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A density-functional study of the structures, binding energies and magnetic moments of the clusters Mo_N ($N = 2\text{--}13$), Mo_{12}Fe , Mo_{12}Co and Mo_{12}Ni

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Abstract

We report the results of density-functional calculations of the structures, binding energies and magnetic moments of the clusters Mo_N ($N = 2\text{--}13$), Mo_{12}Fe , Mo_{12}Co and Mo_{12}Ni that were performed using the SIESTA method within the generalized gradient approximation for exchange and correlation. For pure Mo_N clusters, we obtain collinear magnetic structures in all cases, even when the self-consistent calculations were started from non-collinear inputs. Our results for these clusters show that both linear, planar and three-dimensional clusters have a strong tendency to form dimers. In general, even-numbered clusters are more stable than their neighbouring odd-numbered clusters because they can accommodate an integer number of tightly bound dimers. As a consequence, the binding energies of pure Mo_N clusters, in their lowest-energy states, exhibit an odd–even effect in all dimensionalities. Odd–even effects are less noticeable in the magnetic moments than in the binding energies. When comparing our results for pure Mo clusters with those obtained recently by other authors, we observe similarities in some cases, but striking differences in others. In particular, the odd–even effect in three-dimensional Mo clusters was not observed before, and our results for some clusters (e.g. for planar Mo_3 and Mo_7 and for three-dimensional Mo_7 and Mo_{13}) differ from those reported by other authors. For Mo_{12}Fe and Mo_{12}Ni , we obtain that the icosahedral configuration with the impurity atom at the cluster surface is more stable than the configuration with the impurity at the central site, while the opposite occurs in the case of Mo_{12}Co . In Mo_{12}Co and Mo_{12}Ni , the impurities exhibit a weak magnetic moment parallelly coupled to the total magnetic moment of the Mo atoms, whereas in Mo_{12}Fe the impurity shows a high moment with antiparallel coupling.

1. Introduction

The properties of clusters of transition metal (TM) atoms have attracted much attention in recent years for both merely scientific reasons (nanoscience) and their potential technological applications as building blocks of nanostructured materials, electronic devices, high-density magnetic data storage materials, nanocatalysts, etc (nanotechnology) (see [1] and references cited therein). Since most physical and chemical properties of clusters are strongly linked to features

of their structural forms, the starting point for understanding the properties of TM clusters is the determination of their geometrical structure, which is a nontrivial task because their atoms include both relatively localized d electrons and relatively delocalized sp electrons.

Experimental information on the structures of TM clusters can be acquired by several means, including the chemical probe method [2–6], in which cluster structure is inferred from the level of the adsorption of molecules such as N_2 onto the cluster surface. However, experimental determinations

are not always unequivocal and, in these cases, elucidation of the structures can be aided by computer simulations based on appropriate theoretical models. These fall into two broad classes: semiempirical methods involving many-body potentials, such as those based on the embedded atom model [7] or on the second-moment approximation of the tight-binding method [8–10]; and *ab initio* calculations, which are generally based on density-functional theory (DFT). The accuracy of both semiempirical and DFT methods naturally depends on the approximations they make, their parametrization (in the case of semiempirical methods) or basis sets, etc (in the case of DFT methods), and how they are used. For example, Chang and Chou [11] have recently investigated the structures of 13-atom clusters of all TMs in the 4d series (and a selection of those belonging to the 3d and 5d series) using the Vienna *ab initio* simulation package (VASP) [12, 13], with a plane-wave basis, Vanderbilt-type ultrasoft pseudopotentials [14, 15] and the spin-polarized generalized gradient approximation (GGA) for exchange and correlation [16, 17], to show that 13-atom clusters of early 4d TMs (Y_{13} , Zr_{13} , Nb_{13} and Mo_{13}) prefer the icosahedral structure, while those of late 4d TMs (Tc_{13} , Ru_{13} , Rh_{13} , Pd_{13} , Ag_{13} and Cd_{13}) prefer a ‘buckled biplanar’ (BBP) structure. According to these results, the BBP structure seems to be favoured when the d shell is more than half-filled. However, in studies of Rh_{13} performed by Bae *et al* [18, 19] using the same computational approach as Chang and Chou [11], and in a recent investigation [20] of Pd_{13} using the numerical atomic orbital DFT method SIESTA (Spanish initiative for electronic simulations with thousands of atoms) [21], Troullier–Martins pseudopotentials [22] and the GGA, it has been found that, at least for these two late 4d TM clusters, there are structures of lower energies than the BBP configuration. These results, and others for 13-atom clusters of some late 3d and 5d TMs that are discussed in [20], question the suggestion that 13-atom clusters of TMs with more than half-filled d shells have BBP ground structures. Mo being a borderline case among all 4d TMs (the electronic structure of the free Mo atom in its ground state, $4d^5 5s^1$, corresponds to just a half-filled d shell), Mo_{13} , and in general clusters of Mo atoms, are a kind of cluster that requires special attention. Moreover, Mo, isoelectronic to Cr, has a large number of d holes, so that, apart from the structural behaviour, interesting magnetic effects (including possible non-collinear magnetic configurations [23, 24]) may also be expected in Mo clusters. Besides its theoretical interest, accurate information on the structures of clusters of Mo is important for technological applications: commercial catalysts based on Mo are used in the petrochemical process known as hydrodesulfuration by which sulfur is removed from organosulfur compounds that are present in petroleum-based feedstocks [25].

The Mo dimer has been extensively investigated both experimentally and theoretically (see [26] and references cited therein). In addition to Mo_2 , some small clusters of Mo have been studied by DFT calculations. The most extensive study in this area has recently been performed by Zhang *et al* [26] who investigated the properties of Mo_N clusters ($N = 2\text{--}55$) using VASP with the GGA. Their results showed that linear (1D) and

planar (2D) Mo clusters, which have a strong tendency to form dimers, exhibit an odd–even effect in binding energy, the even-numbered clusters being more stable than their neighbouring odd-numbered clusters. By contrast, the binding energy of three-dimensional (3D) Mo clusters, which are their predicted ground-state structures beyond $N = 4$, was found to increase monotonically with cluster size. In the particular case of Mo_{13} , Zhang *et al* [26] investigated three different structures, none of them the BBP structure analysed by Chang and Chou [11], to find that the initial icosahedral structure was severely distorted after relaxation. The ground-state Mo_{13} structure predicted by Chang and Chou [11] also showed strong distortions from the ideal icosahedral geometry after this latter was allowed to relax, but its magnetic moment, $0.62 \mu_B/\text{atom}$, is different from that of the ground-state structure predicted by Zhang *et al*, $0.15 \mu_B/\text{atom}$.

In the work described here we present a comprehensive DFT study of the structural and magnetic properties of Mo_N clusters ($N = 2\text{--}13$) using the fully unconstrained version of the SIESTA [21, 27] method with the GGA. In addition, we investigate the properties of the binary clusters Mo_{12}Fe , Mo_{12}Co and Mo_{12}Ni , i.e. clusters formed when one of the Mo atoms of the Mo_{13} cluster is replaced by an ‘impurity’ atom of a ferromagnetic metal. This kind of study has proven to be of interest in the case of other binary clusters (see, e.g., [28–30]). In general, accurate predictions of how the atoms are distributed in a binary cluster (in particular, which atoms are segregated on the cluster surface) are of importance for both theoretical and technological reasons due to the use of this kind of cluster as a catalyst.

Details of the computational method used in this paper are given in section 2. In section 3 we present and discuss our results, and in section 4 we summarize our main conclusions.

2. Details of the computational procedure

We performed DFT calculations for Mo_N clusters ($N = 2\text{--}13$) using the SIESTA [21, 27] method, which employs a linear combination of pseudoatomic orbitals as basis sets. The calculations were performed without assuming the same spin-quantization axis for each Mo atom, thus allowing for possible non-collinear spin configurations. The atomic Mo core was replaced by a nonlocal norm-conserving Troullier–Martins [22] pseudopotential that was factorized in the Kleinman–Bylander form [31] and included nonlinear core corrections to account for the significant overlap of the core charge with the valence d orbitals. For the exchange and correlation potential we used the GGA as parametrized by Perdew *et al* [32]. The ionic Mo pseudopotential was generated using the atomic configurations $4d^5 5s^1 5p^0$, with 1.67, 2.30 and 2.46 au cutoff radii, respectively. The core corrections were included using a radius of 1.2 au. We tested that the $4d^5 5s^1$ configuration reproduced accurately the eigenvalues of different excited states of the isolated Mo atom. Using a conjugate gradient algorithm [33], the atomic and electronic degrees of freedom were allowed to relax simultaneously and self-consistently without any symmetry or spin constraints until interatomic forces were smaller than $0.005 \text{ eV } \text{\AA}^{-1}$. As

Table 1. Binding energies, average magnetic moments, range of interaction distances (and the average value), number of short bonds, number of total bonds and ratios of short to the total number of bonds for linear (1D) clusters. The bold numbers in the first column indicate that these clusters are the global minima (or ground states) among all the clusters of the same size.

<i>N</i>	E_B (eV/atom)	μ (μ_B /atom)	Distances ($\text{\AA}$)	Short bonds	Total bonds	Ratio
2	2.225	0.00	1.65, 1.65	1	1	1.00
3	1.962	2.00	1.61–2.89, 2.25	1	2	0.50
4	2.709	0.00	1.59–2.95, 2.04	2	3	0.66
5	2.345	1.20	1.62–2.91, 2.27	2	4	0.50
6	2.921	0.00	1.55–2.98, 2.13	3	5	0.60
7	2.613	0.86	1.57–2.95, 2.26	3	6	0.50
8	3.034	0.00	1.56–2.98, 2.27	4	7	0.57

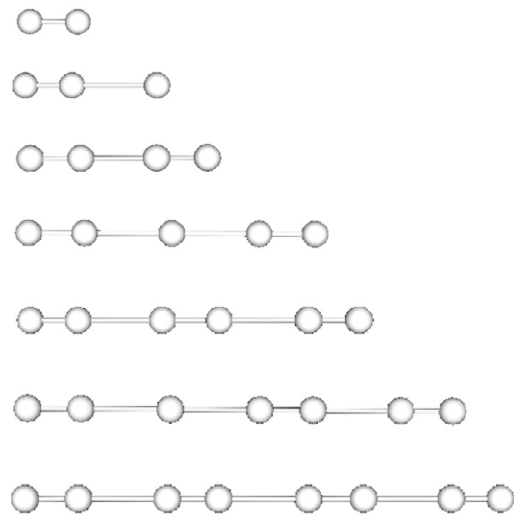
starting geometries we used a variety of configurations with different symmetries and shapes (1D, 2D and 3D), and as starting magnetic structures a variety of collinear and non-collinear arrangements of the atomic spins.

In order to ensure the stability of our calculations, we performed careful tests to check the basis sets employed and the energy cutoff used to define the real space grid for numerical calculations involving the electron density. In general, we described the valence states of the Mo clusters using triple- ζ doubly polarized (TZP) basis sets, i.e. basis that contains three orbitals with different radial forms to describe the 5s shell and three orbitals for each of the angular functions of the 4d shell, the 5s shell being polarized by the inclusion of a double set of p orbitals. We considered an electronic temperature of 25 meV and used a 250 Ryd energy cutoff to define the real space grid for numerical calculations involving the electron density. For some Mo clusters, however, we also used larger cutoffs, but the results were virtually the same. Similar results were obtained by considering an electronic temperature of 10 meV (the reduction did not produce any effect on the total energies and on the occupancy of the 5p states of the Mo atoms). The results were also hardly modified, in general, when the TZP basis was replaced by a double- ζ doubly polarized (DZP) basis.

The calculations for the binary clusters Mo_{12}Fe , Mo_{12}Co and Mo_{12}Ni were performed using only DZP basis sets in view of the similar results obtained with DZP and TZP basis for pure Mo clusters; calculations with TZP basis sets were observed to be extremely demanding. Moreover, on the basis also of the results obtained for pure Mn clusters, the study of the binary clusters was performed by assuming collinear spin arrangements. The ionic Fe pseudopotential was generated using the valence configuration $3d^7 4s^1$ because, although that of the free Fe atom in its ground state is $3d^6 4s^2$, studies of Fe clusters [34, 35] suggest that in these structures the Fe atom is mainly in the former configuration. The pseudopotentials of Co and Ni were generated using the ground-state valence configurations of the Co and Ni atoms, $3d^7 4s^2$ and $3d^9 4s^1$, respectively. The core radii were 2 au for the s, p and d orbitals of Fe and Co, and 2.05 au for the s, p and d orbitals of Ni.

3. Results and discussion

Tables 1–4 show the calculated binding energies, average magnetic moments and structural data of the low-lying isomers found for 1D, 2D and 3D Mo_N clusters, respectively; bold

**Figure 1.** Linear (1D) structures of Mo_N clusters ($N = 2$ –8).

characters in the first columns of these tables mean that those isomers are the global minima (or ground states) among the clusters of the same size. The corresponding geometries are shown in figures 1–4.

Due to the exact half-band filling of Mo, we obtain that the formation of tightly bound dimers dominate the cluster growth sequence, regardless of the dimensionality of the clusters, at least up to the size considered here. This effect is illustrated in figures 1–3, where two types of distances, short and long, characterize the structures, particularly those of the even-numbered clusters for which an integer number of tightly bound dimers can be formed (in this paper, short bonds were considered those whose interatomic distances were smaller than 2.05 $\text{\AA}$, i.e. 25% smaller than the bulk interatomic distance, 2.73 $\text{\AA}$, and long bonds those whose interatomic distances were comprised between 2.05 $\text{\AA}$ and a distance 25% larger than the bulk value). In tables 1–4, the ranges of variation of the interatomic distances are provided together with the number of short bonds relative to the total number of bonds (named Ratio). An odd–even effect is obtained for this Ratio as a function of cluster size, as a consequence of which the binding energies, shown also in tables 1–4, reflect the same odd–even trend. As a general rule, even-numbered clusters are more stable than their neighbouring odd-numbered clusters because they accommodate an integer number of tightly bound dimers. These dimers are weakly bound among themselves

Table 2. Binding energies, average magnetic moments, range of interaction distances (and the average value), number of short bonds, number of total bonds and ratios of short to the total number of bonds of the lowest-lying isomers of planar (2D) or quasi-planar clusters. The bold numbers in the first column indicate that these clusters are the global minima (or ground states) among all the clusters of the same size.

<i>N</i>	E_B (eV/atom)	μ (μ_B /atom)	Distances ($\text{\AA}$)	Short bonds	Total bonds	Ratio
3-1	1.710	0.67	1.93–2.35, 2.21	1	3	0.33
3-2	1.681	0.67	2.08–2.42, 2.19	2	3	0.66
4-1	2.554	0.50	1.64–2.97, 2.40	2	5	0.40
	2.493	0.00				
4-2	2.468	0.00	1.62–3.00, 2.31	2	4	0.50
5-1	2.499	0.80	1.68–2.88, 2.50	2	7	0.29
	2.439	0.40				
6-1	2.990	0.00	1.62–2.94, 2.28	3	6	0.50
6-2	2.756	0.00	1.65–2.98, 2.49	3	9	0.33
7-1	2.953	0.29	1.71–2.91, 2.49	3	12	0.25
	2.922	0.00				
8-1	3.123	0.00	1.58–2.98, 2.28	4	8	0.50
9-1	3.162	0.44	1.59–2.94, 2.59	4	16	0.25
10-1	3.202	0.00	1.58–3.00, 2.29	5	10	0.50

Table 3. Binding energies, average magnetic moments, range of interaction distances (and the average value), number of short bonds, number of total bonds and ratios of short to the total number of bonds of the lowest-lying isomers of three-dimensional (3D) clusters.

<i>N</i>	E_B (eV/atom)	μ (μ_B /atom)	Distances ($\text{\AA}$)	Short bonds	Total bonds	Ratio
4-1	2.457	0.50	1.71–2.96, 2.54	2	6	0.33
	2.417	0.00				
5-1	2.426	0.40	1.67–3.08, 2.59	2	9	0.22
	2.399	0.00				
5-2 Rect.	2.300	0.40	1.90–3.00, 2.49	2	8	0.25
5-3	2.265	0.00	2.31–2.83, 2.48		9	
	2.246	0.40			9	
5-4 Square	2.011	0.00	2.42, 2.42		8	
6-1	2.918	0.00	1.65–2.98, 2.57	3	10	0.30
6-2 Trap.	2.661	0.00	1.75–3.254, 2.64	1	13	0.08
6-3 Rect.	2.480	0.33	2.02–3.23, 2.59		12	
	2.453	0.66				
6-4 Square	2.299	0.00	2.50, 2.50		12	
7-1	2.844	0.00	1.85–3.06, 2.65	3	16	0.19
7-2	2.775	0.29	1.96–3.36, 2.59	3	15	0.20
	2.753	0.00				

Table 4. Binding energies, average magnetic moments, range of interaction distances (and the average value), number of total bonds and ratios of short to the total number of bonds of the lowest-lying isomers of three-dimensional (3D) clusters. The bold numbers in the first column indicate that these clusters are the global minima (or ground states) among all the clusters of the same size.

<i>N</i>	E_B (eV/atom)	μ (μ_B /atom)	Distances ($\text{\AA}$)	Short bonds	Total bonds	Ratio
8-1	3.315	0.00	1.62–3.03, 2.68	4	18	0.22
	3.230	0.25				
8-2	2.834	0.00	2.45–2.49, 2.47		16	
	2.780	0.25				
9-1	3.187	0.22	1.63–3.15, 2.68	3	21	0.14
9-2	3.059	0.00	1.67–2.97, 2.66	2	21	0.09
10-1	3.397	0.00	1.62–3.31, 2.72	5	25	0.20
10-2	3.100	0.80	2.35–2.87, 2.59		24	
10-3	2.984	0.00	2.23–2.81, 2.52		20	
11-1	3.361	0.18	1.66–3.20, 2.69	5	27	0.18
11-2	3.206	0.00	1.68–3.13, 2.72	3	30	0.10
12-1	3.579	0.17	1.68–2.93, 2.67	6	30	0.2
12-2	3.085	0.17	2.41–2.73, 2.54		28	
	3.073	0.00				
13 ICO	3.561	0.00	1.59–3.61, 2.76	6	37/42	0.16/0.14
	3.507	0.15	1.62–3.39, 2.76	6	38/42	0.16/0.14
	3.334	0.62	1.71–3.79, 2.91	6	39/45	0.15/0.13
13 BBP	3.543	0.31	1.59–3.37, 2.74	6	32/36	0.19/0.16
13 Cubo	3.063	0.31	2.60, 2.60		36	

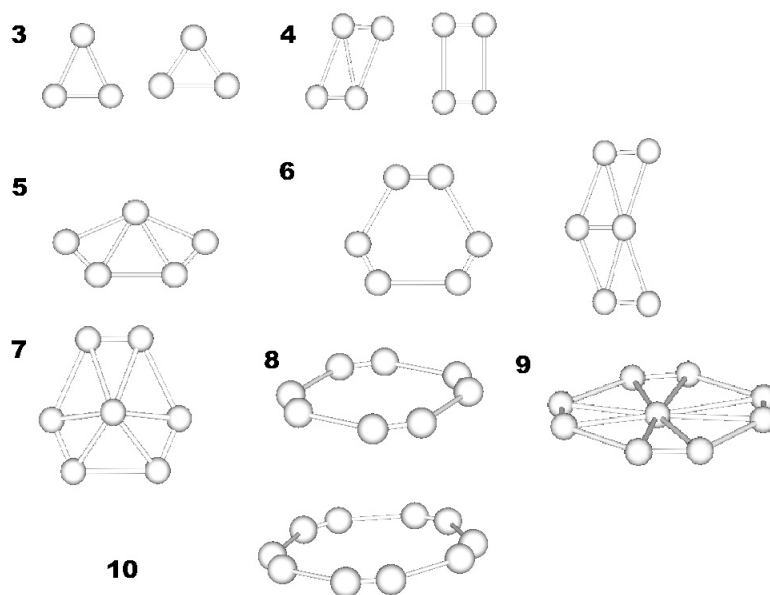


Figure 2. Planar (2D) and quasi-planar structures of Mo_N clusters ($N = 3\text{--}10$). Where several isomers were found, they are placed in decreasing order of stability.

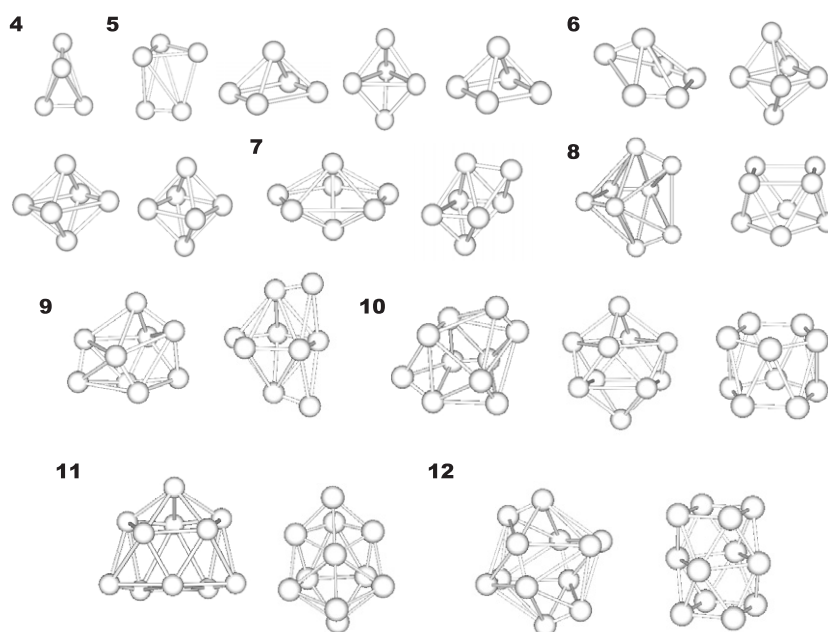


Figure 3. Three-dimensional (3D) structures of Mo_N clusters ($N = 4\text{--}12$). Where several isomers were found, they are placed in decreasing order of stability.

since most of the valence electrons participate in the bonding of the dimers (covalent bonds). Therefore, distances separating the dimers, or separating a dimer from an atom in the case of odd-numbered clusters, are noticeably larger than the interatomic dimer distances. Of course, this odd–even effect should decrease as increasing cluster size, when the tendency to form more compact structures maximizing the total number of bonds will dominate. It is, therefore, expected that, when the dimensionality of the cluster is increased, the average interatomic distance will reflect less odd–even effect. This trend is clear in figure 5, which shows that for 3D

clusters the average interatomic distance increases much more monotonically towards the bulk value, as compared to their 1D and 2D counterparts.

Figure 6 shows the binding energies of the most stable Mo clusters of each dimensionality. Two interesting trends come out: (i) odd–even effects exist in all dimensionalities; and (ii) a strong competition between low-dimensional and 3D structures takes place up to about 8 Mo atoms, which is unusual in TM clusters. The odd–even effect in Mo clusters has also been observed by Zhang *et al* [26], but only in 1D and 2D structures. Moreover, Zhang *et al* found that the low-

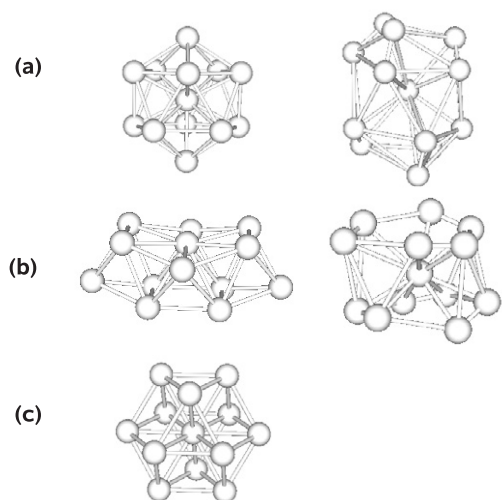


Figure 4. Starting configurations for determining the lowest-energy state of Mo_{13} : (a) ideal icosahedron, (b) buckled biplanar (BBP) structure and (c) octahedron. The structures obtained by relaxing these initial configurations using SIESTA are shown on the right-hand side (in the case of the octahedron, the relaxation is almost uniform).

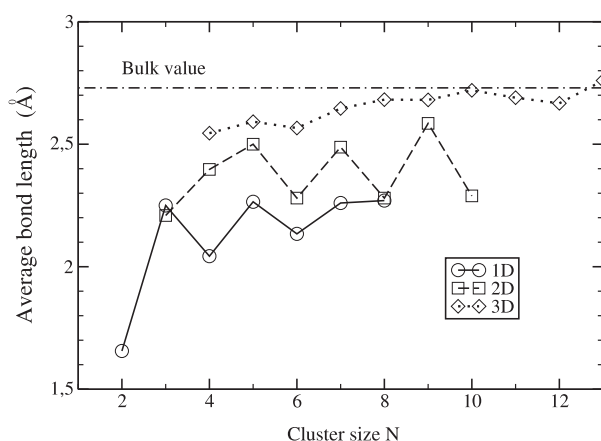


Figure 5. Average interatomic distances of the lowest-energy structures of 1D, 2D and 3D clusters.

dimensional structures do not compete with the 3D structures for Mo clusters with more than four atoms. Our results are consistent with the formation of tightly bound dimers during the cluster growth in all dimensionalities. This dimerization effect has also been obtained in clusters of Cr (isoelectronic with Mo) with up to 11 atoms [36, 37].

Concerning the magnetic moments of the Mo clusters, we obtain collinear magnetic structures in all cases, even when the self-consistent calculations started from non-collinear inputs. In general, the magnetic order is ferromagnetic, although there is a weak antiferromagnetic character when the cluster skeleton contains triangles or pentagons. The values of the average magnetic moment per atom of the most stable clusters of each dimensionality, shown in figure 7, are generally small and decrease as the cluster size increases in a non-monotonic fashion. An odd–even effect in the magnetic moment is obtained in 1D clusters, for which odd-numbered clusters

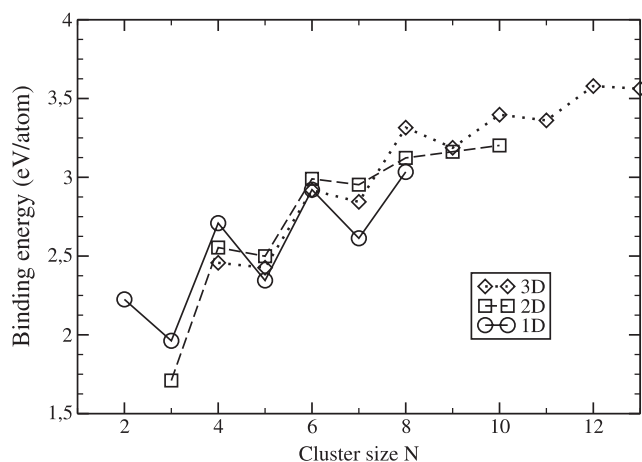


Figure 6. Binding energies of the lowest-energy states of 1D, 2D and 3D clusters.

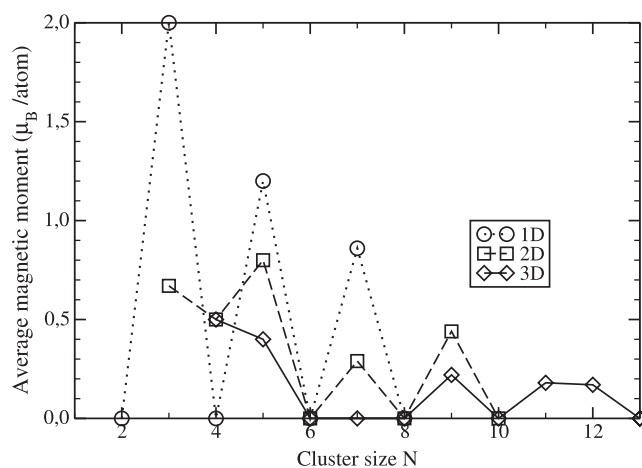


Figure 7. Average magnetic moments of the lowest-energy states of 1D, 2D and 3D clusters.

have total spin 6, whereas even-numbered clusters have total spin 0. For 2D clusters, not all the even-numbered clusters have spin 0 (Mo_4 has spin 2), but those with spin 0 are even-numbered clusters. Finally, for 3D clusters we find some odd-numbered clusters with spin 0 (Mo_7 and Mo_{13}). Thus, our results indicate that odd–even effects are less noticeable in the magnetic moments than in the binding energies.

We now discuss in more detail the results obtained in our calculations, comparing with available theoretical and experimental data. For 1D clusters, the local magnetic moments of odd-numbered clusters are very small and show an antiparallel coupling, except in the atom that does not form a tightly bound dimer, which has $\approx 5 \mu_B$ due to its having nearly half of the 4d electrons available to be spin-polarized. This atom contributes with $\approx 5 \mu_B$ to the value of the total magnetic moment, $6 \mu_B$. The dimer Mo_2 has been theoretically studied by different methods, the predicted bond lengths and binding energies being in the ranges 1.63–1.98 Å and 1.36–2.67 eV/atom, respectively; the experimental values are in the ranges 1.93–1.94 Å and 1.68–2.44 eV/atom (see [26] and references therein). Our results, 1.65 Å and

2.23 eV/atom (table 1), are in the ranges of other theoretical calculations. On the other hand, although our computed bond length is somewhat smaller than the experimental values (the value obtained with SIESTA using a DZP basis was slightly greater, 1.71 Å), our computed binding energy is in the range of experimental data. The linear trimer has been studied by several authors. Min *et al* [38] obtained a symmetric structure with 2.16 Å and 1.75 eV/atom. Our calculation gives a non-symmetric chain (1.61 Å and 2.89 Å with 1.96 eV/atom) with a magnetic moment of $2 \mu_B$ /atom, in agreement with the results of Pis-Diez [39] (2.19 Å and 2.40 Å with 2.01 eV/atom) and Zhang *et al* [26] (1.80 Å and 2.92 Å with 1.96 eV/atom). For larger chains, our results (table 1) are similar to those of Zhang *et al* [26] which are, to our knowledge, the only results available in the literature.

With regard to 2D clusters, all theoretical calculations for $N = 3$ found the most stable structure to be an obtuse isosceles triangle with two short bonds and one long bond. Specifically, Pis-Diez [39] obtained a structure with 2×2.19 Å, 2.40 Å and 2.01 eV/atom, Zhang *et al* [26] a structure with 2×2.04 Å, 2.34 Å and 2.25 eV/atom, and Bérces *et al* [40] a structure with 2×2.20 Å and 2.42 Å. We also found an obtuse isosceles triangle (2×2.08 Å, 2.42 Å and 1.68 eV/atom), but as the second lowest-energy isomer, the lowest-energy state being an acute isosceles triangle with 1.93 Å, 2×2.35 Å and 1.71 eV/atom (see table 2). It is worth noting that a similar lowest-energy structure (with one short bond + two long bonds) has been predicted for Cr₃ [36, 37], and this structure has been considered as the building block for Cr clusters of larger sizes. In the case of $N = 4$, two geometries have been predicted, the rectangular and the rhombic. Min *et al* [38] obtained the rectangular geometry (2.12 Å, 2.48 Å and 2.93 eV/atom), whereas we obtained the rhombic structure (2×1.64 Å, 2.78 Å, 2×2.97 Å and 2.55 eV/atom), in agreement with the results of Zhang *et al* [26] (2×1.83 Å, 2.76 Å, 2×3.09 Å and 2.84 eV/atom). However, our rhombic cluster is magnetic whereas Zhang *et al*'s is nonmagnetic. Both calculations give, as a closer isomer, a nonmagnetic rectangular cluster. For $N = 5$, we obtain a fan-like ground-state structure, like in Zhang *et al*'s calculations [26]. For $N = 6$, the ground-state structure is a closed ring with alternated short (1.62 Å) and large (2.94 Å) bonds and 2.99 eV/atom. By bending the linear chain to form a closed ring, the system gains 0.07 eV/atom. We also find an Mo₆ isomer that corresponds to Zhang *et al*'s lowest-energy state. Since the cluster stability is mainly determined by the ratio of shorter to larger bonds, the closed ring structure is more likely to be the real ground-state structure of Mo₆ than the fan-like structure. In the case of $N = 7$, we found the ground state to have a centred hexagonal geometry, as in Zhang *et al*'s calculations, although our geometry is not completely planar (the shape is of clam-like type). This effect suggests that a volumetric (3D) transition is expected to take place around this size (see figure 6). It is worth noting the high stability obtained in the closed ring configurations (hexagonal, octagonal and decagonal), formed with alternated short and long bonds, in comparison with the respective linear chains. For 2D clusters with $N \geq 7$, the structures maximize the ratio of shorter to longer bonds,

whereas those reported by Zhang *et al* do not follow this trend. Apart from the results by Zhang *et al*, we did not find any result for 2D Mo clusters with more than four atoms.

Concerning 3D clusters, for $N = 4$ we obtain a tetrahedral-like structure (2×1.71 Å and 4×2.96 Å with 2.46 eV/atom). The tetrahedral symmetry has been generally observed in other studies: Min *et al* [38] (2.63 Å, 2.75 Å and 4×2.31 Å with 2.99 eV/atom), Bérces *et al* [40] (2×3.02 Å and 4×2.24 Å), Pis-Diez [39] (2×3.00 Å and 4×2.23 Å with 2.59 eV/atom)—all of them thus predicting two long bonds and four short bonds—and Zhang *et al* [26] (2×1.86 Å and 4×2.89 Å with 2.83 eV/atom), thus predicting two short bonds and four long bonds, in keeping with our results, although the total spin predicted by Zhang *et al* was 0 instead of the value 2 obtained in our calculation. For $N = 5$, we obtain the lowest-energy structure to be tetrahedron-like plus an additional atom (1.67 Å, 1.93 Å, $2 \times (2.74$ Å, 3.0 Å and 3.08 Å), average distance of 2.59 Å and binding energy 2.43 eV/atom), not reported in any other previous calculation. The next isomer has a rectangular pyramidal structure (2×1.90 Å, 2×3.00 Å and 4×2.53 Å, with 2.30 eV/atom and magnetic moment of $0.4 \mu_B$ /atom), being followed by a triangular bipyramidal isomer (3×2.83 Å and 6×2.31 Å, 2.27 eV/atom and no net magnetic moment). The triangular bipyramidal structure of Mo₅ has been reported by Min *et al* [38] (3×2.84 Å, 6×2.33 Å and 3.56 eV/atom) and by Zhang *et al* [26] (3×2.77 Å, 6×2.26 Å and 2.84 eV/atom with no net magnetic moment). The rectangular pyramidal structure has been predicted, as a close isomer, by Min *et al* (2×2.23 Å, 2×2.72 Å, 4×2.46 Å and 3.37 eV/atom) and by Zhang *et al* (2×1.94 Å, 2×2.94 Å, 4×2.48 Å, 2.82 eV/atom and no net magnetic moment).

The most common 3D structures for $N = 6$ are the octahedron and the deformed pentagonal pyramid. Min *et al* [38] obtained a deformed octahedron (with non-flat square base plane and 3.96 eV/atom), whereas our calculations, in keeping with the results of Zhang *et al* [26], predict a nonmagnetic deformed pentagonal pyramid, the octahedron being a close isomer. We note that we obtain a noticeable deformation associated with the dimerization effect, while Zhang *et al*'s octahedron is more regular. Our calculation also gives a regular rectangular octahedron and a square octahedron, but both isomers are far in energy from the lowest-energy state. For $N = 7$ our calculation predicts a pentagonal bipyramid to be the lowest-energy structure (the bonds of the atoms in the ring ranging from 2.01 to 3.46 Å and in the apex atoms from 2.01 to 2.95 Å, the binding energy being 2.84 eV/atom). The same symmetry was predicted by Min *et al* [38] (the atoms in the ring ranging from 2.33 to 2.42 Å and in the apex atoms from 2.45 to 3.0 Å, with 4.12 eV/atom). In both calculations, the capped octahedra is a close isomer. By contrast, in Zhang *et al*'s calculations the lowest-energy structure is the capped octahedral, while the pentagonal bipyramid is the closest isomer. The magnetic character is similar in both calculations (Zhang's and ours). For $N = 8$, a twisted square prism and a double capped octahedra are found. Min *et al* [38] predicted the twisted square prism, with a top (bottom) bond length of 2.48 Å (2.44 Å) and a height of 2.08 Å, to be the lowest-energy state. Our calculations, like those of Zhang *et al*, predict that

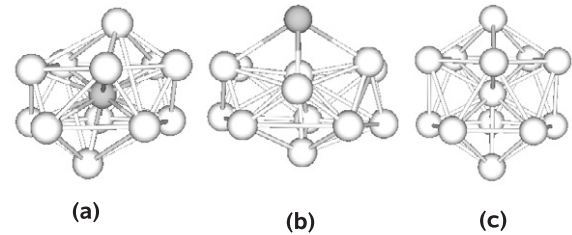
Table 5. Binding energies, magnetic moments and bond distances of the binary icosahedral clusters Mo_{12}Fe , Mo_{12}Co and Mo_{12}Ni , with the impurity (I) atom at the centre (C) and at the surface (S). Bond distances correspond to I–Mo, Mo–Mo and total average distances.

Cluster	E_B (eV/atom)	μ_I (μ_B)	μ_{Mo} (μ_B)	Distances ($\text{\AA}$)
Mo_{12}Fe (C)	3.005	1.96	−0.96	2.66, 2.78, 2.74
Mo_{12}Fe (S)	3.027	3.18	−1.18	2.71, 2.79, 2.78
Mo_{12}Co (C)	3.043	0.09	0.91	2.63, 2.75, 2.72
Mo_{12}Co (S)	3.029	1.91	1.09	2.68, 2.77, 2.76
Mo_{12}Ni (C)	2.982	0.14	1.86	2.64, 2.76, 2.73
Mo_{12}Ni (S)	3.010	0.49	1.51	2.66, 2.78, 2.77

the ground state is a nonmagnetic doubly capped octahedra, although again we obtain a more noticeable deformation than in Zhang *et al*'s study. Both calculations predict that the highly symmetric twisted square prism is a close isomer. For 3D clusters with $N = 9$ –13, there are no results available in the literature except those of Zhang *et al* [26] (the case $N = 11$ was not analysed by Zhang *et al*). In general, we obtain similar structures except for $N = 10$, but, as in cases indicated above, our geometries are more deformed. For $N = 10$, our lowest-energy state is a nonmagnetic hollow amorphous-like cluster with five short bonds. The next isomer, formed by two twisted squares, corresponds to the ground state obtained by Zhang *et al*. Fractions of icosahedral clusters are obtained for $N = 11$, which has four short bonds, and for $N = 12$. Ground-state Mo_{12} is the empty icosahedral cluster with strong deformations.

The 3D cluster with $N = 13$ is a very special case, as indicated in section 1. Our calculations predict that the lowest-energy state has a deformed icosahedral structure with no net magnetic moment (table 4). The next isomers, in decreasing order of energy, are: a BBP structure with $\mu = 0.31 \mu_B/\text{atom}$ (the second lowest-energy isomer identified by Chang and Chou [11]), a deformed icosahedral cluster with $\mu = 0.15 \mu_B/\text{atom}$ (the lowest-energy state predicted by Zhang *et al* [26]), a deformed icosahedral cluster with $\mu = 0.62 \mu_B/\text{atom}$ (the lowest-energy state obtained by Chang and Chou [11]) and a cubo-octahedral cluster with $\mu = 0.31 \mu_B/\text{atom}$ (Zhang *et al* predicted also a cubo-octahedral cluster as one of the lowest-energy isomers of Mo_{13} , but with a large magnetic moment of $0.46 \mu_B/\text{atom}$).

We finally focus on the results obtained for the binary clusters Mo_{12}Fe , Mo_{12}Co and Mo_{12}Ni , i.e. clusters formed when one of the Mo atoms in the icosahedral Mo_{13} cluster is replaced by an 'impurity' atom of a ferromagnetic metal. SIESTA relaxations for the two possible locations of the impurity, one at the cluster centre and the other at the surface, show that in both cases the final structure is strongly deformed. This result is shown in figure 8 for the cluster Mo_{12}Fe ; the other binary clusters behave similarly. The computed binding energies, magnetic moments and bond distances are given in table 5. For Mo_{12}Fe and Mo_{12}Ni , the configuration with the single impurity atom at the cluster surface is more stable than the configuration with the impurity at the central site, while the opposite occurs in the case of Mo_{12}Co . In principle, given that the surface energies of Fe, Co and Ni are smaller than the surface energy of Mo [41], the impurity atom is expected to be placed at the cluster surface in all cases. However, it has

**Figure 8.** Geometrical structures of Mo_{12}Fe with the Fe impurity at the centre (a) and at the surface (b) (dark spheres correspond to the impurity atom). To illustrate the deformations of the clusters, the ideal icosahedral structure is also shown (c).

been shown that arguments based on macroscopic properties such as the surfaces energies of the components are rather questionable when applied to small clusters (see, e.g., [42]). With regard to the magnetic behaviour, in general strong antiferromagnetic order is observed among the Mo atoms. In Mo_{12}Co and Mo_{12}Ni , the impurities exhibit weak magnetic moments parallelly coupled to the total magnetic moment of the Mo atoms, whereas in Mo_{12}Fe the impurity shows high moment with antiparallel coupling. In the latter case, the frustration is relieved, making zero the magnetic moments of two neighbouring sites in the two pentagonal rings.

4. Summary and conclusions

In this paper, we used the DFT method SIESTA to investigate the structures, binding energies and magnetic moments of the clusters Mo_N ($N = 2$ –13), Mo_{12}Fe , Mo_{12}Co and Mo_{12}Ni . The calculations for pure Mo_N clusters were performed without assuming the same spin-quantization axis for each atom, thus allowing for possible non-collinear magnetic configurations. However, we obtained collinear magnetic structures in all cases, even when self-consistent calculations were started from non-collinear inputs. Our results for these clusters showed that both linear, planar and three-dimensional clusters have a strong tendency to form dimers. In general, even-numbered clusters are more stable than their neighbouring odd-numbered clusters because they can accommodate an integer number of tightly bound dimers. As a consequence, the binding energies of pure Mo_N clusters, in their lowest-energy states, exhibit an odd–even effect in all dimensionalities. A strong competition is found between low-dimensional and three-dimensional structures up to about $N = 8$. Our results indicate that odd–even effects are less noticeable in the magnetic moments than in the binding energies.

When comparing our results for pure Mo clusters with those obtained recently by Zhang *et al* [26], we observe similarities in some cases, but striking differences in others. In particular, the odd–even effect in three-dimensional clusters was not obtained by Zhang *et al*, and our results for some clusters (e.g. planar Mo₃ and Mo₇ and three-dimensional Mo₇ and Mo₁₃) differ from those reported by these authors. For Mo₁₃, we found that the lowest-energy state has a deformed icosahedral structure with no net magnetic moment, while Zhang *et al* obtained a deformed icosahedral cluster with $\mu = 0.15 \mu_B/\text{atom}$. Our results for Mo₁₃ confirm the conclusion by Chang and Chou [11] that the BBP structure is less stable than the (deformed) icosahedral structure, although the icosahedral structure obtained by Chang and Chou had a magnetic moment of $\mu = 0.62 \mu_B/\text{atom}$ instead of 0.

Our calculations for the binary clusters Mo₁₂Fe, Mo₁₂Co and Mo₁₂Ni were performed by assuming collinear spin arrangements. For Mo₁₂Fe and Mo₁₂Ni, we obtained that the icosahedral configuration with the impurity atom at the cluster surface is more stable than the configuration with the impurity at the central site, while the opposite occurs in the case of Mo₁₂Co. In principle, since the surface energies of Fe, Co and Ni are smaller than the surface energy of Mo [41], the impurity atom is expected to be placed at the cluster surface in all cases. However, it has been shown that arguments based on macroscopic properties such as the surface energies of the components are rather questionable when applied to small clusters [42]. In Mo₁₂Co and Mo₁₂Ni, the impurities exhibit a weak moment parallelly coupled to the total magnetic moment of the Mo atoms, whereas in Mo₁₂Fe the impurity shows high moments with antiparallel coupling.

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