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Performance of Density Functional Methods. Some Difficult Cases for Small Systems Containing Cu, Ag, or Au

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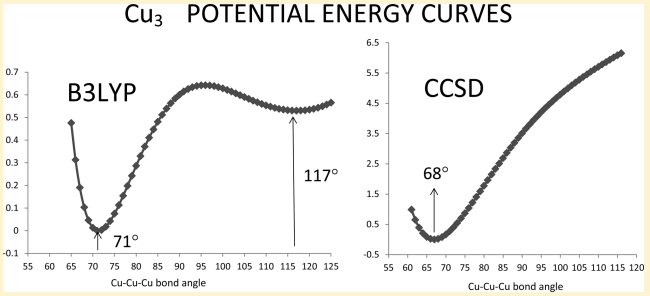
Supporting Information

ABSTRACT: Twenty-six density functional theory (DFT) methods were tested in conjunction with three different effective core potentials (ECPs) and their corresponding valence basis sets, for studying the behavior of DFT methods in small systems containing Cu, Ag, or Au where it is well-known that some functionals fail. The DFT results were compared with those obtained with post Hartree−Fock methods: second-order many-body perturbation theory (MP2), coupled cluster singles-doubles (CCSD), and coupled cluster singles-doubles with perturbative triples, CCSD(T). Calculations were carried for M_3 (M = Cu, Ag, Au); M_4^-, (M = Cu, Ag) and $[H_2O{-}Cu]^{+2}$. The comparison of the DFT calculated values with the Post Hartree−Fock values showed that, in general, all generalized gradient approximation (GGA) type functionals fail to describe these systems. The hybrid GGA functionals (H-GGA) showed a better behavior; however, when the Lee−Yang−Parr (LYP) exchange-correlation functional was used, wrong results were obtained. The results with the hybrid meta (HM-GGA) functionals, as in the case of H-GGAs, showed that, to obtain similar results to MP2 or CCSD(T), it is necessary to have a high Hartree−Fock exchange percentage. Spurious results obtained with the H-GGA or HM-GGA methods can be eliminated increasing the Hartree−Fock exchange percentage in the H-GGA or HM-GGA type functionals. Among the different functionals tested, the BB1K and MPWB1K functionals showed the best agreement with the MP2 and CCSD(T) results.



INTRODUCTION

Presently, common computational quantum chemistry applications include calculations of minimum energy structures, activation energies, thermodynamic properties, vibrational frequencies, atomic charges, and so forth. These types of calculations aid scientists in their interpretation of experimental results, and therefore, it is very important to know the limitations of the quantum chemistry methods to avoid false conclusions extracted from the calculations. Nowadays, quantum chemical calculations performed using density functional theory (DFT) have become a very common application.[1,2] However, since the exact exchange-correlation functional is not known, only approximate functionals can be used,[2] which introduces limitations and errors in the calculation results. There are a large number of papers devoted to validating the density functionals.[1−3] Experimental or high level wave function theory data are used for the functional validation, and in general, but not always,[4] the mean unsigned error (MUE) is reported. The MUE value gives an idea of the precision of the density functionals; for example, Barden et al.[5] analyzed the behavior of some density functionals in the calculation of nine homonuclear 3d dimers. The authors found that, for B3LYP, the bond distance MUE value was 0.053 Å; therefore, one cannot expect values for 3d bond distances better than ±0.05 Å.

Recently, some authors have reported limitations, failures, or wrong answers in the calculations with some density functionals. Ramírez-Solís[6] in a systematic study about the performance of local density approximation (LDA), generalized gradient approximation (GGA), and nonlocal hybrid and meta type functionals on transition metal molecules found that the hybrid functionals were able to correctly reproduce the ordering for the lowest five electronic states of $CuCl_2$ and $AgCl_2$. However, they are incapable of reproducing a potential curve for the lowest triplet state of AgI. Sodupe and co-workers[9] have shown that the popular B3LYP functional along with G96LYP, BLYP, and MPW1PW91 are unable to reproduce the relative energies of the ground and low-lying electronic states of the $[H_2O{-}Cu]^{+2}$ complex. B3LYP wrongly predicts that the $^2A'$ state (Cs symmetry) is the ground state and the $^2A_1$ state (C_{2v} symmetry) the second low-lying state, in complete disagreement with CCSD(T) results where the $^2A'$ state does not exist and the ground state corresponds to the $^2A_1$ state. Li et al.,[7] in a theoretical study on Au_n^+ (n = 4−6) clusters, found that the DFT relative energy between C_{2v} and quasi-D_{3h} structure for Au_6^+ clusters was positive or negative

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Table 1. Summary of the Density Functionals Employed in This Work[a]

type	HF exchange weight factor	functional	exchange functional	correlation functional
GGA	0	BLYP[22,23]	Becke88	Lee−Yang−Parr
GGA	0	OLYP[22,24]	OptX	Lee−Yang−Parr
GGA	0	MPWLYP[23,25,26]	modified Perdew−Wang91	Lee−Yang−Parr
GGA	0	MPWP86[25,27]	modified Perdew−Wang91	Perdew86
GGA	0	BP86[27,23]	Becke88	Perdew86
GGA	0	MPWPW91[25,26]	modified Perdew−Wang91	Perdew−Wang91
GGA	0	BPW91[27,23]	Becke88	Perdew−Wang91
GGA	0	MPWPBE[25,28]	modified Perdew−Wang91	Perdew−Burke−Ernzerhof
GGA	0	PBEPBE[28]	Perdew−Burke−Ernzerhof	Perdew−Burke−Ernzerhof
H-GGA	0.1161	O3LYP[23,24]	OptX	Lee−Yang−Parr
H-GGA	0.200	B3LYP[23,24,30]	Becke88	Lee−Yang−Parr
H-GGA	0.200	B3PW91[26,23,31]	Becke88	Perdew−Wang91
H-GGA	0.200	B3P86[27,22,29]	Becke88	Perdew86
H-GGA	0.210	B97-1[32]	B97-1	B97-1
H-GGA	0.218	X3LYP[23,23,33]	Becke88 + Perdew−Wang91	Lee−Yang−Parr
H-GGA	0.218	MPW3LYP[23,25,26]	modified Perdew−Wang91	Lee−Yang−Parr
H-GGA	0.250	PBE1PBE[28]	Perdew−Burke−Ernzerhof	Perdew−Burke−Ernzerhof
H-GGA	0.428	MPW1K[25,26,34,35]	modified Perdew−Wang91	Perdew−Wang91
H-GGA	0.500	BH&HLYP[22,31]	Becke88	Lee−Yang−Parr
HM-GGA	0.150	MPW1KCIS[25,27,36,37]	modified Perdew−Wang91	Krieger−Chen−Iafrate−Savin
HM-GGA	0.220	PBE1KCIS[28,36,38]	Perdew−Burke−Ernzerhof	Krieger−Chen−Iafrate−Savin
HM-GGA	0.280	B1B95[22,31]	Becke88	Becke95
HM-GGA	0.310	MPW1B95[25,26,33,33]	modified Perdew−Wang91	Becke95
HM-GGA	0.420	BB1K[22,31,39]	Becke88	Becke95
HM-GGA	0.420	BMK[40]	BMK	BMK
HM-GGA	0.440	MPWB1K[25,26,31,41]	modified Perdew−Wang91	Becke95

[a]See ref 1 for a complete review on DFT functionals.

depending on the density functional. On the other hand, with ab initio correlated methods, such as second-order many-body perturbation theory (MP2), coupled cluster singles-doubles (CCSD), or coupled cluster singles-doubles with perturbative triples (CCD(T)), the relative energy was always negative. Schwerdtfeger and co-workers[10] studied the interaction of CO with anionic, neutral, and cationic Au_2 molecules. From the analysis of their results, the authors found that the different density functionals studied by them were not able to correctly describe the interaction between CO and gold. Unfortunately, Schwerdtfeger et al.[10] only studied two GGA type functionals and one hybrid type functional, namely, B3LYP. In regard to Sodupe and co-workers,[9] they did not include hybrid-meta type functionals in their study, and Li et al.[7] did not analyze the influence of the Hartree−Fock exchange of the hybrid functionals on their results.

Schaefer III et al.[8] studying Ag_3 clusters and using 23 density functional methods found that the density functionals with the LYP and B97 correlation functionals predict only one minimum with an obtuse apex angle of ∼140° for the neutral silver trimer while CCSD(T) predicts one minimum with an apex angle of ∼69°; moreover, other group of functionals predicted wrongly the existence of two minima. This last result along with the previous ones seem to point out that the problem found for Ag_3 clusters could be more general and would be present in other small metallic clusters as well as in complexes such as $[H_2O−Cu]^{+2}$.

According to the former discussion, it seems that the limitations, weakness, or strength of the density functionals proposed in the literature are not totally clear. Despite theoretical studies performed, some important questions remain unanswered: Which one is the most reliable functional at the moment for calculation of small metallic clusters? Is there some kind of diagnostic that can be applied to know how reliable the results are? In this work we study the following systems: M_3, M = Cu, Ag, Au; M_4^-, M = Cu, Ag and $[H_2O−Cu]^{+2}$ where it is known that the many density functionals fail. The aim of the present work is to aid in the understanding of the failures and limitations and help to improve the behavior proposed as functional in the literature.

METHODOLOGY

All geometry optimizations, energy, and frequency calculations were performed with the Gaussian-03 program.[11] A total of 26 density functionals were tested. The functionals were chosen as follows: 9 GGA, see Table 1. These types of functionals include in the exchange-correlation expression not only the density, 0as in the local density approximation methods, but also the gradient of the density. Ten H-GGA functionals which employ the generalized gradient approximation adding to the exchange-correlation part of the GGA, the Hartree−Fock exchange weighted by a factor, which is lower than 1. Seven HM-GGA functionals which include higher order density gradients than the corresponding to the GGA and the kinetic energy density; these expressions are not included in the standard GGA methods. As in the case of the H-GGA, the HM-GGA also includes the Hartree−Fock exchange.[1] Table 1 presents a summary of the density functionals employed in this work. Post-HF calculations were performed using the CCSD,[12] CCSD(T),[13] and the Møller−Plesset method truncated at second order, MP2.

Three effective core potentials (ECPs) along with their valence basis sets were employed in this work. All ECPs include explicitly the 19 valence electrons $ns^2np^6nd^{10}(n+1)s^1$. The

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LanL2DZ or Los Alamos ECP[14] has a double-ζ quality basis sets; [5s,6p,4d/3*s*,3*p*,2*d*] for Cu and Ag, and [5s,6p,3d/3*s*,3*p*,2*d*] for Au. The medium size CEP-121 or compact effective potentials[15] has a triple-split or triple-ζ quality basis sets; [8s,8p,6d/4*s*,4*p*,3*d*] for Cu, [8s,8p,5d/4*s*,4*p*,3*d*] for Ag and [7s,7p,5d/4*s*,4*p*,3*d*] for Au. The SDD ECP or the energy-consistent pseudopotentials of the Stuttgart/Cologne Group known as Stuttgart−Dresden[16] has the largest basis sets [8s,7p,6d/6s,5p,3d] for Cu, Ag, and Au. To avoid numerical problems in the calculation of the exchange-correlation energies, all calculations were performed with the grid ultrafine. All optimization were performed with a tight criterion. The root-mean-square (RMS) force is equal to 1×10^{-5}, and the RMS of the displacement is equal to 4×10^{-5}. For the optimization processes, two techniques were employed: (a) relaxed potential energy surface scans with regular intervals sampling of the angles and relaxing the bond distances and, (b) global optimization from a given starting structure. The spin−orbit coupling and the BSSE corrections were not included in the calculations.

RESULTS AND DISCUSSION

A. Diatomic Molecules: Cu_2, Ag_2, and Au_2. To have a look at the goodness of the density functionals to reproduce experimental data, we performed DFT calculations for Cu_2, Ag_2, and Au_2 using the 26 functionals reported in Table 1 and the three sets of ECP/valence basis sets. We calculated the MUEs using the experimental data reported on ref 17. The calculated MUE values of the bond lengths for GGA methods were 0.07, 0.07, and 0.06 Å for LanL2DZ, CEP-121, and SDD, respectively. The average mean unsigned errors (AMUEs), which is the average of the MUEs with the LanL2DZ, CEP-121, and SDD ECP/valence basis sets, was 0.07 Å. This last value compare well with the reported value by Truhlar et al.[18] (0.09 Å) in their study on density functionals where the authors analyzed the bond lengths as well as atomization energies of eight transition metal dimers, including Cu_2 and Ag_2. For the H-GGA methods, our MUE values were 0.07, 0.07, and 0.07 Å for LanL2DZ, CEP-121, and SDD, respectively, and the AMUE 0.07 Å. For HM-GGA methods, the calculated MUE values were 0.07, 0.07, and 0.06 Å for LanL2DZ, CEP-121, and SDD, respectively, and the AMUE 0.07 Å. All our AMUE values are lower than the reported for the set of eight metallic dimers[18] (0.09 Å for GGA, 0.18 Å for H-GGA, and 0.15 Å for HM-GGA) but higher than the corresponding to the subset composed by Ag_2, AgCu, Cu_2, and Zr_2 (0.05 Å for GGA, 0.05 Å for H-GGA, and 0.04 Å for HM-GGA).[18]The reason for this is that the set of eight metallic dimers includes the Cr_2 molecule where, according to Truhlar et al.,[18] the DFT methods fail to reproduce the experimental Cr_2 bond distance. On the other hand, our set includes the Au_2 molecule where it is well-known[10] that the DFT methods do not reproduce the bond length and the dissociation energy; therefore, our MUEs values are larger than the corresponding to the subset of Ag_2, AgCu, Cu_2, and Zr_2.

B. Neutral Trimer Structures: Cu_3, Ag_3, and Au_3. Schaefer III et al.[8] reported that, for neutral and ionic Ag_3 clusters, the molecular geometry are highly depend on the correlation functional employed in the calculation. The authors studied 23 DFT methods and found a better performance when the uniform electron gas limit is incorporated into the correlation functional, whereas in those methods with LYP type functionals or variations of the B97 the performance was worse. In this section, we study the Cu_3, Ag_3, and Au_3 clusters with 26 different density functionals and with the ab initio post-Hartree−Fock methods CCSD, CCSD(T), and MP2. According to Table 2 at CCSD, CCSD(T), and MP2/SDD levels, the

Table 2. Distances (in Å) and Bond Angles (in Degrees) for $Cu_3(C_{2v})$ Clusters. $^2B_2$ State Using Some GGA Type Functional[a]

functional	*R* (Å)	angle (deg)	*R* (Å)	angle (deg)
BLYP	2.319	71.96	2.310	122.98
	2.338	*68.62*	*2.329*	*125.35*
	2.308	**69.85**	**2.304**	**128.70**
OLYP	2.367	72.39	2.370	121.06
	2.357	*68.95*	*2.364*	*116.50*
	2.339	**70.00**	**2.351**	**124.27**
MPWLYP	2.317	71.87	2.307	122.50
	2.335	*68.53*	*2.326*	*124.54*
	2.305	**69.67**	**2.300**	**128.43**
MPWP86	2.303	68.94	**2.275**	**117.04**
	2.310	*67.12*		
	2.286	**67.59**		
BP86	2.306	68.98	*2.299*	*114.26*
	2.313	*67.17*		
	2.289	**67.68**	**2.279**	**118.43**
MPWPW91	2.312	68.96		
	2.316	*67.11*		
	2.293	**67.58**		
BPW91	2.315	69.00		
	2.319	*67.16*		
	2.296	**67.66**		
MPWPBE	2.312	68.83		
	2.315	*67.02*		
	2.292	**67.48**		
PBEPBE	2.317	68.75		
	2.319	*66.96*		
	2.297	**67.45**		

[a]LanL2DZ plain. *CEP-121 italic*. **SDD bold**. **MP2:** LanL2DZ *R* = 2.402, angle = 69.34; *CEP-121 R = 2.290, angle = 66.69*; **SDD *R* = 2.297, angle = 66.59**. **CCSD:** LanL2DZ *R* = 2.432, angle = 70.75; *CEP-121 R = 2.336, angle = 68.56*; **SDD *R* = 2.334, angle = 68.40**. **CCSD(T):** LanL2DZ *R* = 2.420, angle = 69.54; *CEP-121 R = 2.322, angle = 67.09*; **SDD *R* = 2.323, angle = 66.86**.

Cu_3 cluster only has one minimum energy structure with an acute bond angle of ∼67°. At the DFT level with a SDD ECP/valence basis set, within GGA approximation, the number of minimum energy structures depends on the correlation functional; that is, for LYP (see Figure 1) and P86 correlation functionals, there are two structures, while for PW91 and PBE there is only one. These results are similar to those reported by Schaefer III et al.[8] Table 3 shows that for Ag_3 cluster at CCSD, CCSD(T), and MP2, there is only one stationary point that corresponds to the geometry with a bond angle of ∼68°. Even though for BLYP, OLYP, and MPWLYP only one structure was found, the angle is above 139°, and therefore these results are in disagreement with the ab initio post-Hartree−Fock results. The others GGA functionals predict two minimum energy structures, one with an acute Ag−Ag−Ag bond angle (∼70°) and other with an obtuse bond angle (∼135°), again in conflict with CCSD, CCSD(T), and MP2 results. In the case of Au_3 clusters, the CCSD/SDD calculations show that there are two stationary points, one at r = 2.700 Å and θ = 65.7°, and the

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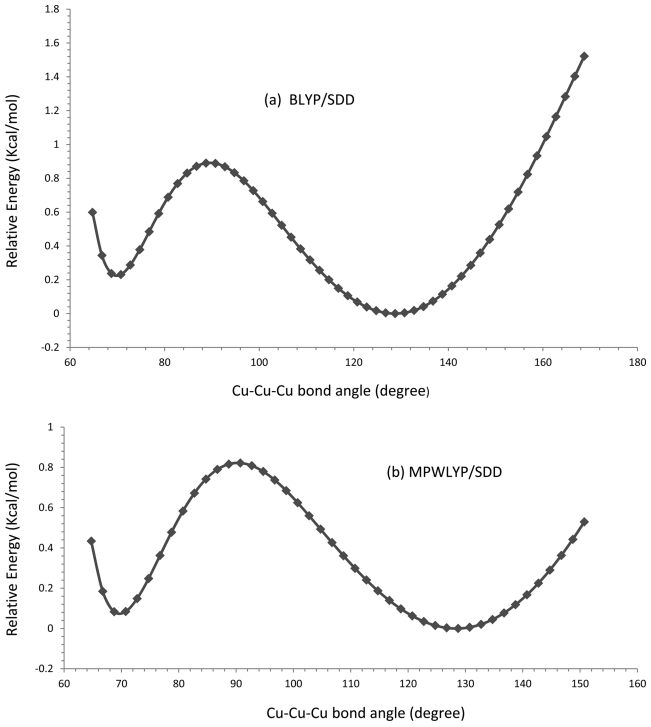

Figure 1. Potential energy curve for the Cu_3 as a function of the Cu−Cu−Cu bond angle. (a) BLYP/SDD, (b) MPWLYP/SDD.

other one at r = 2.625 Å and θ = 122.4°. Surprisingly, all of the GGA functionals tested with CEP-121 predict two minima, one at ∼68° and the other at ∼136° in agreement with the CCSD results. On the other hand when LanL2DZ is used, only the structure with the obtuse bond angle (∼ 147°) is obtained with BLYP, OLY, and MPWLYP functionals. The other functionals with LanL2DZ predict qualitatively the two minimum energy structures. With SDD, all GGA functionals predict two minima in agreement with the CCSD/SDD result except the OLYP functional where only the structure with the obtuse bond angle was obtained. To know if the trend found with the GGA type functionals remains when increasing the quality of the valence basis set, calculations with def2-QZVP ECP basis set[19,20] and four functionals: BLYP, MPWLYP, MPWPW91 and PBEPBE, were performed. The results show that for Cu_3, similarly to the results obtained with LANL2DZ, CEP-121, and SDD (see Table 2), the BLYP and MPWLYP functionals predict two minima at ∼69° and ∼126°, while the MPWPW91 and PBEPBE predict only one minimum near to 67°. For Ag_3, the BLYP and MPWLYP functionals predict one minimum near to 144°, while with the MPWPW91 and PBEPBE functionals two minimums at ∼69° and ∼133° were obtained. Regarding the H-GGA type functionals, calculations with a new split LanL2DZ and CEP-121 valence basis sets were performed. The new valence basis sets corresponding to LanL2DZ ECP for Cu and Ag (5s, 5p,3d) have two s, two p, and one d extra functions. These valence basis sets are known in the literature as LanL2TZ.[20] For CEP-121 ECP, the original (4s,4p,3d) valence basis set was extended to (6s,6p,4d). Calculation for Cu_3 and Ag_3 using the X3LYP functional with these new extended valence basis sets only shows a change of bond distance and bond angle values but not in the number of minimum energy structures. The number of minima obtained with def2-QZVP ECP/basis set, LanL2TZ, and the extended CEP-121 is qualitatively similar to those obtained with the

Table 3. Distances (in Å) and Bond Angles (in Degrees) for $Ag_3(C_{2v})$ Clusters. $^2B_2$ State Using Some GGA Type Functional[a]

functional	R (Å)	angle (deg)	R (Å)	angle (deg)
BLYP			2.697	144.86
			2.692	*140.14*
			2.676	**157.19**
OLYP			2.743	151.75
			2.723	*144.25*
			2.709	**180.0**
MPWLYP			2.693	144.36
			2.688	*139.30*
			2.672	**159.87**
MPWP86	2.653	71.40	2.651	135.89
	2.649	*69.21*	*2.644*	*131.06*
	2.635	**70.17**	**2.629**	**142.85**
BP86	2.655	71.73	2.653	136.34
	2.651	*69.42*	*2.648*	*131.93*
	2.637	**70.48**	**2.632**	**141.99**
MPWPW91	2.661	72.08	2.661	135.03
	2.655	*69.54*	*2.653*	*131.04*
	2.672	**70.54**	**2.638**	**142.80**
BPW91	2.663	72.48	2.663	135.51
	2.658	*69.78*	*2.657*	*131.87*
	2.644	**70.88**	**2.641**	**141.72**
MPWPBE	2.658	71.76	2.658	133.99
	2.652	*69.34*	*2.650*	*130.08*
	2.639	**70.26**	**2.635**	**141.54**
PBEPBE	2.664	71.58	2.663	133.86
	2.656	*69.27*	*2.654*	*129.40*
	2.644	**70.16**	**2.640**	**141.06**

[a]LanL2DZ plain. *CEP-121 italic*. **SDD bold**. **MP2:** LanL2DZ R = 2.750, angle = 68.29; *CEP-121 R = 2.678, angle = 67.20;* **SDD *R* = 2.668, angle = 67.31**. **CCSD:** LanL2DZ R = 2.778, angle = 69.09; *CEP-121 R = 2.701, angle = 68.38;* **SDD *R* = 2.691, angle = 68.28**. **CCSD(T):** LanL2DZ R = 2.775, angle = 68.53; *CEP-121 R = 2.693, angle = 67.44;* **SDD *R* = 2.684, angle = 67.57**.

other ECPs and their corresponding valence basis sets (see Tables 2 and 3) when the same density functional is used. Consequently, all of these results suggest that the geometry of the Cu_3 and Ag_3 obtained with GGA type functionals, depends not only on the correlation functional but also on the pseudopotential and the valence basis set. In conclusion, the GGA type density functionals do not seem to be very reliable for calculation of transition metal trimers of the 1b group.

Tables 4 and 5 show that, for H-GGA methods in general with CEP-121 and SDD ECP/valence basis set, the calculations with LYP correlation functional predict two structures regardless of the Hartree−Fock exchange percentage is in the functional. Only PBE1PBE and MPW1K agree with the CCSD, CCSD(T), and MP2 results for Cu_3 and Ag_3, independently of the pseudopotential employed. It is noteworthy that CCSD as well as CCSD(T) and MP2 methods predict one minimum only, with all ECPs/valence basis sets. For Au_3 cluster all functionals predict correctly two structures except for calculations done with B3LYP/LanL2dz, O3LYP/LanL2DZ, and O3LYP/SDD where only a single minimum near 140° was found. The seven tested HM-GGA functionals (see Supporting Information, Table S1) behave better than the GGA or H-GGA, for Cu_3. All functional predict correctly a single Cu_3 minimum near θ = 70 in agreement with the ab initio post-

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Table 4. Distances (in Å) and Bond Angles (in Degrees) for Cu_3 (C_{2v}) Clusters. $^2B_2$ State Using Some H-GGA Functional[a]

functional	weight factor	R (Å)	angle (deg)	R (Å)	angle (deg)
O3LYP	0.1161	2.364	73.58	**2.344**	**116.75**
		2.357	*69.89*		
		2.334	**70.88**		
B3LYP	0.200	2.327	73.94	*2.339*	*113.62*
		2.340	*70.04*		
		2.308	**71.30**	**2.310**	**117.10**
B3PW91	0.200	2.325	70.63		
		2.326	*68.43*		
		2.300	**68.91**		
B3P86	0.200	2.312	70.43		
		2.315	*68.34*		
		2.288	**68.78**		
B97-1	0.210	2.342	74.85		
		2.347	*70.54*		
		2.319	**72.07**		
MPW3LYP	0.218	2.326	73.95	*2.336*	*110.01*
		2.338	*70.03*		
		2.307	**71.18**	**2.307**	**114.81**
X3LYP	0.218	2.327	73.93	*2.337*	*110.81*
		2.339	*70.04*		
		2.308	**71.24**	**2.308**	**115.18**
PBE1PBE	0.250	2.334	70.40		
		2.331	*68.35*		
		2.306	**68.73**		
MPW1K	0.428	2.347	71.91		
		2.342	*69.51*		
		2.313	**69.77**		
BH&HLYP	0.500	2.360	78.72		
		2.365	*72.79*		
		2.330	**74.48**		

[a]LanL2DZ plain. *CEP-121 italic*. **SDD bold**.

Table 5. Distances (in Å) and Bond Angles (in Degrees) for Ag_3(C_{2v}) Clusters. $^2B_2$ State Using Some H-GGA Functional[a]

functional	weight factor	R (Å)	angle (deg)	R (Å)	angle (deg)
O3LYP	0.1161			2.732	149.70
				2.715	*142.15*
				2.701	**179.99**
B3LYP	0.200	*2.683*	*75.92*	2.694	141.83
				2.688	*135.62*
				2.673	**153.04**
B3PW91	0.200	2.668	73.19	2.669	126.80
		2.661	*70.32*	*2.660*	*118.65*
		2.645	**71.24**	**2.646**	**133.62**
B3P86	0.200	2.654	72.13	2.653	128.90
		2.649	*67.76*	*2.645*	*119.43*
		2.634	**70.59**	**2.631**	**134.14**
B97-1	0.210	2.669	78.32	2.696	142.48
		2.682	*75.37*	*2.688*	*135.89*
		2.669	**78.32**	**2.674**	**153.70**
MPW3LYP	0.218	*2.680*	*74.57*	2.692	140.82
				2.685	*134.14*
				2.670	**154.61**
X3LYP	0.218	*2.681*	*74.84*	2.693	140.98
				2.686	*134.44*
				2.671	**152.95**
PBE1PBE	0.250	2.670	72.13		
		2.661	*69.72*		
		2.648	**70.38**		
MPW1K	0.428	2.676	72.61		
		2.664	*70.04*		
		2.652	**70.61**		
BH&HLYP	0.500	*2.697*	*75.57*	2.714	133.11
				2.704	*121.51*
		2.682	**78.21**	**2.690**	**137.05**

[a]LanL2DZ plain. *CEP-121 italic*. **SDD bold**.

Hartree−Fock results. Regarding Ag_3 (Supporting Information, Table S2), the results are not as good as in the Cu_3 case. Only the BB1K and MPWB1K functionals predict correctly a single Ag_3 minimum with all ECPs/valence basis sets used. The MPW1KCIS, PBE1KCIS, and BMK functionals predict two minima, one with an acute bond angle and other with an obtuse bond angle. It is worth noticing that, even though the BMK functional has the same Hartree−Fock exchange percentage that the BB1K functional, the results are completely different. On the other hand the B1BB5 and MPW1B95 functionals work well with LanL2DZ and CEP-121 pseudopotentials but no with SDD where two minimum energy structures appear.

Regarding the Au_3 clusters in general, all HM-GGA functionals predict two structures with LanL2DZ and CEP-121 ECP/valence basis set in agreement with the CCSD/SDD calculations (see Table S3). On the contrary, in the case of the HM-GGA/SDD: B1B95, MPW1B95, BB1K, and MPWB1K, even though two stationary points were found with acute and obtuse bond angles, the structures with the obtuse bond angle have imaginary frequencies and therefore are not real minimum energy structures.

To analyze the influence of the HF-exchange percentage in the H-GGA functional, we performed a series of calculation changing the HF-exchange weight factor in a given functional and keeping the correlation part constant. Considering that the exchange-correlation energy E^{XC} can be written as:

$$E^{XC} = \alpha E^{X}_{HF} + (1 - \alpha)E^{X}_{DFT} + E^{C}_{DFT} \quad (1)$$

where α is the Hartree−Fock exchange weight factor, E^{X}_{HF} the HF-exchange energy, and E^{X}_{DFT} and E^{C}_{DFT} are the exchange and correlation density functionals, respectively. The α value can be changed systematically without changing the correlation functional E^{C}_{DFT}.[21] We chose the MPW1K functional because this functional has a high α value (α = 0.428) and the calculations with the three ECPs/valence basis sets predict correctly only one structure. In eq 1 when the α value is 0.250, the E^{XC} corresponds to MPW1PW91 functional, while when α = 0.428, E^{XC} corresponds to MPW1K. Figure 2 displays the potential energy curves using the MPW1K functional with α = 0.26, 0.27, and 0.28, and the SSD ECP/valence basis set for Ag_3. The minimum in the potential curves around 120−125° disappears as the α value increases from 0.26 to 0.28 which shows the importance of α in the stabilization/destabilization of certain structures. Table 6 shows that the effect of the α value on the predicted structure with the acute angle (~71°) is not as dramatic as the effect on the second structure where increasing slightly the α value from 0.250 to 0.270, the bond angle changes from 126° to 118°; furthermore, in the range of 0.280−0.428, this last structure completely disappears, and the calculations predict that there is only one structure with an acute angle. From now in the text, the structures that show instabilities with small changes in α will be called spurious structures. These

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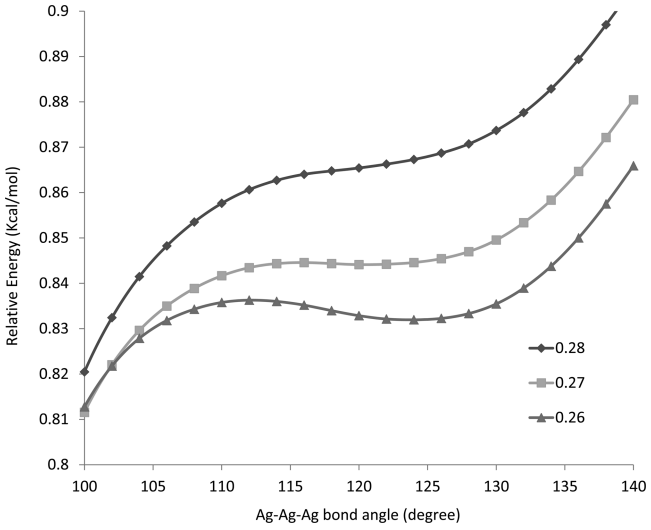

Figure 2. Detail of the potential energy curves for Ag_3 as a function of the Ag−Ag−Ag angle using eq 1 and α values of 0.26, 0.27, and 0.28. MPW1K(α)/SDD.

Table 6. HF Weight Factor, Distances (in Å), and Bond Angles (in Degrees) for Ag_3 (C_{2v}) $^2B_2$ H-GGA Functional/SDD

weight factor	R (Å)	angle (deg)	R (Å)	angle (deg)	ΔE kcal/mol
0.250[a]	2.646	70.69	2.645	126.53	0.80
0.260	2.647	70.69	2.645	123.91	0.84
0.270	2.647	70.69	2.645	118.41	0.87
0.280	2.647	70.69			
0.300	2.648	70.68			
0.428[b]	2.652	70.61			

[a]MPW1PW91 functional. [b]MPW1K functional.

results show that there is a compensation of errors between the Hartree−Fock exchange percentage in the functional and the exchange-correlation functional that can be manipulated partially changing the α value. As stated by Yang, Cohen, and Mori-Sanchez in their review on DFT methods[2] "B3LYP is successful as a result of some cancellation of errors". The density functionals are successful due to the appropriate cancellation of errors.[1,2,6,42]

As in the case of the diatomic molecules, the MUE and AMUE values were calculated. Because there is not experimental data available, we used the CCSD(T) method as the reference method for the geometrical parameter values. In general, for GGA, H-GGA, and HM-GGA methods, the bond length AMUE values are all equal to 0.04 Å . Regarding to the bond angles, the following AMUE values were obtained: GGA 2.6°, H-GGA 5.1°, and HM-GGA 3.2°. The maximum MUEs for the GGA, H-GGA, and HM-GGA methods corresponding to the bond length and bond angle were obtained with the LanL2DZ ECP/valence basis set. GGA-(LanL2DZ): bond length (MUE = 0.09 Å), bond angle (MUE = 2.35); H-GGA(LanL2DZ): bond length (MUE = 0.09 Å), bond angle (MUE = 6.13); HM-GGA(LanL2DZ): bond length (MUE = 0.08 Å), bond angle (MUE = 3.73).

C. Anionic Tetramers: Cu_4^-, Ag_4^-. In this section, the results for Cu_4^- and Ag_4^- using the H-GGA and HM-GGA type functionals are presented. Four geometry types are possible for M_4^- M = Cu, Ag clusters: D_{2h}, C_{2v}, C_{2h}, and $D_{\infty h}$, as shown in Figure 3. At MP2 and CCSD level, the

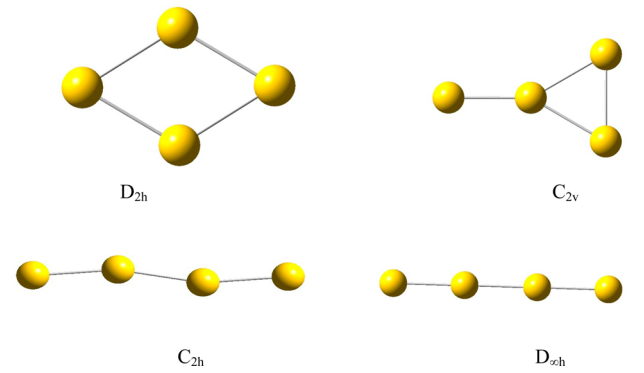

Figure 3. M_4^- structures, M = Cu, Ag.

relative energy of the Cu_4^- clusters follows the order: $D_{2h} < C_{2v} < D_{\infty h}$, as shown at the footnote in Table 7. No C_{2h} type structures were found at MP2 or CCSD level of theory. In general for Cu_4^- clusters (see Table 7), the H-GGA functionals reproduce qualitatively the MP2 and CCSD trend. On the other hand; calculations with CEP-121 and LanL2DZ and functionals with α values lower or equal to 0.218 predict the C_{2h} structure as the real minimum and the lineal structure $D_{\infty h}$ with two imaginary frequencies. It is worth noticing that there is a change in the order of stability of the $D_{\infty h}$ and C_{2v} structures when O3LYP/SDD and BH&HLYP/SDD are used, which is in disagreement with the MP2/SDD and CCSD/SDD results. These two functionals have the lower and higher values of the Hartree−Fock exchange factor, 0.1161 and 0.500, respectively. Noteworthy, unlike calculations with SDD, BH&HLYP calculations with LanL2DZ and CEP-121 predict the right energy order; i.e., $D_{2h} < C_{2v} < D_{\infty h}$. This result suggests that the cancellation of errors in the functionals is affected by the ECP/valence basis set employed.

Table 8 shows that, for Ag_4^- clusters, only the PBE1PBE and MPW1K functionals reproduce the ab initio post-Hartree−Fock relative energy order with all ECP/valence basis sets. On the other hand, all functionals with Lee−Yang−Parr correlation functional predict wrongly the lineal structure $D_{\infty h}$ as the ground state structure.

Tables 9 and 10 show that the behavior of the HM-GGA functionals is better than the H-GGAs, except the functionals with low α values such as MPW1KCIS and PBE1KCIS. To see the influence of the α factor on the results obtained with HM-GGA functionals, we change the α value of the MPW1B95(α = 0.31) functional. This functional with SDD ECP/valence basis set fails in the case of Ag_3 (see Table S2) predicting two stable structures, one with a bond angle of 69.2° and other one with a bond angle of 130.3°. Changing the α value from 0.310 to 0.330, the false minimum at 130.3° obtained with MPW1B95/SDD disappears. The relative energy order for Ag_4^- clusters obtained using MPW1B95(α = 0.33)/SDD and MPW1B95(α = 0.33)/CEP-121 was: $D_{2h}(E_{rel.}$ = 0.00 kcal/mol) < $C_{2v}(E_{rel.}$ = 2.99 kcal/mol) < $D_{\infty h}(E_{rel.}$ = 3.96 kcal/mol) and $D_{2h}(E_{rel.}$ = 0.00 kcal/mol) < $C_{2v}(E_{rel.}$ = 3.8 kcal/mol 0) < $D_{\infty h}(E_{rel.}$ = 5.41 kcal/mol), respectively. Comparing these results with those reported in Table 10 it is clear that there is not a significant change in the relative energy values. Therefore, one can conclude that the effect of α on the relative energies of true minimums is lower than the corresponding effect on the spurious structures.

D. $[H_2O-Cu]^{+2}$ Case. Sodupe et al.[9] analyzed the ground and low-lying states of the $[H_2O-Cu]^{+2}$ complex. Using two

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Table 7. Relative Energies in kcal/mol for Cu_4^- Clusters. H-GGA Type Functional[a]

functional	HF weight factor	D_{2h} ($^2B_{2u}$)	C_{2v} ($^2B_2$)	C_{2h} (^2A_g)	$D_{\infty h}$ ($^2\Sigma_g^+$)
O3LYP	0.1161	0.00	3.88	6.05, θ = 172.21	6.05[b]
		0.00	*3.60*	*5.47*, θ = *174.03*	*5.47*[b]
		0.00	**4.46**		**2.93**
B3LYP	0.200	0.00	3.70	*5.33*, θ = *176.25*	5.86
		0.00	*3.48*		*5.33*[b]
		0.00	**2.40**		**3.04**
B3PW91	0.200	0.00	5.50	9.71, θ = 174.76	9.72[b]
		0.00	*5.28*	*9.16*, θ = *176.58*	*9.16*[b]
		0.00	**4.39**		**7.25**
B3P86	0.200	0.00	5.81	*9.65*, θ = *177.60*	9.96
		0.00	*5.67*		*9.65*[b]
		0.00	**4.75**		**7.70**
B97-1	0.210	0.00	5.58	*6.94*, θ = *177.42*	7.72
		0.00	*5.17*		*6.94*[b]
		0.00	**4.08**		**4.70**
MPW3LYP	0.218	0.00	3.89	*5.71*, θ = *177.31*	6.17
		0.00	*3.72*		*5.72*[b]
		0.00	**2.63**		**3.46**
X3LYP	0.218	0.00	3.80	*5.53*, θ = *177.41*	6.02
		0.00	*3.61*		*5.53*[b]
		0.00	**2.54**		**3.29**
PBE1PBE	0.250	0.00	6.10		10.78
		0.00	*5.91*		*10.18*
		0.00	**5.09**		**8.45**
MPW1K	0.428	0.00	8.08		7.83
		0.00	*4.60*		*7.30*
		0.00	**4.10**		**6.36**
BH&HLYP	0.500	0.00	2.10		2.62
		0.00	*2.02*		*2.07*
		0.00	**1.40**		**0.88**

[a]LanL2DZ plain. CEP-121 italic. **SDD bold**. MP2/LanL2DZ relative energy: D_{2h} (0.00) < C_{2v} (+9.2 kcal/mol) < $D_{\infty h}$ (+13.6 kcal/mol); *MP2/CEP-121 relative energy*: D_{2h} (0.00) < C_{2v} (+13.5 kcal/mol) < $D_{\infty h}$ (+19.2 kcal/mol); MP2/SDD relative energy: D_{2h} (0.00) < C_{2v} (+11.7 kcal/mol) < $D_{\infty h}$ (+17.2 kcal/mol); CCSD/LanL2DZ relative energy: D_{2h} (0.00) < C_{2v} (+3.9 kcal/mol) < $D_{\infty h}$ (+5.6 kcal/mol); CCSD(T)/LanL2DZ relative energy: D_{2h} (0.00) < C_{2v} (+5.1 kcal/mol) < $D_{\infty h}$ (+9.3 kcal/mol); CCSD/SDD relative energy: D_{2h} (0.00 kcal/mol) < C_{2v} (+3.5 kcal/mol) < $D_{\infty h}$ (+5.1 kcal/mol). [b]Two imaginary frequencies.

Table 8. Relative Energies in kcal/mol for Ag_4^- Clusters. H-GGA Type Functionals[a]

functional	HF weight factor	D_{2h} ($^2B_{2u}$)	C_{2v} ($^2B_2$)	$D_{\infty h}$ ($^2\Sigma_g^+$)
O3LYP	0.1161	4.75	3.60	0.00
		5.43	*3.78*	*0.00*
		3.27	**2.67**	**0.00**
B3LYP	0.200	2.30	2.10	0.00
		2.93	*2.48*	*0.00*
		0.82	**1.46**	**0.00**
B3PW91	0.200	0.00	1.12	0.60
		0.00	*1.03*	*0.37*
		0.00	**2.22**	**2.00**
B3P86	0.200	0.00	1.62	1.29
		0.00	*1.52*	*1.01*
		0.00	**2.56**	**3.00**
B97-1	0.210	0.91	2.24	0.00
		1.47	*2.49*	*0.00*
		0.58	**1.62**	**0.00**
MPW3LYP	0.218	1.70	1.83	0.00
		2.47	*2.30*	*0.00*
		2.30	**2.28**	**0.00**
X3LYP	0.218	1.90	1.90	0.00
		2.51	*2.27*	*0.00*
		2.50	**2.27**	**0.00**
PBE1PBE	0.250	0.00	1.87	2.05
		0.00	*1.81*	*1.89*
		0.00	**2.77**	**3.64**
MPW1K	0.428	0.00	1.21	1.25
		0.00	*2.05*	*2.70*
		0.00	**1.39**	**1.51**
BH&HLYP	0.500	2.41	1.76	0.00
		1.32	*1.36*	*0.00*
		2.61	**1.94**	**0.00**

[a]LanL2DZ plain. *CEP-121 italic*. **SDD bold**. MP2/LanL2DZ relative energy: D_{2h} (0.00 kcal/mol) < C_{2v} (+7.2 kcal/mol) < $D_{\infty h}$ (+9.0 kcal/mol); *MP2/CEP-121 relative energy*: D_{2h} (0.00 kcal/mol) < C_{2v} (+9.4 kcal/mol) < $D_{\infty h}$ (+11.7 kcal/mol); **MP2/SDD relative energy**: D_{2h} (0.00 kcal/mol) < C_{2v} (+8.5 kcal/mol) < $D_{\infty h}$ (+11.9 kcal/mol); CCSD/LanL2DZ relative energy: D_{2h} (0.00 kcal/mol) < C_{2v} (+1.7 kcal/mol) < $D_{\infty h}$ (+2.4 kcal/mol); CCSD(T)/LanL2DZ relative energy: D_{2h} (0.00 kcal/mol) < C_{2v} (+2.9 kcal/mol) < $D_{\infty h}$ (+4.3 kcal/mol); **CCSD/SDD relative energy**: D_{2h} (0.00 kcal/mol) < C_{2v} (+1.9 kcal/mol) < $D_{\infty h}$ (+3.2 kcal/mol).

GGA type and three H-GGA type functionals they concluded that the relative stability of the electronic states, $^2A_1$ < $^2B_1$ < $^2B_2$ < $^2A_2$, depends on the degree of mixing of exact HF and DFT exchange functional. For GGA and H-GGA with α lower or equal to 0.25, the $^2B_1$ state is more stable than the $^2A_1$ one. Moreover, with these functionals the structure with C_s geometry is the groundstate; at the CCSD(T) level this structure does not exist. We reanalyzed the $[H_2O{-}Cu]^{+2}$ case and found that in general, with GGA type functionals, the $^2A'$ state (C_s symmetry) is the ground state in agreement with Sodupe's results. On the other hand the $^2B_1$ state, which is lower in energy that the $^2A_1$, has one imaginary frequency and corresponds to a transition state between two C_s symmetry structures. The performance of the H-GGA and HM-GGA type functionals are better than the GGA; however, it is necessary to reach at least one α value of 0.420 (see Tables S5 and S6) to obtain the same CCSD(T) relative stability order without the spurious C_s symmetry structures. This result point out that, for $[H_2O{-}Cu]^{+2}$ case, it is more important to have a high HF exchange percentage than the exchange-correlation type functional in the density functionals.

CONCLUSIONS

Results for M_3 and M_4^-, M = Cu, Ag, Au, clusters seem to point out that it is necessary to develop more confident funcionals. GGA type functionals, in general, failed in all studied cases. The inclusion of the Hartree−Fock exchange in the functional (H-GGA) seems to have improved results; however, the results with these H-GGA types functional show dependence with the ECP/valence basis set used; i.e., some false minima can appear with some ECP/valence basis sets, inducing wrong conclusions on the existence of isomers. This type of dependence was not found in MP2, CCSD or CCSD(T) calculations. On the other hand, H-GGA functionals with LYP correlation functional fail in the description of M_3 and M_4^- clusters, M = Cu, Ag. Some authors have proposed[8,42] that this fail is due to the fact that the

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Table 9. Relative Energies in kcal/mol for Cu_4^- Clusters. HM-GGA Type Functionals[a]

functional	HF weight factor	D_{2h} ($^2B_{2u}$)	C_{2v} ($^2B_2$)	C_{2h} (^2A_g)	$D_{\infty h}$ ($^2\Sigma_g^+$)
MPW1KCIS	0.150	0.00	5.35	9.24, θ = 169.35	9.26[b]
		0.00	*4.99*	*8.42,* θ = *173.00*	*8.43*[b]
		0.00	**3.97**		**6.25**
PBE1KCIS	0.220	0.00	5.23		8.82
		0.00	*4.86*		*7.87*
		0.00	**3.97**		**5.98**
B1B95	0.280	0.00	6.99		11.99
		0.00	*6.58*		*10.85*
		0.00	**6.08**		**9.74**
MPW1B95	0.310	0.00	7.07		12.04
		0.00	*6.69*		*10.96*
		0.00	**6.24**		**9.99**
BB1K	0.420	0.00	6.35		10.68
		0.00	*6.00*		*9.52*
		0.00	**5.77**		**9.06**
BMK	0.420	0.00	5.97		9.57
		0.00	*4.98*		*6.57*
		0.00	**4.78**		**6.35**
MPWB1K	0.440	0.00	6.46		10.81
		0.00	*6.12*		*9.69*
		0.00	**5.92**		**9.31**

[a]LanL2DZ plain. *CEP-121 italic*. **SDD bold**. [b]2 imaginary frequencies.

Table 10. Relative Energies in kcal/mol for Ag_4^- Clusters HM-GGA Type Functionals[a]

functional	HF weight factor	D_{2h} ($^2B_{2u}$)	C_{2v} ($^2B_2$)	$D_{\infty h}$ ($^2\Sigma_g^+$)
MPW1KCIS	0.150	0.54	1.28	0.00
		0.00	*1.57*	*0.54*
		1.10	**1.61**	**0.00**
PBE1KCIS	0.220	0.11	1.04	0.00
		0.00	*1.75*	*1.30*
		0.62	**1.36**	**0.00**
B1B95	0.280	0.00	2.67	3.42
		0.00	*3.56*	*4.94*
		0.00	**2.69**	**3.35**
MPW1B95	0.310	0.00	2.94	3.90
		0.00	*3.83*	*5.42*
		0.00	**2.99**	**3.91**
BB1K	0.420	0.00	2.57	3.55
		0.00	*3.45*	*4.97*
		0.00	**2.76**	**3.79**
BMK	0.420	0.00	1.71	1.65
		0.00	*2.71*	*3.14*
		0.00	**1.37**	**0.65**
MPWB1K	0.440	0.00	2.80	3.94
		0.00	*3.67*	*5.35*
		0.00	**3.00**	**4.22**

[a]LanL2DZ plain. *CEP-121 italic*. **SDD bold**.

LYP correlation functional does not satisfy the correct electron gas limit[8] and underestimate the correlation energy of the homogeneous electron gas;[42] therefore, it is important to work with correlation functionals that satisfy the electron gas limit such as PW91, PBE, B95, and so forth, to obtain the correct results. Even though our results support this conclusion, it is clear that it is necessary but not sufficient to satisfy the electron gas limit. Density functionals with B95 correlation functional such as B1B95 or MPW1B95 and functionals with PW91 such as MPW1PW91 fail in the calculation of the Ag_3 cluster (Tables 6 and S2).

Our results point out that the HF-exchange percentage in the H-GGA functionals helps to improve the results, compensating in some way the functional errors. Changing slightly the α value, some minima in the energy potential surface can completely disappear. These minimums or spurious structures do not appear when ab initio correlated methods such a as MP2, CCSD, or CCSD(T) are used. The existence of the spurious structures is an indication of the delicate balance in the compensation of errors in the functionals. On the other hand, there is not a straightforward correlation between the α values, and the final results, for example, the relative energy order for Cu_4^- calculated with O3LYP(α = 0.1161)/SDD or BH&HLYP (α = 0.500)/SDD is in disagreement with the MP2/SDD or CCSD/SDD results but the MPW3LYP(α = 0.218)/SDD and X3LYP(α = 0.218)/SDD, reproduce the relative energy order given by the post Hartree−Fock methods. The HM-GGA type functionals seem to behave better than the H-GGA type functionals, been the BB1K(α = 0.420) and MPWB1K(α = 0.440) functionals with all ECP/valence basis sets those that reproduce in almost all cases studied herein, the MP2, CCSD, and CCSD(T) results. These two functional have in common that have the B95 correlation functional. Others functional with the B95 correlation functional but with low α values such as MPW1B95(α = 0.310) fail in the calculation of Ag_3 structures with SDD showing once more, the delicate compensation of errors between the Hartree−Fock exchange percentage and the exchange-correlation functional. In spite of the fact that more theoretical studies are necessary to improve the functional, the BB1K and MPWB1K functionals seem to be the logical choice at the moment to calculate small metallic clusters. One possible strategy to check if the structures are spurious or not, is to perform calculations increasing slightly the α value in the functional, if the structure disappears or drastic change are observed in its geometrical parameters, it was a false minimum. Regarding the $[H_2O{-}Cu]^{+2}$ case, our and the Sodupe et al.[9] results show that it is more important the Hartree−Fock exchange percentage than the type of exchange or correlation functional and at least one α value of 0.400 in the functional to reproduce the electronic state and relative energy order given by high correlated ab initio methods such as CCSD(T).

■ ASSOCIATED CONTENT

Supporting Information

Distances and bond angles for Cu_3 (C_{2v}) clusters using HM-GGA type functional (Table S1), distances and bond angles for Ag_3 (C_{2v}) clusters using HM-GGA type functional (Table S2), distances and bond angles for Au_3 (C_{2v}) clusters using HM-GGA type functional (Table S3), relative energies between the first electronic states of $[H_2O{-}Cu]^{+2}$ complex using GGA type functional (Table S4), relative energies between the first electronic states of $[H_2O{-}Cu]^{+2}$ using H-GGA type functional (Table S5), and relative energies between the first electronic states of $[H_2O{-}Cu]^{+2}$ complex using HM-GGA type functional (Table S6). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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(21) We have made use of the G03 program feature that allows one to vary the functionals standard parameter set through internal options. To do this, one must define the Gaussian route as # MPWPW91 IOp(3/76 = *P1P2*). The new E^{XC} energy is therefore given by $E^{XC} = p2E^{X}_{HF} + p1(E^{X}_{LDA} + E^{X}_{MPW}) + E^{C}_{PW91}$, where $pi = Pi/10000$, for i= 1,2. The MPW1K correspond to the set: $p1 = 0.4280$ and $p2 = 0.5720$.

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