Ab initio study of structural, electronic and magnetic properties of iron clusters Fe_n (n=2-13)

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Structures, binding energies, and magnetic moments of Fe_n (n = 2–13) clusters have been obtained by pseudopotential density functional theory. A Troullier-Martin scheme was used to generate the iron's pseudopotential and we have successfully reproduced results (lattice constant and magnetic moment) for the bulk BCC iron. The results indicate that the magnetic moment per atom varies slowly around a mean value 3.0 μ_B/atom. With increasing atom number the mean binding energy monotonically decreases.

Keywords: Iron clusters; pseudopotentials; density functional theory; density of states.

En este trabajo se obtienen estructuras de energías de enlace y momentos magnéticos de cúmulos de Fe_n (n = 2–13) mediante la teoría funcional de la densidad con pseudopotenciales. Se usó el esquema de Troullier-Martin para generar el pseudopotencial del fierro, lo que ha permitido reproducir resultados exitosamente (constante de red y momento magnético) para el fierro en configuración BCC. Los resultados indican que los momentos magnéticos por átomo varían lentamente alrededor del valor central de 3.0 μ_B/atom. Al incrementar el número atómico la energía central de enlace decae monótonamente.

Descriptores: Cúmulos de fierro; pseudopotenciales; teoría funcional de densidad; densidad de estados.

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1. Introduction

Nanometer clusters are the focus of a fascinating interest in recent years because they constitute a new state of matter with new physical and chemical properties, as well as for their potential applications in a diverse range of new materials, electronic-devices and chemical sensors [1,2]. In contrast to bulk materials, the properties of nanomaterials are also correlated to their large fraction of surface atoms, or their high surface/volume ratio.

The electronic and magnetic properties of small iron clusters exhibit a large variation with cluster size. They have been targeted by several studies both experimentally and theoretically. On the experimental side, the information about iron clusters is limited. Only a few data is collected about dimer and trimer clusters [3-7]. On the theoretical side, several calculations have been performed to predict the geometries and electronic structures of iron clusters. Chen *et al.*, [8] attributed a ferromagnetic behavior in their study of Fe_n (n from 2 to 7) clusters using the all-electron and linear combination of atomic orbitals method. For larger clusters (up to n=7), we can cite the work of Castro and Salabub [9], Ballone and Jones [10] Gutsev and Bauschlicher [11] ,Dieguez *et al.* [12] Kohler *et al.* [13] and S. Yu *et al.* [14]. The theoretical results of these authors except Fe_2, agree well but there are controversies for larger clusters about the assignment of the ground-state structures.

The present research work is devoted to study the electronic and magnetic properties of iron clusters using the Siesta code based on pseudopotentials method. It will be noted that no such study was cited elsewhere in our knowledge.

2. Computational method

Our calculations were performed using the SIESTA [15-17] package, which implements DFT with the pseudopotential approximation and a basis set of linear combination of atomic orbital. We used the generalized gradient approximation (GGA) for the exchange-correlation functional parameterized by Perdew, Burke and Ernzerhof [18]. The pseudopotentials were constructed using the Troullier and Martin scheme [19] to describe the valence electron interaction with the atomic core.

The atomic-orbital basis set employed throughout was a split-valence double zeta polarized basis for iron atom (Fe).The charge density was calculated in a regular real-space grid with a cutoff energy of 250 Ry. Structural optimizations were performed for all configuration using the conjugate gradient (CG) algorithm until the residual forces were smaller than 0.0016 Ry/Bohr. We used periodic boundary conditions and a supercell greater than 40^3 Å to make sure that there was no additional interaction between image clusters. For a given cluster, several geometrical configurations are generated and tested.

In order to test the pseudopotential we have firstly, calculated the lattice parameter and the magnetic moment for the bulk BCC iron. Using a k-sampling with four thousand (4000) points, we have obtained the values of 2.87 Å and 2.35 μ_B as lattice parameter and magnetic moment respectively, with good agreement with both experimental [20] and theoretical [21] data.

3. Results and discussion

The ground state (optimized geometries) of iron clusters, Fe_n (n$\leq$13), obtained in our calculations is shown on Fig. 1. Only the most relaxed geometries are illustrated below.

Fe_2, Fe_3 and Fe_4 clusters

Fe_2 cluster is a complicated molecule. The bond length in iron dimer Fe_2 is 1.99Å, in good agreement with many other results such as those obtained by J.L. Chen *et al.* [8] using LSDA method and Calaminici [22] based on a DFT calculation. The magnetic moment equals 3.00 μ_B per atom.

There are controversies about the assignment of the ground-state structure for Fe_3 cluster. Most previous DFT calculations on Fe_3 [8-10,12,13] proposed an equilateral triangle with eight unpaired electrons as the most stable isomer. Gutsev and Bauschlicher [11] have predicted an isosceles triangle as ground state. In our computational study, we have tested all possible geometric configurations for Fe_3 cluster. The lowest-energy structure is the C_{2v} structure (a distorted form of D_{3h}) with a magnetic moment of 3.33 μ_B per atom. The two values of bond lengths are 2.07 and 2.38 Å. These results agree well with those obtained by Ma *et al* [23].

Most theoretical calculations for Fe_4 have predicted that the most stable isomer is a regular [8,9] or distorted [10,35,12] tetrahedron with μ= 3.0 μ_B/atom. In the present work, we have investigated the tetrahedron structures D_{2d}, D_{4h} and D_{2h}. The D_{2d} structure is the most stable of them. The second and the third one belong energetically above 0.14 and 0.08 eV/per atom, respectively. D_{2d} and D_{2h} exhibit a magnetic moment equal to 3.00 and the D_{4h} form gives 3.50 μ_B. Ballone and Jones [10] were the first to show that the energy can be lowered when the symmetry is broken. They found the same results by molecular dynamics simulations. Elsewhere, Yuan *et al.* [42], starting from a free regular tetrahedral structure, have obtained as the ground state the distorted tetrahedral structure (D_{2d} symmetry). The Jahn-Teller effects on ground state geometries of iron clusters was extensively studied by Castro [43].

In our calculations, D_{2d} ground state isomer has two short and four longer bonds of 2.19 and 2.41Å. These lengths seem to be longer than those obtained by Chen *et al.* [8] and Ballone *et al* [10]. Comparing with Fe_2 and Fe_3, it becomes evident that bigger cluster are favored with bigger interatomic distances and higher number of bonds [14].

Fe_5 to Fe_8 cluster

It should be pointed out that among all the candidates for Fe_5, four configurations are found and tested. The most stable of them is C_{2v} structure with a magnetic moment equal to 3.21 μ_B/atom with excellent agreement with several studies (see the Table I). Contrary to Boyakata *et al.* [40] the energy of D_{3h} is higher by 0.016 eV. They retrieved a trigonal geometry for the Fe_5 clusters with 1.31 eV/atom. The minimum displacement of pair atoms is 2.49Å. The C_{2v} (distortion of D_{3h}) is the most stable structure for Fe_5 with bond length of 2.34–2.41 Å and magnetic moment of 3.21 μ_B/atom.

In the case of Fe_6 cluster, two geometries seem to be as the most stable possible configurations. Regular octahedron (O_h) structure with atomic displacement equals to 2.40 Å with good agreement with Boyakata *et al.* [25] work. The obtained results contradict the results of Ballon *et al.* [10] who found that capped trigonal bipyramid is the minimum energy structure, but agrees with that of Gutsev and Bauschlicher [11] and Dieguez *et al.* [12].

The second stable Fe_6 cluster is the capped trigonal bipyramid which is isoenergetic with the first configuration and agree well with references [31,13]. Both geometries exhibit a magnetic moment equal to 3.33 μ_B/atom.

Three stable structures are obtained for Fe_7 cluster: D_{2h}, C_{3v} and the C_s geometries. On Table I, we saw that the bicapped trigonal bipyramids (D_{2h}) and the capped octahedron (C_{3v}) are above the most stable structure (the pentagonal bipyramid) (C_s) by 0.02 and 0.4 eV, respectively. Our results for Fe_7 can be compared only with those obtained by Dieguez *et al.* [12] and Kohler *et al.* [13]. The bond lengths are 2.28 and 2.89Å. Similar results are obtained elsewhere [12,40,10].

To determine the stable structure of Fe_8, four most probable geometries are studied. After relaxation, we have found surprisingly that there are two isoenergetic stables configuration having C_s and C_{2v} as a point groups symmetry with bond lengths of 2.27 to 2.68Å. These atomic distances seem to be shorter then those found by Dieguez *et al,* [12]. We can conclude that the C_s and C_{2v} structures are two energetic isomers with the same magnetic moment (3.00 μ_B/atom).

Fe_9 to Fe_{12} clusters

Three most probable structures for Fe_9 cluster are studied. The lowest energy structure obtained is C_s. The second isomer exhibits C_1 point group with very slightly different atomic distances (2.27-2.73Å), energetically above the most stable with 0.02 eV. The third cluster is crystallized in the C_{2v} structure with an energy higher with 0.15 eV. All these seeds have the same magnetic moment (equal to 2.89 μ_B/atom).

For Fe_{10}, the C_1 structure has the lowest energy . Three other candidates can be found having C_1 , C_2 and D_2 symmetries, energetically less stable, and have sensitively the same magnetic moment. The results concerning the magnetic moment (3.00 μ_B/atom) are different with those obtained by Kohler *et al,* [13].

Icosahedral like structure of Fe_{11} cluster is the lowest energy configuration (C_1) with a binding energy per atom equal to 4,999 eV and an average magnetic moment of 3,25 μ_B/atom. The C_2 structure (which is a distortion of D_{4d}) and another isomere with C_1 symmetry seem to be a probable geometry of the Fe_{11} cluster. Both clusters have the same value of magnetic moment (2.91 μ_B/atom). This value is bigger than those obtained by Pastor *et al.* [29], Kohler [13] and Bobadova *et al,* [28].

TABLE I. Space group (SG), bond lengths, binding energy and magnetic moment of Fe_n (n=2 to 13)

n	Cluster	SG	bond lengths	Comparison with other works	Binding Energy	Magnetic moment/atom	Comparison with other works
2	Fe2		1.99	2.09[32], 1.98[8], 1.96[41],2.01[22], 2.02[34],2.00[41] ; 2.03[31]	-1552.83	3.00	3.00[28,29,31,13,34]
3	Fe3-a	C2v	2.07 - 2.38	2.10[41], 2.60[31]	-2330.96	3.33	2.67[28,31,13],
	Fe3-b	C2v	2.07 - 2.39	2.31-2.18[22],	-2330.96	3.33	2.33[29], 3.53[32];
	Fe3-c	C2v	2.2 - 2.36	2.28-2.27[34]	-2330.94	3.28	1.87-3.33[34]
4	Fe4-a	D2d	2.19 – 2.41	2.28-2.18[28]	-3110.08	3.00	
	Fe4-b	D4h	2.28	2.22[41],	-3109.52	3.50	3.00[28,29,31,13],
	Fe4-c	D2h	2.22-2.43	2.22-2.61[41], 2.23-2.63[41], 3.07[31] , 2.52[33], 2.28[22],2.30[34]	-3109.76	3.00	3.01[32], 3.5[34]
5	Fe5-a	C4v	2.31 – 2.44	2.43-2.37[34]	-3889.32	3.56	3.20[28], 3.00[29],
	Fe5-b	D3h	2.32 – 2.63	2.49[33],	-3889.44	3.60	2.8[13], 3.31[32] ;
	Fe5-c	C2v	2.30 – 2.77		-3889.52	3.21	3.41[34]
	Fe5-d	D3h	2.36- 2.54		-3889.46	3.56	
6	Fe6-a	D2h	2.30 – 2.70	2.48[33]	-4669.68	3.33	3.33[28,13] 3.00[29]
	Fe6-b	0h	2.40 – 2.41		-4669.67	3.33	3.30[32]
7	Fe7-a	D2h	2.28 – 2.48	2.46[33],	-5446.28	3.07	
	Fe7-b	C3v	2.26 – 2.67	2.24-2.52[28]	-5449.29	3.14	3.14[28], 3.00[29],
	Fe7-c	Cs	2.28 – 2.89		-5449.45	3.14	3.14[13,32]
8	Fe8-a	Cs	2.27 – 2.68		-6229.19	3.00	3.00[28,13,29]
	Fe8-b	C2v	2.28 – 2.69		-6229.19	3.00	
	Fe8-c	C2	2.23 – 2.67		-6228.06	3.00	
	Fe8-d	0h	2.30		-6226.41	3.00	
9	Fe9-a	C1	2.27 – 2.73		-7007.96	2.89	2.89[28,13], 2.33[29]
	Fe9-b	C2v	2.22 – 2.80		-7007.83	2.89	
	Fe9-c	Cs	2.28 – 2.71		-7007.98	2.89	
10	Fe10-a	C2	2.28 – 2.76	2.25-2.48[28] 2.27-2.61[28]	-7787.28	3.00	2.80[28,13]
	Fe10-b	C1	2.31 – 2.78		-7787.24	3.00	
	Fe10-c	D2	2.28 – 2.85		-7787.20	3.02	
	Fe10-d	C1	2.33 – 2,70		-7798.41	3.00	
11	Fe11-a	C1	2.33 – 2.75		-8567.08	2.91	2.73[28,13], 3.00[29]
	Fe11-b	C2	2.31 – 2.69		-8567.11	2.91	
	Fe11-c	C1	2,32 – 2,80		-8579.00	3,25	
12	Fe12-a	D2h	2.35 – 2.63		-9346.27	2.83	2.67[28,13]
	Fe12-b	C1	2.21 – 2.48		-9339.22	3.00	
	Fe12-c	D2h	2,33 – 2,77		-9359.28	3,17	
13	Fe13-a	C2v	2.29 – 2.71		-10126.27	2.92	2.62[28,13], 2.54[29]
	Fe13-b	C1	2.27 – 2.70		-10125.69	2.92	
	Fe13-c	C2	2,33 – 2,66		-10140.33	3,07	

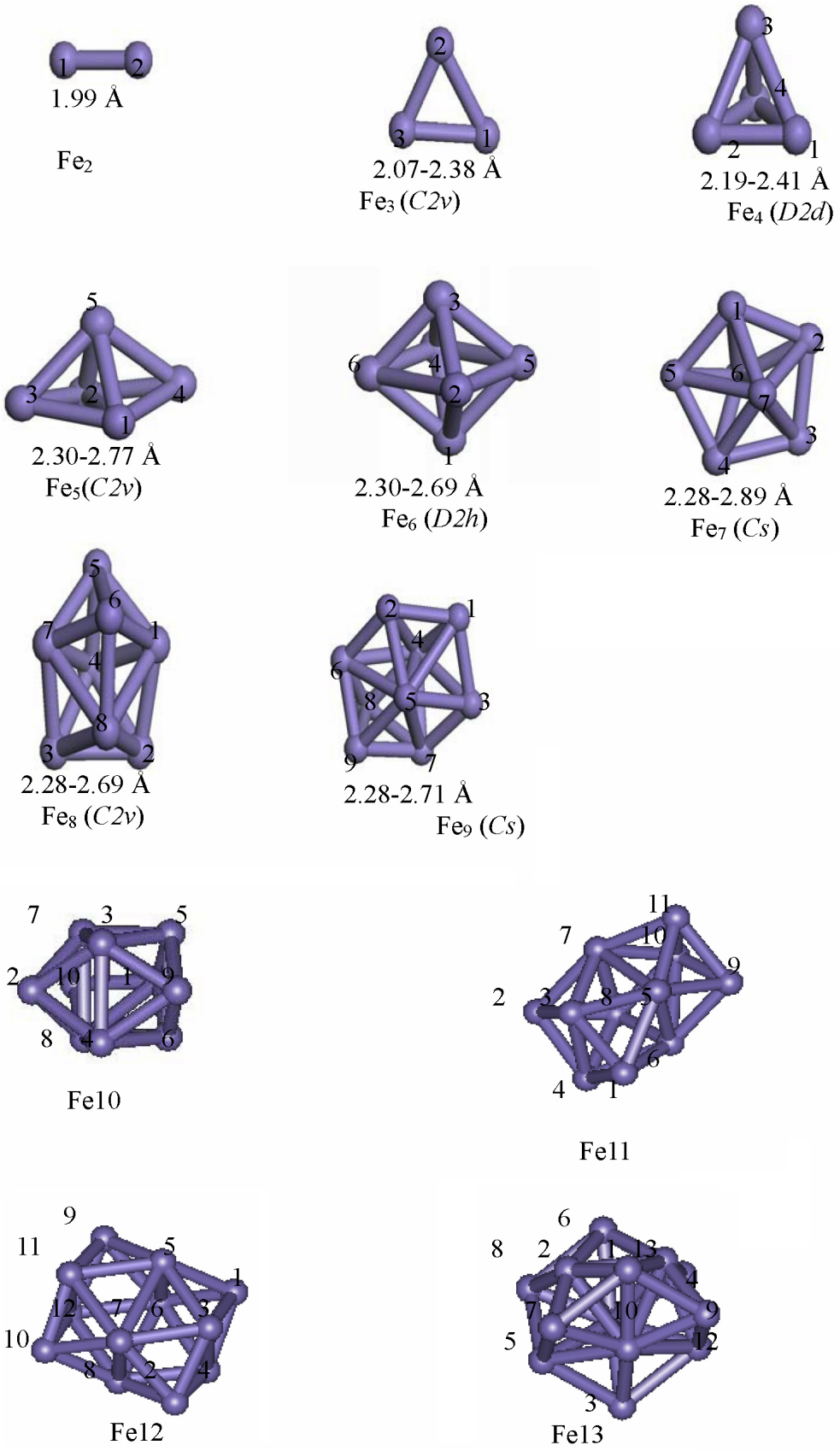

FIGURE 1.Structural sketches and their symmetries for Fe_n (n = 2–13) clusters.

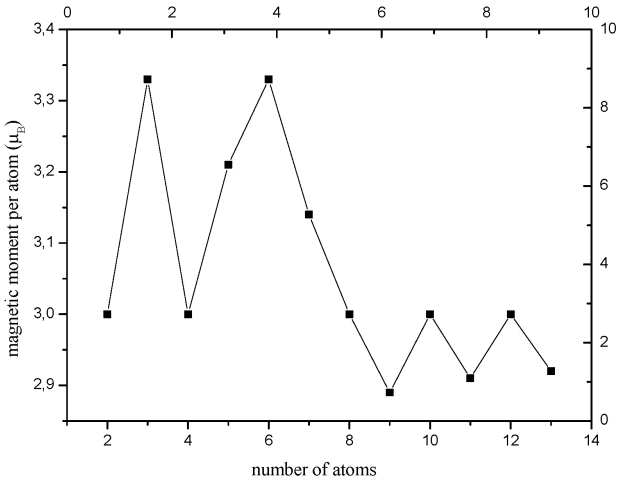

FIGURE 2. Variation of the magnetic moment per atom with the number of atoms in iron clusters

The lowest energy structure obtained for Fe_{12} has the D_{2h} symmetry which is a distortion of I_h. It is necessary to note that this distortion has completely lifted the fivefold degeneracy of the HOMO state, though the binding energy does not show much reduction [14]. The value of magnetic moment is about 3,17 μ_B/atom.

For Fe_{13}, there are many potential modes for constructing the cluster: icosahedral, hexagonal, cuboctahedral and decahedral isomers. The C_2 structure seems to be the most stable. Atomic distances are between 2.33 and 2.66Å and the magnetic moment is 3,07 μ_B/atom, exactly the same value obtained by Aguilera-Granja *et al* [44].

In Fig. 2 we present the mean magnetic moments of Fe_n (n = 2–13) clusters versus number of atoms in the cluster. The diagram shows only small variations in the magnetic moment per atom over this size range and shows that the magnetic moment remains in the vicinity of 3.0 μB/atom [36,37]. Billas *et al.* [36,37] in Stern–Gerlach deflection experiments indicated that the magnetic moment of small Fe_n clusters was around 3.0 μ_B/atom and decreased to about the bulk value. We can understand this large value of n from geometrical effects as follows: increasing interatomic spacing enhances magnetic moments and increasing coordination number has the reverse effect as a function of the cluster size [38-40].

In Fig. 3 we present as an example the density of states of Fe_{13} cluster (C_{2v} symmetry).Both spin curves (sp and d orbitals) are illustrated in this figure with a well visible energy shift. One can directly see that the mean contribution of the total DOS becomes from d orbitals. Also the DOS curve is mainly shaped from this orbital.

Electronic composition of the different peaks was investigated. We have performed a Mulliken analysis per eigenstate, atom and basis function. Below the fermi level located at -1.24 eV, the total DOS is mainly composed by $3d_{xy}$, $3d_{yz}$, $3d_{z2}$, $3d_{xz}$ and $3d_{x2-y2}$ functions. Above the Fermi level, the DOS is predominantly composed by the sp orbitals.

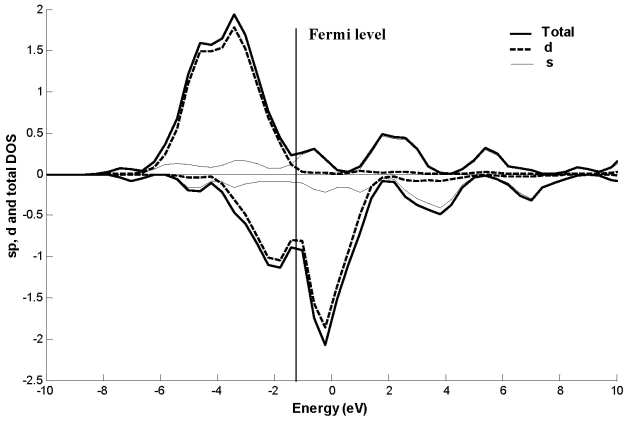

FIGURE 3. Total and partial electronic densities of states (DOS and PDOS) for Fe13 cluster. The minority spin DOS is drawn in opposite direction than the majority spins DOS. The literature usually report several results on Fe_7 and its electronic properties. For comparison, the Fe_7 Dos is shown bellow (on Fig. 4). Adding the spin contributions (up+down) we obtain sensitively the same DOS spectra obtained by Wang *et al* [45] and Castro [43].

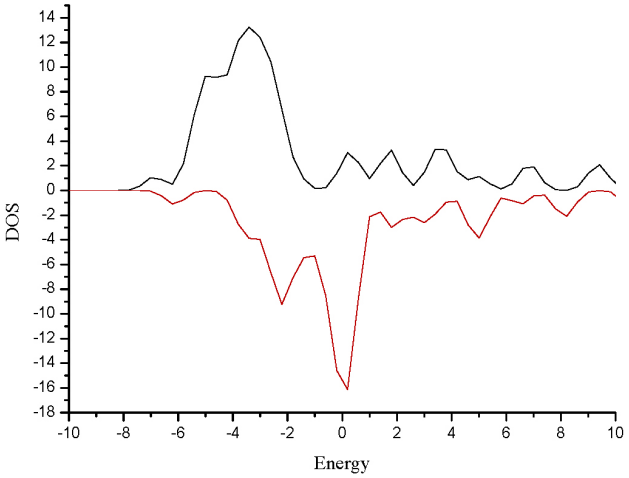

FIGURE 4. Total electronic densities of states for Fe7 cluster (down and up spins are shown)

4. Conclusion

In this paper, we have studied the Fe_n (n = 2–13) clusters using the DFT based on pseudopotential method. All possible configurations are investigated and the ground states are depicted and agree well with several precedent works. We note also that the same cluster with different geometries can exhibit the same magnetic moment and the same energy. Electronic study shows that only small variations in the magnetic moment per atom over this size range, is obtained and the magnetic moment remains in the vicinity of 3.0 μ_B/atom [36,37]. With increasing number of atoms, the mean binding energy monotonically decreases. Mullikan analysis demonstrates that below the fermi level, the total DOS is mainly composed by $3d_{xy}$, $3d_{yz}$, $3d_{z2}$, $3d_{xz}$ and $3d_{x2-y2}$ orbitals. Above the Fermi level, the sp orbital dominates the DOS.

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