{Cu-Cu}}$ (Å)	IP (eV)
Pt ₁₂	D_{3d}	4.883	0.0	2.52	7.14
Pt ₁₁ Cu ₁		4.807	3.0	2.60	2.57	...	7.11
Pt ₁₀ Cu ₂		4.719	2.0	2.57	2.55	4.39	6.94
Pt ₉ Cu ₃		4.641	3.0	2.61	2.54	2.39	6.93
Pt ₈ Cu ₄		4.554	2.0	2.63	2.50	2.45	6.78
Pt ₇ Cu ₅		4.474	1.0	2.59	2.52	2.40	6.70
Pt ₆ Cu ₆		4.380	2.0	2.63	2.50	2.45	6.69
Pt ₅ Cu ₇	C_s	4.291	1.0	2.61	2.49	2.54	6.41
Pt ₄ Cu ₈		4.189	0.0	2.62	2.50	2.43	6.30
Pt ₃ Cu ₉	D_{3h}	4.033	1.0	2.82	2.52	2.48	5.18
Pt ₂ Cu ₁₀	C_2	3.896	0.0	2.86	2.50	2.44	5.87
Pt ₁ Cu ₁₁	C_s	3.665	1.0	...	2.46	2.42	4.94
Cu ₁₂	D_{3d}	3.388	0.0	2.40	4.65

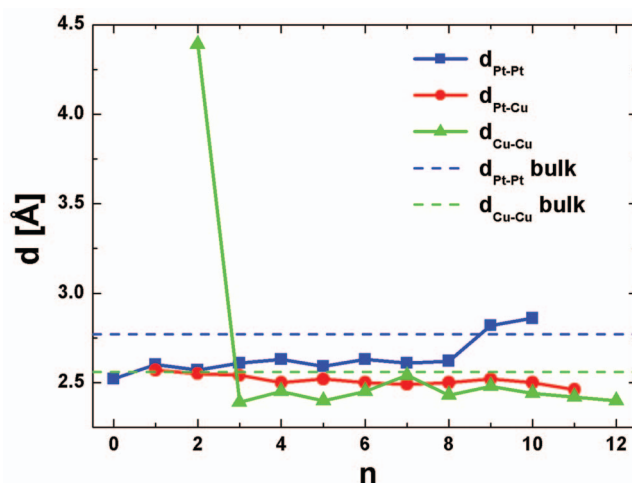
small atom number on the two ends (Cu or Pt atoms less than 3), those species with small number like to sit as far as possible, which indicates that the cluster prefers to keep the chemical coordination for the larger atomic species and there is segregation for the smaller atom composition. This effect is also consistent with recent calculations for Pt–Cu alloy surfaces for particular compositions.⁵² The trend is that when the concentration of copper is lower than that of platinum, the most stable structure found has no symmetry, while if the concentration of Cu is higher, there is a change in the structure with some point group symmetry (see Table I). There is an exception which is the case of Pt₄Cu₈ where the most stable structure has no symmetry, but this could be due to the presence of a relative number of both species, that is, if we consider that the structure is composed of a single atom, then the symmetry group of the structure would be C_s , which can be related to the difference in the chemical potential of Cu on Pt within the Pt–Cu alloys.

The distribution of energies of the three lowest energy isomers is shown in Fig. 3. There one can see that the difference in binding energy between the ground state and these isomers is typically less than 0.03 eV; this suggests that an ensemble of energetically low-lying isomers will be thermally available already at room temperature. In addition, Fig. 3 shows that larger the number of Cu atoms becomes, the isomers get closer to the lowest energy configuration. With respect to magnetic moments, we can see that when the copper atom concentration is less than 50%, the isomers have quite different values; on the contrary, they have practically the same value. According to this distribution of the magnetic moments, we can infer that the thermal average of the total magnetic moment of these ensembles will follow the same qualitative behavior.

For each case of the reported minimal energy structures, there exists charge transfer from the Cu atoms to Pt atoms. In general, this transfer is not symmetrical for spins up and down and, as a consequence, the clusters acquired a net magnetic moment. In the particular case of Pt₁₁Cu₁, the presence of the Cu atom leads to a distorted structure, in which the average binding distance between two Pt atoms is increased

relative to that in the cluster of pure Pt. Moreover, the cluster becomes magnetic with a magnetic moment of $3\mu_B$ because of charge transfer from the Cu atom toward the Pt atoms. Mainly, the charge redistribution is more noticeable on Pt atoms farther away from the Cu atom. Even though there is a large charge redistribution with different spin channels, we find that a simple model of atomic spins could rationalize the magnetic behavior overall considered lowest energy structures. Taking into account that in a single Cu atom, the difference between spin up and spin down charge happens to be 1, the value $3\mu_B$ for this particular cluster can be explained as due to a spin flip of one electron. In particular, if we compare the charge per spin channel with a system of isolated 11 Pt atoms and 1 Cu atom, we note that there is a transfer of one electron charge from spin up to spin down; this gives $2\mu_B$ plus $1\mu_B$ which contributes an isolated atom of Cu, explaining the magnetic moment value obtained for this concentration.

When the Cu concentration increases to 16% (Pt₁₀Cu₂), the structure is more distorted and the two Cu atoms are farther apart from each other. The charge transfer from the

FIG. 2. Atomic distances as a function of the number of Cu atoms in the clusters with Pt_{12-n}Cu_n composition between different species.

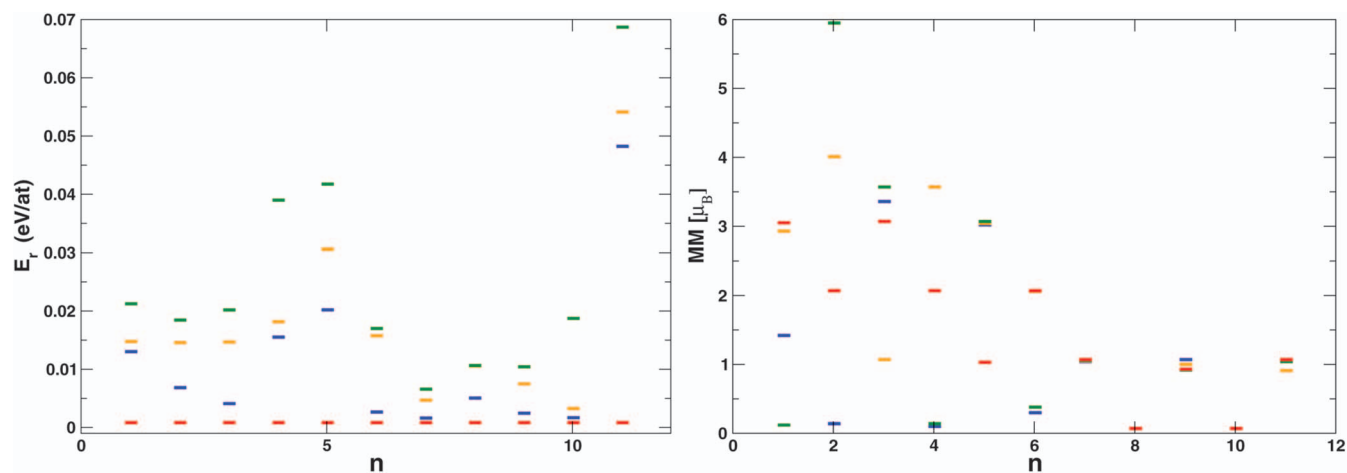


FIG. 3. Left panel: the relative energy of the lowest energy isomers with respect to the lowest energy configuration as a function of the Cu composition. Right panel: magnetic moment per atom of the lowest energy isomers as described on the left panel.

Cu atoms to Pt atoms gives to the system a magnetic moment of $2\mu_B$. In the picture mentioned before, this would mean that this transfer does not induce any spin flip. When the Cu concentration increases to 25% (Pt₉Cu₃), the binding distance between two out of the three Cu is roughly equal to that of the pristine Cu cluster. The structure has a magnetic moment of $3\mu_B$, i.e., there is no spin flip. For the concentration of 33% (Pt₈Cu₄), the average binding distance between Cu atoms is made slightly larger than the pristine Cu cluster, while the binding Pt atoms continuously increases; it seems that Cu atoms expand the cluster and increase the distance of the Pt atoms with respect to the center of mass. The magnetic moment of $2\mu_B$ means that there is one spin flip with respect to the free atom case.

For Cu concentrations of 42% and 50%, we need two spin flips from the single Cu atom to explain the magnetic moment, whereas the number of required spin flips increases as the number of Cu atoms increases within the cluster. Such that for 56%, three spin flips are required, for 67% and 75%, four spin flips are required, and for 83% and 92%, five spin flips are necessary.

Therefore, it is important to notice that besides a change in the electronic structure, there is a large dependence of the cluster magnetic properties on the concentration of Cu atoms. This could lead to potential uses in magnetic environments, where this property can be of use.

IV. ELECTRONIC PROPERTIES

In Fig. 4, we report a set of different electronic properties calculated for the lowest energy structures for the bimetallic clusters considered here. It is concluded from this figure that there is an almost monotonic increase in the binding energy, as well as for the ionization potential (IP), starting from the pristine Pt cluster. Even though the binding energy decreases, the clusters remain stable. This depletion in the binding energy is related then to the charge transfer. This is related to the fact that Cu has a lower electron binding energy than Pt; therefore, as we increase the number of Cu atoms, the formed bonds are weaker compared to Pt–Pt bonds. Interestingly enough, the hardness is more indepen-

dent for small and medium concentrations of Cu atoms, and then it becomes oscillatory from even and odd number of Cu atoms on the Pt_{12-n}Cu_n. The hardness is always higher in clusters with an even number of Cu atoms, being the maximum when the cluster has ten Cu atoms. This is due to the increase/decrease in the energy gap, which is related to the deformation resistance of the electronic density in such clusters and the number of even/odd number of the total electrons. In the cases of open shell systems, the electronic gap becomes smaller. Therefore, the cluster electronic stability is quite related to the odd/even number of electrons. The electrophilicity decays very slowly for small Cu concentration, showing that the electronic density is less affected, at least for those concentrations. After six Cu atoms, the electrophilicity decays much faster, where now the electronic properties are controlled by the large presence of copper atoms. Due to the dependence of the electrophilicity on the elec-

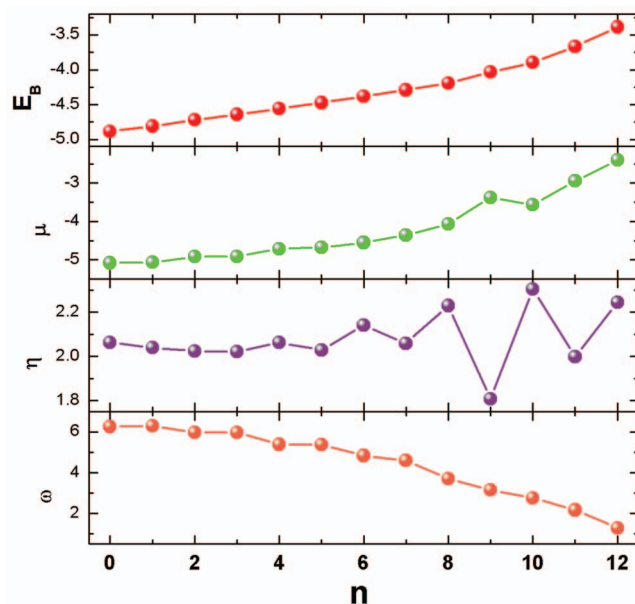


FIG. 4. Binding energy, chemical potential, hardness, and electrophilicity as a function of the number of Cu atoms in the clusters with Pt_{12-n}Cu_n composition.

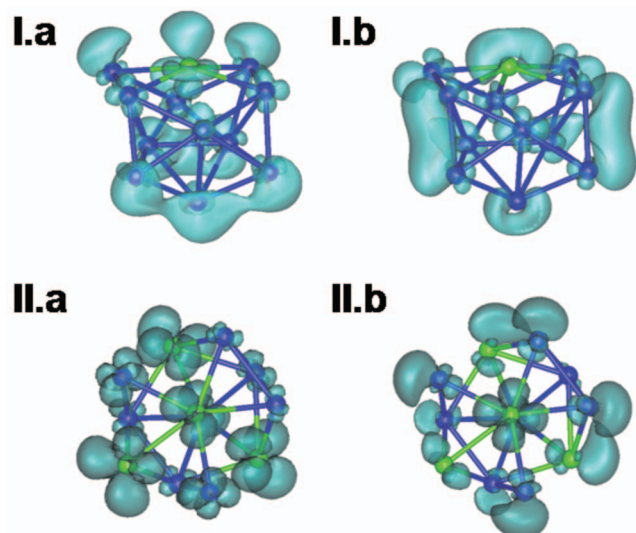


FIG. 5. HOMO and LUMO of two different bimetallic clusters. (I.a) HOMO for Cu_{11}Pt , (I.b) LUMO for Cu_{11}Pt , (II.a) HOMO for Pt_4Cu_8 , and (II.b) LUMO for Pt_4Cu_8 .

tronegativity power and the potential electron flow toward the cluster, we can see that even there is an oscillatory behavior on the hardness, ω is largely controlled by the monotonic behavior of the chemical potential. From our analysis, we can see that there is an important interplay between the structure and the global reactivity parameters.⁵³

An important feature we can also analyze is the spatial reactivity of the clusters. For that purpose, we consider the HOMO and LUMO or all lowest energy configurations, which are a good measure for nucleophilic and electrophilic attacks.⁴⁸ In particular, for the discussion, we have chosen two examples with two different Cu atomic fractions, as shown in Fig. 5. For the case of the PtCu_{11} , it is observed that the LUMO has different features to point out. There is a large charge delocalization on Cu atoms which are away from the Pt atom, for those Cu atoms close to the Pt atom, the electronic density is much smaller. There is also a large contribution from the Pt atom, with a $d\text{-}z^2$ atomiclike contribution. The LUMO for this cluster happens to be also quite interesting. There is a large delocalization from Cu atoms close to the Pt atom and no atomiclike contribution from the Pt atom; this will indicate that for this orbital, there is a large hybridization from the Cu and Pt atoms. Therefore, the cluster is quite sensitive to nucleophilic attack on the Pt atom and to electrophilic attack on Cu atoms away from the Pt atom. As we increase the presence of Pt atoms in the cluster, as in the case of Pt_4Cu_8 , the different orbitals become largely hybridized. As it happens on the single Pt atom, the electronic density at the HOMO is larger for Cu atoms away from the Pt atoms, whereas the LUMO is reverse and the delocalization is larger on Cu atoms closer to the Pt atoms. In any case, as the number of Pt atoms is increased, the HOMO and LUMO resemble a combination of d -orbitals with four ellipsoids coming from every atom in the cluster. It seems that there exists an electronic balance between the two different species, which help strengthen the idea that the combination

of those atoms could also increase the reactivity, and depending on the composition, the cluster could be more nucleophilic or electrophilic.

V. CONCLUSION

In this work, we report a theoretical study of bimetallic clusters of the type $\text{Pt}_{12-n}\text{Cu}_n$ with the purpose of studying the possibility of increasing the catalytic potential of such clusters by the combination of those atoms. We find that the bimetallic clusters are stable with a monotonic dependence of different electronic properties as a function of n .

Even though the electronegativity increases and the electrophilicity decreases monotonically with increasing Cu concentration, the hardness has an oscillatory dependence as a function of even or odd number of Cu atoms. Such dependence is also observed for the magnetic moment. We see that by changing the Cu atoms, the magnetic properties are largely modified and they could go from nonmagnetic to magnetic with a magnetic moment of as large as $3\mu_B$. It can also be inferred that by changing the concentration of Cu atoms, the system decreases the HOMO volume (to the same isodensity), which means that the nucleophilic probability is diminished and the electrophilic reactivity sits on the Cu atoms, as demonstrated from the IP dependence, as well as the analysis on the HOMO and LUMO. The large dependence of the chemical properties, as well as magnetization, as a function of Cu concentrations on Pt clusters opens the interest in using binary nanoalloy in many different fields and, in particular, in nanomagnets and catalysis.

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