CO-EXISTENCE OF LOCALIZED MAGNETIC MOMENT AND DELOCALIZED ELECTRONIC SHELL IN SUB-NANOMETER KONDO-LIKE SYSTEMS

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Abstract: *Looking for the smallest limit that the Kondo-like effect can be observed has been a long-standing interest in the field of fundamental physics. In this regard, we have investigated the interaction between a countable number of free electrons and a single impurity magnetic moment in two typical quantum systems $Cu_{12}Cr$ and $Au_{19}Cr$ clusters. Both icosahedral $Cu_{12}Cr$ and tetrahedral $Au_{19}Cr$ clusters tend to form a closed-shell electron structure. However, their magnetic moments are completely different. Using density functional theory calculations, we analyzed, discussed and proposed a co-existence picture of electronic and magnetic shell to explain the quenched and unquenched magnetic moment of $Cu_{12}Cr$ and $Au_{19}Cr$. The finding results are expected to contribute to the understanding of molecular magnetism in bimetallic nanoclusters.*

Keywords: Metal clusters; Transition metal Kondo-effect; Electronic shell; Magnetic moment.

1. INTRODUCTION

During the last decades, the behavior of the magnetic impurities in nonmagnetic hosts in bimetallic clusters has posed problems to challenge the condensed matter theorists. The geometry, chemical and physical properties of clusters system depend on cluster size composition which has been extensively investigated for pure metal clusters and alloy species [1-4]. It is interesting that a small concentration of magnetic impurities – atoms or ions can dramatically affect the behavior of conduction electrons in non-magnetic host clusters, where the occurrence (or not) of the so-called Kondo effect [5] can be observed for physically confined systems [6-8]. The physics of the Kondo effect arises from the hybridization of localized spins in magnetic impurities, which occur almost exclusively in partially filled *d* shells, and the *s* orbitals of the nonmagnetic host. This hybridization is shown to reduce or even quench the TM dopant's local magnetic moment. In this context, small copper and gold metal clusters doped with single transition metal atoms is an ideal quantum system to investigate the interplay between the electronic shell and cluster geometry. Copper and gold atoms (Cu and Au) lie at the end of the 3*d* and 5*d* row in the periodic table, respectively. The electronic configuration of copper and gold are characterized by closed *d* shell and a single *s* valence electron [Cu: $3d^{10}4s^1$ and Au: $5d^{10}6s^1$], respectively. Due to the presence of single *s* electrons in the atomic outer shell, the noble-metal cluster is expected to exhibit certain similarities to the Akali metal ones. The electronic structure of noble cluster can be described by the geometrical shell model. The characteristics of geometric structure, electronic structure, bonding of atoms in pure Cu_n and Au_n clusters have been studied [9-10]. For instance, a spin-compensating electron cloud surrounding the magnetic impurity in a symmetric endohedral geometry silver clusters $Ag_{10}Co^+$ and $Ag_{10}Fe$ are well controlled by the number of constituent atoms in clusters, and finally quenching the magnetic moment of $Ag_{10}Co^+$ and $Ag_{10}Fe$ cluster's [11, 12]. The quenching behavior was then attributed to the closed 18-e shell of a spherical electronic model [13]. Meanwhile, the magnetic moments of Cu_nV clusters are mainly localized on the V atom and decrease with the increase of cluster size [14]. Bin Zhu and his co-worker have demonstrated that the magnetic moment of Ni atom in the nonmagnetic gold cluster is obviously reduced and even completely quenched [15].

In this paper, we reproduce on the structure and spin optimization of $Cu_{12}Cr$, $Au_{19}Cr$ clusters using DFT calculations [16, 17]. The magnetic moment which explore by the interaction between *d-s* orbitals of noble host metal and transition dopant. The magnetic moment of $Cu_{12}Cr$ and $Au_{19}Cr$ can be understood by incompletion electronic shell configuration $1S^21P^61D^{10}$ for $Cu_{12}Cr$ and $1S^21P^62S^21D^{10}$ for $Au_{19}Cr$ [18-22]. In the following, we perform a quantitative analysis on the local magnetic moment, molecular diagram, and cluster-spin density in order to explain the magnetic behavior in $Cu_{12}Cr$ and $Au_{19}Cr$ clusters.

2. THEORETICAL APPROACH

Theoretical studies of the electronic structure and ground-state geometric of $Cu_{12}Cr$ and $Au_{19}Cr$ have been carried out by density theory (DFT) calculations implemented in the Gaussian 09 package [16, 17]. We used the BP86 functional in conjunction with cc-pvTZ-pp for Cu and Au atoms and cc-pvTZ for transition metal - Cr to confirm the results presented in Refs [18-22]. The search for energy minima followed by frequency was conducted using this approach. The total magnetic moments (TMM) and local magnetic moments (LMM) were defined as the difference between the numbers of spin-up and spin-down electron occupying the molecular/atomic orbitals of the cluster/atom.

3. RESRULTS AND DISCUSSION

3.1. Geometrical structures and spin multiplicities

In order to investigate the effect of transition metal atoms (Cr) dopant on pure copper and gold metal clusters, we perform the optimization process to find the ground-state geometrical and electronic structure of the clusters. First the pure copper and gold metal clusters (Cu_{13} and Au_{20} clusters) are calculated to obtain all possible structures and spin states. Then a Cr atom have been substituted by Cu and Au atoms on the lowest-lying isomers of Cu_{13} and Au_{20} clusters at different positions as the input structures for the optimization calculations. The most stable $Cu_{12}Cr$ and $Au_{19}Cr$ clusters are displayed in Fig 1. In the following, structure for isomers with increasing order of energy are donated as A, B and C. The spin multiplicity and energy difference compared to each ground-state structures are also presented.

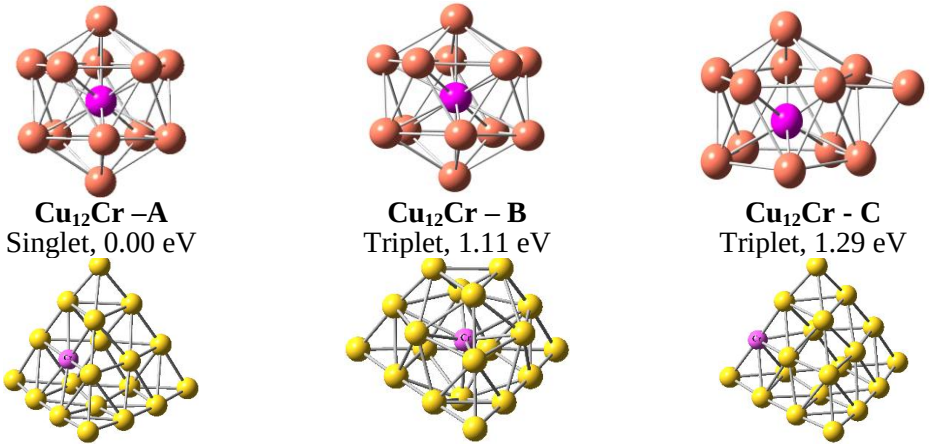


Figure 1. *Optimized structures, spin multiplicities, and relative energies (in eV) of the lowest lying isomers of $Cu_{12}Cr$ and $Au_{19}Cr$ clusters. The orange, yellow and blue balls show Cu, Au and Cr atom, respectively.*

$Cu_{12}Cr$. The computed global minimum-energy structure $Cu_{12}Cr$ –A is the high-symmetry icosahedral singlet. The structural identification for the ground state of $Cu_{12}Cr$ cluster illustrated that the Cr atom dopant locates at the central position of a Cu_{12} icosahedral cage. The relative energy of the triplet icosahedron $Cu_{12}Cr$ – B is significantly higher than that of the ground-state by 1.11 eV. The next isomer triplet $Cu_{12}Cr$-C is very unstable at 1.29 eV compared to the ground-state.

$Au_{19}Cr$. Our computed lowest-energy isomer sextet $Au_{19}Cr$ – A prefers high symmetry tetrahedral in which Cr atom impurity favorably substitutes for a gold atom on the surface center. The next isomer sextet $Au_{19}Cr$-B experiences a distortion of truncated pyramid with the dopant atom Cr is located at the central. The difference energy of $Au_{19}Cr$-B and the corresponding ground state is 0.33 eV. The relative energy of less stable sextet $Au_{19}Cr$-C is higher than the ground state by 0.48 eV and the geometric again tends to retain a tetrahedral symmetry with a substituted dopant atom on the edge.

3.2. Electronic and magnetic properties

Cr dopant atom is known as a strong magnetic element that has an outermost $3d^5 4s^1$ atomic shell. Nevertheless, doping a Cr atom into Cu_{12} and Au_{19} clusters result is a completely different picture. It is found that the magnetic moment in $Cu_{12}Cr$ is entirely quenched while that of $Au_{19}Cr$ is 5 μ_B. The aim of this section is to find the underlying physics for magnetic difference between two cluster systems and possibly generalize a mechanism to predict the magnetic behavior in similar quantum systems. While we doped exactly the same dopant, there are two main differences between the host systems. First, the geometry of $Cu_{12}Cr$ is icosahedral while that of $Au_{19}Cr$ is tetrahedral. Owning to their icosahedral and tetrahedral geometries, $Cu_{12}Cr$ and $Au_{19}Cr$ clusters exhibit slightly different molecular shell of electrons, respectively [22-24]. In particular, $Cu_{12}Cr$ has a nearly spherical structure and its valence electrons can be described as moving inside a spherical potential, resulting in an electronic shell ordering as 1S 1P 1D 2S 2P … Meanwhile, the valence electrons in $Au_{19}Cr$ can be approximated as moving inside a tetrahedral potential, yielding an electronic shell ordering as 1S 1P 2S 1D 2P …The second point is that the number of valance electrons provided by the host is different. Assuming that each copper or gold atom delocalizes one $4s^1$ or $6s^1$ electron, $Cu_{12}Cr$ and $Au_{19}Cr$ clusters will provide totally 18 and 25 valence electrons, respectively. So how will the electronic shell order and the total number of valence electrons influence the electronic and magnetic properties of the clusters? In order to visualize the electronic shell structure of the clusters, we plot their corresponding molecular orbital diagrams in Fig. 2. For the case of $Cu_{12}Cr$ cluster, it can be seen that all $4s^1 3d^5$ valence of Cr delocalizes and join with *s* valence electrons of the Cu host. The total number of valence electrons in $Cu_{12}Cr$ cluster is 18 (12 from Cu atoms and 6 from Cr dopant), which completely fills the $1S^2 1P^6 1D^{10}$ to form a closed shell and stable structure. In the other words, the strong hybridization of 4s-Cu and 3d-Cr results in an electronic shell closure and consequently a quenched magnetic moment of the Cr dopant. By contrast, $Au_{19}Cr$ cluster has a magic number of 20 with an electronic configuration of $1S^2 1P^6 2S^2 1D^{10}$. The molecular orbital diagram confirms that only one valence electron of Cr dopant transfers to fill into the molecular orbitals together with 19 *s*-electron of Au host, forming 20-electron shell closure. The remaining 5 electrons are localized on 3*d*-Cr atomic orbitals, responding to the magnetic moment of the cluster. Now the magnetic picture of two systems somewhat can be revealed. We consider two different systems but the same dopant atom Cr with 6 ($4s^1 3d^5$) valence electrons. However, their magnetic moment is completely difference. The total magnetic moment of $Cu_{12}Cr$ is completely quenched while $Au_{19}Cr$ has a large total magnetic moment of 5 μ_B. The molecular orbital diagram clearly indicates that the magnetic feature of $Cu_{12}Cr$ and

$Au_{19}Cr$ depends on the hybridization of 3*d* dopant electrons and *s* host electrons. The 3*d* dopant electrons are believed to undergo the following process. Firstly they prefer to be delocalized to form the molecular electron shell. The required number of valance electrons will depend on the typical electronic configuration of each cluster. In this case, the shell closure will be at 18 and 20 electrons. Upon the shell completion, the remaining valence electrons of the dopant localizes in the atomic orbital to trigger the magnetic shell. Similar to $Cu_{12}Cr$, Dong and co-worker [7] have observed the completely quenched magnetic moment in $Ag_{10}Fe$ whose valence electrons fulfill the 18-electrons counting rule ($4s^2 3d^6$ for the Fe atom and ten $5s^1$ electrons for silver atoms). The predicted electronic shell closure, where all valence electrons of $Cu_{12}Cr$ cluster are occupied, has been believed to be the reason of their completely quenched magnetic behavior. The magnetic moment of $Au_{19}Cr$, therefore, is originated from the co-existence of delocalized electron shell and (localized) magnetic shell.

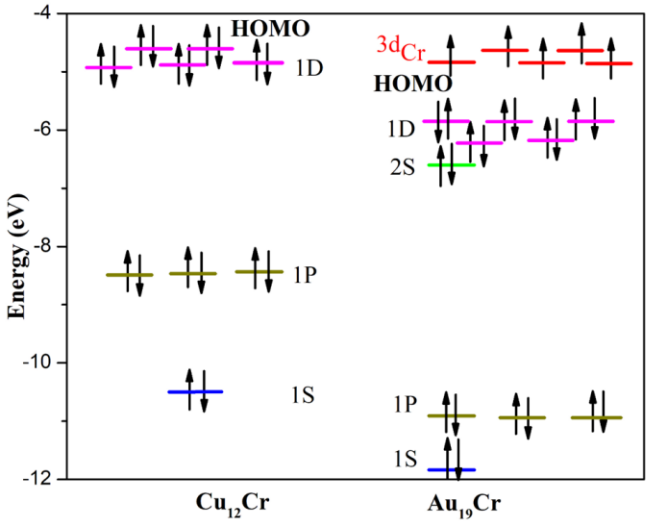


Figure 2. *Orbital levels and electronic configuration of $Cu_{12}Cr$ and $Au_{19}Cr$ clusters.*

Table 1. *Local magnetic moments (LMM in μ_B) of Cr atom, and total magnetic moment (TMM in μ_B) of $Cu_{12}Cr$ and $Au_{19}Cr$, respectively.*

Clusters	LMM (μ_B)			TMM (μ_B)
	3d (Cr)	4s	6s	
$Cu_{12}Cr$	0	0	-	0
$Au_{19}Cr$	4.19	-	0.81	5

To gain insight into the magnetic behavior of icosahedral $Cu_{12}Cr$ and tetrahedral $Au_{19}Cr$ clusters, we analyzed the local magnetic moments (LMM) and total magnetic moments (TMM) (in μ_B) of these clusters. Table 1 presents the magnetic moment on 3*d*-Cr, 4*s*-Cu and 6*s*-Au and total magnetic moment (in μB) of $Cu_{12}Cr$ and $Au_{19}Cr$ clusters. It can be seen that for the case of $Cu_{12}Cr$, the local 3*d* magnetic moment of Cr atom and 4*s* of Cu atoms is zero. This finding is in line with the molecular orbital picture that predicts the pairing of Cr and Cu valence electrons in the molecular shell. The case of pyramid $Au_{19}Cr$ is more interesting since the LMM in 3*d*-Cr is more than $4\mu_B$ while that of 6*s*-Au is nearly 1 μ_B. Together with the molecular orbital diagram in Fig. 2, it can be concluded that while electrons from 3*d*-Cr orbitals partially delocalize and joint the molecular shell with 6*s*-Au electrons, there is one 6*s*-Au electron moves to 3*d*-Cr orbitals to contribute to the total magnetic moment of the cluster.

In the following, we further verify the origin of the cluster magnetic behavior by mapping cluster spin up and spin down densities in $Cu_{12}Cr$ and $Au_{19}Cr$. The results are presented in Fig. 3.

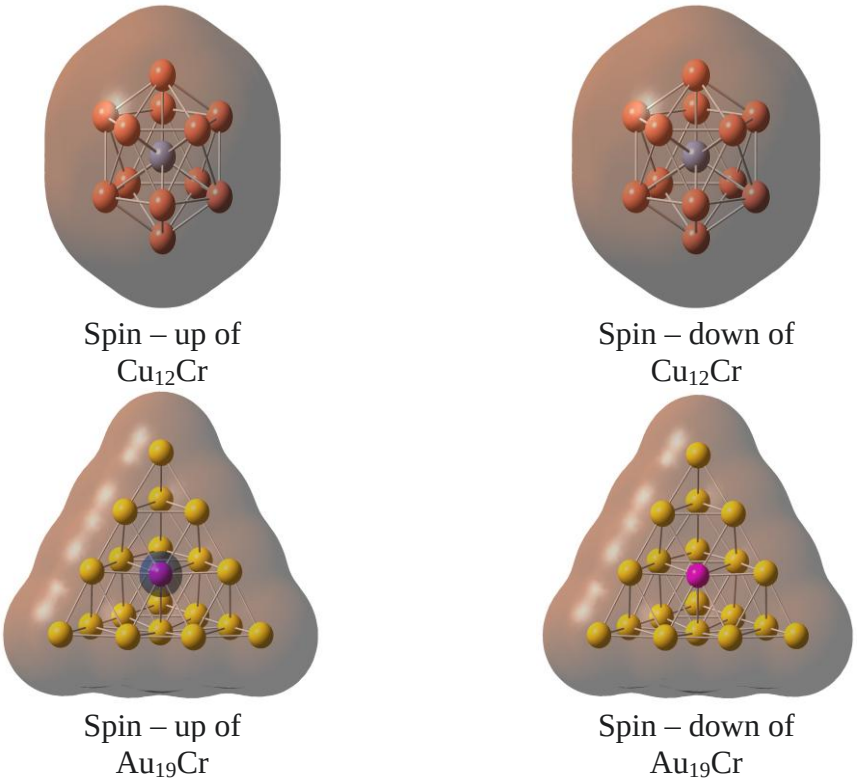


Figure 3. *Spin density of the ground-state $Cu_{12}Cr$ and $Au_{19}Cr$ clusters.*

The picture shows that the total spin of $Au_{19}Cr$ cluster is mainly located at the dopant atom position. It is supported by our above-mentioned argument that the total magnetic moment is $Au_{19}Cr$ cluster essentially results from the localized 3*d*-dopant. The exact electronic configuration can be assigned as $1S^21P^62S^21D^{10}3d^5_{Cr\uparrow}$. By contrast, for $Cu_{12}Cr$ the local magnetic moment of the Cr dopant atom disappears and the spin-up and spin-down clouds are entirely overlapped with each other. This can be explained by the fact that after completely filling the $1S^21P^61D^{10}$ shell closure. This is the reason why we observe the superposition of spin-up and spin-down clouds in $Cu_{12}Cr$. In the other words, the Kondo-like effect zero magnetic moment of $Cu_{12}Cr$ is resulted from the formation of a molecular shell closure in the central Cr dopant.

4. CONCLUSION

Density functional calculations have been performed for the structural, electronic, and magnetic properties of $Cu_{12}Cr$ and $Au_{19}Cr$ clusters. The icosahedral $Cu_{12}Cr$ and tetrahedral $Au_{19}Cr$ clusters are found nonmagnetic and has the largest magnetic at 5μB in accordance to an 18-electrons $1S^21P^61D^{10}$ and 20-electrons $1S^21P^62S^21D^{10}$ molecular shell closure. The behavior of magnetic moment quenched –like Kondo effect in icosahedral $Cu_{12}Cr$ system can be explained by filling of the orbital energy levels form to electronic shell closure. The tetrahedral Cr has open-shell with 25-electrons $1S^21P^62S^21D^{10}3d^5_{Cr\uparrow}$ with co-existence of the electronic shell and magnetic shell, the total magnetic moment of $Au_{19}Cr$ is 5μB.

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REFERENCES

[1]. Nguyen Thi Mai, Nguyen Thanh Tung, Phan Thi Thuy, Nguyen Thi Minh Hue, Ngo Tuan Cuong, "*A Theoretical Investigation on $Si_nMn_2^+$ Clusters (n =1-10): Geometry, Stability, and Magnetic Properties*," computational and theoretical chemistry, 1117, (2017), 124-129.

[2]. Yejun Li, Nguyen Minh Tam, Alex P. Woodham, Jonathan T. Lyon, Zhe Li, Peter Lievens, André Fielicke, Minh Tho Nguyen, Ewald Janssens, *"Structure Dependent Magnetic Coupling in Cobalt-Doped Silicon Clusters,"* J. Phys. Chem. C, 120, 34, (2016), 19454-19460.

[3]. Zheng Ben-Xia, Die Dong, Wang Ling, and Yang Ji-Xian, *"Density Functional Study on the Structural, Electronic, and Magnetic Properties of 3d Transition-Metal-Doped Au_5 Clusters*," J. Phys. Chem. *A*, 22, (2014), 118.

[4]. Xibo Li, Yuqi Chen, Pradip Basnet, Jiangshan Luo and Hongyan Wang, "*Probing the properties of size dependence and correlation for tantalum clusters: geometry, stability, vibrational spectra, magnetism, and electronic structure,"* RSC Adv. 9, (2019), 1015-1028.

[5]. J. Kondo, *"Resistance Minimum in Dilute Magnetic Alloys,"* Progress of Theoretical Physics, 32, (1964), 37.

[6]. C. Verdozzi, Y. Luo, and Nicholas Kioussis, *"Disordered Kondo nanoclusters: Effect of energy spacing,"* Phys. Rev. B, 70, (2004), 132404.

[7]. H. C. Manoharan, C. P. Lutz and D. M. Eigler *"Quantum mirages formed by coherent,"* Nature, 403, (2000), 512.

[8]. Michael Grobis, Ileana G. Rau, Ronald M. Potok, David Goldhaber- Gordon, *"Kondo Effect in Mesoscopic Quantum Dots,"* Handbook of Spintronics and Magnetoelectronics Exotic Materials, (2007).

[9]. Pham Vu Nhat, Nguyen Thanh Si, Minh Tho Nguyen, "*Structural Evolution and Stability Trend of Small-Sized Gold Clusters Au_n (n=20-30)*," Phys. Chem. A, (2020), Doi: 10.1021/acs.jpca.9b09287.

[10]. Dong Die, et al., "*Insights into the structural, electronic and magnetic properties of V-doped copper clusters: comparison with pure copper clusters*," Scientific reports, (2016), Doi: 10.1038/srep31978.

[11]. E. Janssens, S. Neukermans, H. M. Nguyen, M. T. Nguyen, P. Lievens, *"Quenching of the Magnetic Moment of a Transition Metal Dopant in Silver Clusters,"*, Phys. Rev. Lett., 94, (2005), 113401.

[12]. Ruibin Dong, Xiaoshuang Chen, Huxian Zhao, Xiaofang Wang, Haibo Shu, Zonglin Ding and Lu Wei, "*Structural, electronic and magnetic properties of Ag_nFe clusters ($n \leq 15$): local magnetic moment interacting with delocalized electrons,"* Journal of Physics B, 44, (2011), 035102.

[13]. R. H. Crabtree, *"The Organometallic Chemistry of the Transition Metals,"* (Wiley, New York, 2001), 3rd ed., (2001).

[14]. D. Die, B. X. Zheng, L. Q. Zhao,Q. W. Zhu, Z. Q. Zhao, *"Insights into the structural, electronic and magnetic properties of V-doped copper clusters: comparison with pure copper clusters",* Scientific Report, 6(1), (2016), 31978.

[15]. Bing Zhu, Dong Die, Ren-Cai Li, Hui Lan, Ben-Xia Zheng, Zhi-Qin Li, *"Insights into the structural, electronic and magnetic properties of Ni-doped gold clusters: Comparison with pure gold clusters,"* Journal of Alloys and Compounds, 696, (2017), 402-412.

[16]. M. J. Frisch, et. al, *"Gaussian 09 (Revision A02),"* Gaussian, Inc., Wallingford CT, (2009).

[17]. P. Hohenberg and W. Kohn, *"Inhomogeneous Electron Gas,"* Phys. Rev. 136, (1964), B864.
[18]. Nguyen Minh Tam, Nguyen Thi Mai, Hung Tuan Pham, Ngo Tuan Cuong, Nguyen Thanh Tung, *"Ultimate Manipulation of Magnetic Moments in the Golden,"* J. Phys. Chem. C, 122, (2018), 16256−16264.
[19]. Nguyen Minh Tam, Ngo Tuan Cuong, Hung Tan Pham, Nguyen Thanh Tung, *"$Au_{19}M$ (M=Cr, Mn, and Fe) as magnetic copies of the golden pyramid.",* Scientific Report, 7, (2017), 16086.
[20]. Hung Tan Pham, Ngo Tuan Cuong, Nguyen Minh Tam, Nguyen Thanh Tung, *"A Systematic Investigation on $CrCu_n$ Clusters with n = 9–16: Noble Gas and Tunable Magnetic Property,"* J. Physics. Chem. A, 37, 120, (2016), 7335-7343.
[21]. Nguyen Thi Mai, Ngo Thi Lan, Nguyen Thanh Tung, "*Insights into the magnetic origin of Cu_nCr (n=9-11) clusters: A superposition of magnetic and electronic shells*", Vietnam Science and Technology, 58 (1) (2020) 31-38.
[22]. K. Clemenger, *"Ellipsoidal shell structure in free-electron metal clusters.",* Phys. Rev. B **32**, (1985), 1359.
[23]. W. A. de Heer *"The physics of simple metal clusters: experimental aspects and simple models."*, Rev. Mod. Phys. **65**, (1993), 611.
[24]. M. Brack, *"The physics of simple metal clusters: selfconsistant jellium and semiclassical approaches.",* Rev. Mod. Phys. **65**, (1993), 677.

TÓM TẮT

TRẠNG THÁI ĐỒNG TỒN TẠI CỦA MÔ MEN TỪ CỤC BỘ VÀ VỎ ĐIỆN TỬ TỰ DO TRONG CÁC HỆ KONDO DƯỚI NANO MÉT

Tìm kiếm giới hạn nhỏ nhất mà hiệu ứng giống như Kondo có thể được quan sát là mối liên quan thú vị trong lĩnh vực vật lý cơ bản. Về vấn đề này, chúng tôi đã nghiên cứu sự tương tác giữa một số điện tử tự do của cụm nguyên tử kim loại quý và nguyên tử kim loại chuyển tiếp trong hai hệ lượng tử điển hình là $Cu_{12}Cr$ và $Au_{19}Cr$. Cả hai cụm thập nhị diện $Cu_{12}Cr$ và tứ diện $Au_{19}Cr$ đều có xu hướng tạo thành cấu trúc electron lớp vỏ đóng kín. Tuy nhiên, tính chất từ của chúng là hoàn toàn khác nhau. Bằng việc sử dụng các tính toán lý thuyết phiếm hàm mật độ, chúng tôi đã phân tích, thảo luận và đề xuất một hệ đồng tồn tại của lớp vỏ điện tử của cụm nguyên tử và lớp vỏ điện tử định xứ trên obital 3d của nguyên tử kim loại chuyển tiếp tạo lên tính chất từ của phân tử, nhằm mục đích giải thích hiện tượng dập tắt từ tính và không dập tắt từ tính của $Cu_{12}Cr$ và $Au_{19}Cr$. Các kết quả thu được dự kiến sẽ đóng góp vào sự hiểu biết về từ tính phân tử trong các cụm nano lưỡng kim.

Từ khóa: Cụm nguyên tử kim loại; Hiệu ứng Kondo; Lớp vỏ điện tử; Mômen từ.

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