PHYSICOCHEMICAL CHARACTERISTICS FOR Feₙ (n = 2–10) CLUSTER BY DENSITY FUNCTIONAL THEORY†

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In this work, we present a theoretical study on the equilibrium geometry and the energetic, electronic and magnetic properties of Fe_n (n = 2–10) based on the use of density functional theory (DFT). The results are obtained using Both Generalized Gradient Approximation according to the scheme described by Perdew-Burke-Ernzerhof (GGA-PBE). More stable structures obtained compared to other isomers have not been previously found. It is shown by the results calculated as the calculated fragmentation energy, and the second-order energy difference that Fe_n (n = 7,8,9) clusters are more stable than the other cluster sizes. The calculated magnetic properties of the most stable clusters display varying magnetic torque between values 3.00 μ_B and 3.35 μ_B, except for the Fe_{10} cluster, which takes the upper value of 3.38 μ_B. These results are very important for experimental experts who are active in designing new nanocatalysis systems in the physical and chemical fields.

Keywords: *Iron clusters; Relative stabilities; Density functional theory DFT; Binding energies;Magnetic properties*
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1. INTRODUCTION

Iron is one of the most important materials due to its physical and magnetic properties among the first transition (TM) metals. It also has high magnetism and in addition to the high value of transverse relaxation, iron metal and its oxides make it a suitable component in magnetic nanoparticles (MNPs). The high values of transverse relaxation result from the external magnetic field, and thus the detection of signals is facilitated through the transverse relaxation of iron as well. The uses of compounds based on MNP materials fall into several fields, the most important of which are in biosensing applications using magnetic resonance [1], as well as the detection of tuberculosis bacteria [2], As for magnetic enrichment, it is used to detect the in vivo circulation of cancer cells [3].

Cluster physicists admit, according to their opinion, the difficulty of conducting accurate studies of iron clusters at experimental levels [4,5]; however, applications have been made using density functional theory (DFT), which has been successful and has become widely used in calculating TM properties during the past years [6]. Among the most important advantages of the DFT theory is the ability to look for the correct and accurate electronic structure among many other possible cases that has lower energy [5], this is what makes us obtain the accurate and correct magnetic and structural properties. Thus, the presence of a strong correlation in partially filled d orbitals leads to the highest magnetic moments. In previous theoretical studies of small iron, clusters [7-10] showed a close correlation between their size and the value of their magnetic moment. The experimental study of clusters containing more than 500 atoms was also addressed. Whereas, the obtained iron cluster structures were in deformed geometries and completely different from the bcc crystal structure of iron, this was predicted by Jahn-Teller [11].

In this work we confirm the value of the quality of the calculations of all electrons within the DFT framework and find the most stable Fe_n clusters compared to other isomers.

In addition, we also calculate the important electronic properties of these clusters such as homo–lumo energy, second-order energy difference, vertical ionization potential (VIP) and vertical electronic affinity (VEA), this is for a deeper understanding of the stability of the clusters and the differences between them. The next section reviews the theoretical methodology used in the calculation briefly, while the third section presents the results of our calculations and their analysis, while this work concludes with a general summary.

2. MATERIALS AND METHODS

Our calculations were performed in order to determine the ground-state structures within the framework of spin-polarized density functional theory [12] with the use of the generalized gradient approximation (GGA) defined by Perdew,

Burke, and Ernzerhof (PBE) [13,14] functional has been used for the exchange correlation energy as implemented in the SIESTA package [15]. Among the features of this program is that it can be used for all kinds of non-local pseudo-standards preservation method for Troullier-Martins [16]. The geometries were optimized without any symmetry constraints by self-consistent field (SCF) solving of the Kohn–Sham equations with a convergence criterion of 10^{-4}a.u. on the electron density and energy.

In order to avoid interaction between neighboring clusters, we used the cubic supercell of 20 Å void, and also used the conjugate gradient (CG) algorithm. Using the Γ point approximation, the k grid integration was carried out. Geometrical optimizations were considered as converged when the residual forces were smaller than 10^{-3} eV/Å.

We employed the double polarizer ξ (DZ) basis with polarization function for all iron atoms. We have performed a relaxation for a large number of possible initial structures for iron clusters in the size (n= 2–10) atom-sized iron clusters in a very recent and previously unpublished work. In this work we could find the most appropriate structures of Fe$_n$ clusters by searching the various possible isomers.

We studied the various properties of iron Fe$_n$ clusters by determining their relative stability, which is represented by the binding energy E$_b$, fragmentation energy E$_f$, second-order energy difference Δ$_2$E. The electronic properties represented by the vertical ionization potential (VIP), vertical electronic affinity (VEA) and Chemical hardness η, were also investigated. All these quantities were calculated according to the following formulas:
The binding energy E$_b$/atom.

$$E_b (Fe_n) = [nE (Fe) – E (Fe_n)]/(n). \tag{1}$$

Fragmentation energy E$_f$

$$E_f (Fe_n) = E (Fe_{n-1}) + E (Fe) – E (Fe_n). \tag{2}$$

Second-order energy difference Δ$_2$E

$$Δ_2E (Fe_n) = E (Fe_{n+1}) + E (Fe_{n-1}) – 2E (Fe_n). \tag{3}$$

The HOMO–LUMO energy ΔE

$$ΔE = E (LUMO) – E (HOMO). \tag{4}$$

Vertical ionization potential (VIP)

$$VIP = E (Fe_n^+) – E (Fe_n). \tag{5}$$

Vertical electronic affinity VEA

$$VEA = E (Fe_n^-) – E (Fe_n). \tag{6}$$

Chemical hardness η

$$η = VIP – VEA. \tag{7}$$

Where E is the total energy of the given system.

3. RESULTS AND DISCUSSION
3.1. Structural Properties

We found a large number of isomers and determined the ground state structure of all Fe$_n$ clusters (n = 2–10) using the above calculation scheme. The most stable structures were selected for each size among the lower energy isomers, as shown in Figure 1.
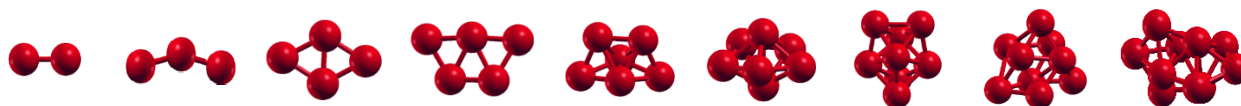
Figure 1. The lowest energy structures of Fe$_n$ (n = 2–10) clusters

In the Table we calculated bond length for Fe-Fe dimer is 1.98 Å and its binding energy per atom of 1.40 eV. In Figure 1 shows the most stable structures in this study, using SIESTA program based on DFT. Actually, this result is close to theoretical results of B.V. Reddy et al. and S. Dhar et al. and J.L. Chen et al. [17-19] and experimental results of the average bond length in the work of P.A. Montano et al. and H. Purdum et al. [20,21].

Table 1. Bond lengths of dimer Fe$_2$(Å).

This work	Other calculations	Experimental
	2.02 [17]	1.87 [20]
1.98	1.96 [18]	2.02 [21]
	1.98 [19]	

Various values of the average bond length of clusters Fe_n where (n= 2–10) are shown in Figure 2. For the clusters of Fe_n where (n=2–6), they are either linear or closed Chains in the plane, with an average bond length estimated as 1.98 Å, 2.11 Å, 2.28 Å, 2.37 Å, 2.53 Å, respectively. Generally, it is observed that the average bond length increases with the cluster size.
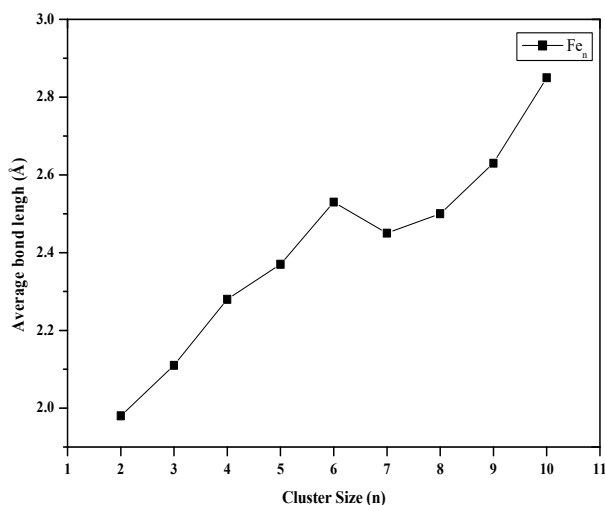

Figure 2. Average bond lengths for Fe_n(n=2–10) clusters

Based on the results shown in Figure 2, we conclude that the values of the average bond length increase in parallel with the increase in the cluster size. This is due to the fact that the ratio of atoms on the surface of the cluster is greater than the ratio of atoms in the core of it. In fact, because they are less compact, they cause the increase in the bond length.

3.2. Relative Stability
One of the most important physical factors that must be studied in the physics of materials and clusters is:

Binding Energy (cohesion)
It shows the stability of clusters obtained by comparing the result of their binding energy to other previous results for the same metal clusters. We report the calculated binding energies of Fe_n (n = 2 –10) clusters their growth with cluster size is plotted for the lowest-energy of each cluster in Figure 3. Through the general form, we notice a direct relationship, as the increase in the binding energy corresponds to the increase in the mass size. This behavior means that the clusters can obtain energy continuously during the growth process.
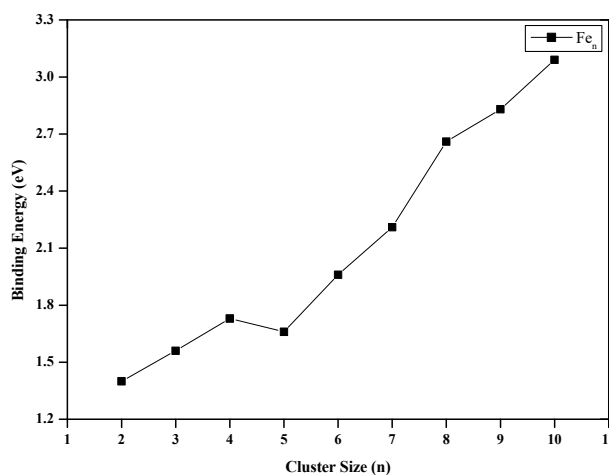

Figure 3. Binding energies per atom for the Fe_n (n = 2–10) clusters

Fragmentation energy
The fragmentation energy can also be considered as an indicator for forecasting the relative stability of the clusters. In Figure 4 we feature the growth of E_f as a function of the size clusters n. Overall through the general shape, fluctuating behavior in the values was detected. The results obtained indicate that the Fe_7, Fe_8 and Fe_9 clusters have bigger values compared to the rest of the neighboring clusters and therefore, so the clusters are relatively more powerful in terms of thermodynamic stability.

Second-order energy difference

In addition to both the fragmentation energy and the binding energy, we can use another amount that has a great indication of the stability of the clusters, which is second-order energy difference. In Figure 5, we show the growth of Δ_2E in terms of changing cluster size. Through the positive values reached at the following clusters for (n = 3,7 and 9) clusters, indicating that these clusters may have special stability compared to the rest of the clusters.
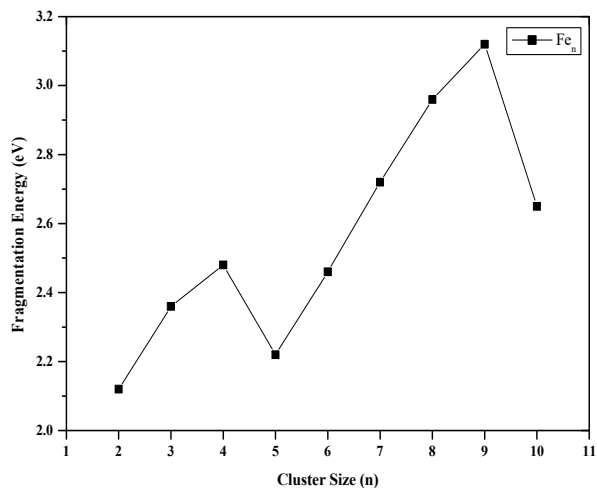
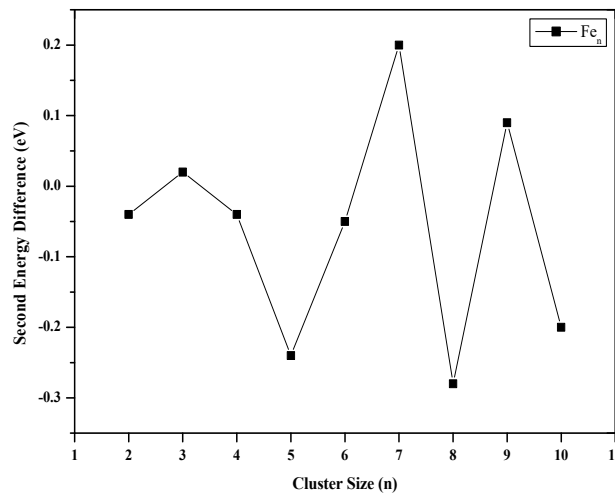**Figure 4.** Fragmentation energy per atom for the Fe$_n$ (n = 2-10) clusters

Figure 5. The Second energy difference for the Fe$_n$ (n = 2-10) clusters

3.3. Electronic Properties
HOMO–LUMO energy

When the value of the energy gap HOMO–LUMO (ΔE) is small, the chemical reactivity is high, whereas a considerable value is ascribed to an even higher chemical stability, for this reason, the HOMO-LUMO energy gap is considered as a milestone and an important criterion for the chemical stability of small clusters. The ΔE change in terms of the cluster size variation, for the most suitable structures, is shown in Figure 6.
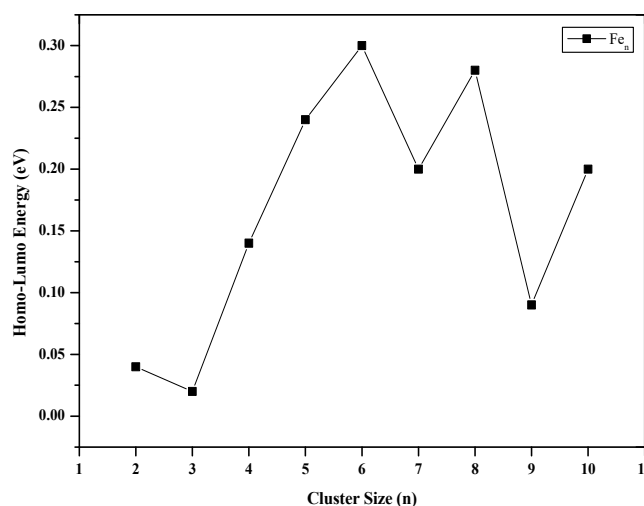
Figure 6. HOMO–LUMO energy for the Fe$_n$ (n = 2–10) clusters

An oscillatory behavior has been recorded in the growth of ΔE values when the volume of clusters is increased. Generally, we note that ΔE of Fe$_n$ (n = 2,3) clusters are smaller than the rest of the existing iron clusters. This means that these clusters come with a greater stability and a low reactivity compared to their neighbors and could be suitable to be utilized as an essential element in developing new materials.

Vertical ionization potential (VIP) and vertical electronic affinity (VEA)

We calculate the vertical electronic affinity and vertical ionization potential for the Fe$_n$ (n = 2–10) ground state, they are plotted in Figures 7 and 8 as a function of the cluster size.

The vertical ionization potential (VIP) is used to determine the chemical stability of small clusters as the proportion between the size of the cluster and its stability is inverse, meaning that the greater the size of the cluster, the less its

chemical activity, and thus its stability. Through Figure 6, we observe a non-monotonic oscillating behavior in the evolution of VIP values of Fe_n clusters. We found the highest values for Fe_6 worth an estimated 5.82 eV, followed by the same value recorded for the Fe_2 and Fe_7 clusters with values of 5.73 eV. The results obtained are close to the theoretical works of Keitel Cervantes-Salguero et al. and Gong and Zheng et al. [22,23].
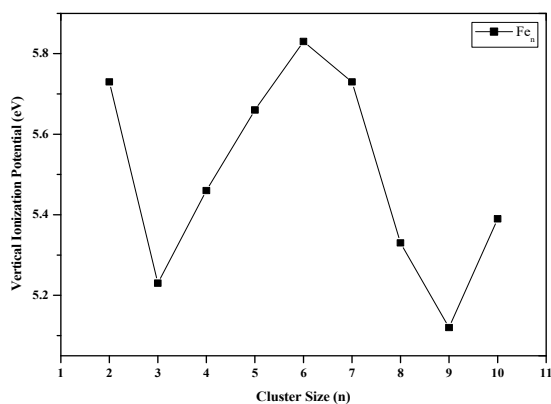

Figure 7. Vertical ionization potential (VIP) for the Fe_n (n = 2-10) clusters
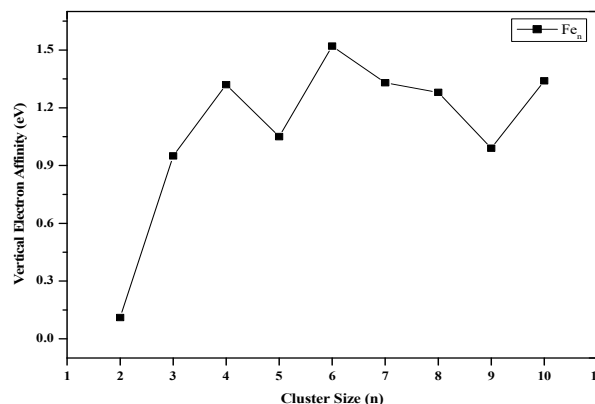
Figure 8. Vertical Electron Affinity for the Fe_n (n = 2-10) clusters

Also, what is recorded for vertical electronic affinity (VEA) values, where a non-monotonic increase with cluster size is observed, this is what the Figure 8 shows. Also, VEA in mass physics shows how stable and coherent a structure is; it is seen that the small clusters approach the metallic state, the VEA values increase with the size of the cluster. Where the following clusters recorded the smallest values of Fe_2 and Fe_9, with values estimated at 0.11 eV and 0.99 eV, respectively. Our results are very close to what has been reached in the theoretical work of Keitel Cervantes-Salguero et al., Chrétien and Salahub, and Castro and Salahub [22,24,25].

Chemical hardness η

Pearson [26] proposed the principle of maximum hardness (PMH) in order to distinguish between the relative stability of the clusters; In general, if the clusters have less interaction, is more stability, the value of their chemical hardness is greater. In Figure 9, we report the growth of η for the lowest-energy structures as a function of the cluster size. The chemical hardness of the Fe_2 and Fe_7 clusters seems to be the largest values recorded compared to all other clusters, this makes these two clusters very inert and they can be considered as good candidates for the fabrication of cluster materials applicable to nanotechnologies and nanoelectronics.
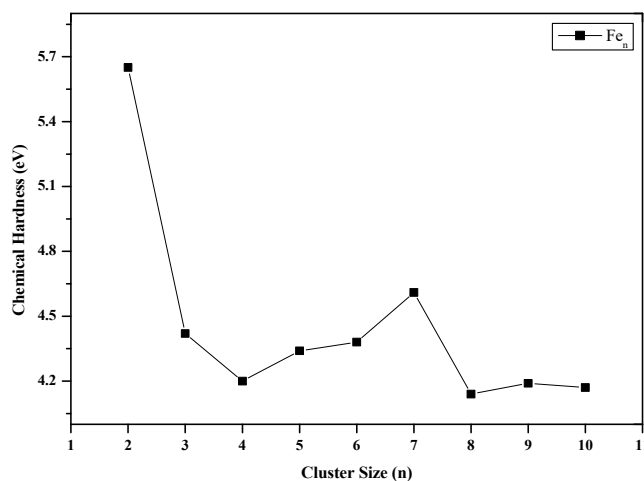

Figure 9. Chemical hardness η for the Fe_n (n = 2–10) clusters

3.3. Magnetic Characteristics

Magnetic behavior can also be considered an important marker for small clusters. In fact, we can find small clusters with specific magnetic moments that qualify them to be used in many important applications in nanotechnology. It is clear from the obtained results that the magnetic torque value of the Fe_{10} cluster takes the largest value and is estimated at 3.38 μ_B which makes it available for use in designing new Nanocatalytic systems, while the rest of the clusters recorded a value of magnetic moment ranging between 3.00 μ_B and 3.354 μ_B values. Our results regarding magnetic moment are close to those reported in the works [27-29]. The magnetic moment results are shown in Figure 10.
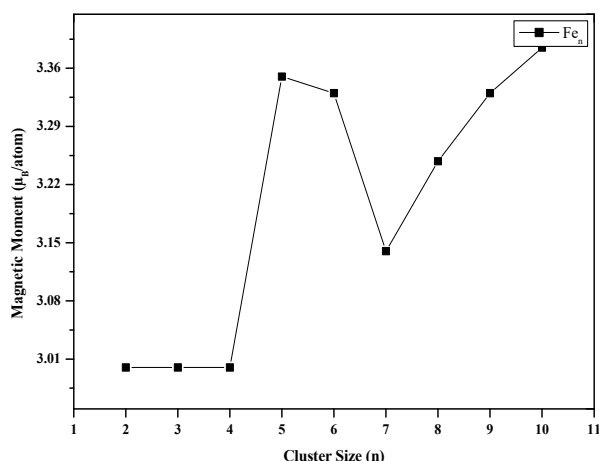
Figure 10. Magnetic moments for the Fe$_n$ (n = 2–10) clusters

4. CONCLUSION

The equilibrium geometries, energetic, electronic and magnetic characteristics of Fe$_n$ (n = 2–10) clusters have been performed by using DFT calculations, with the use of generalized gradient approximation GGA. The geometric structures of the clusters are in good agreement with previous computational studies; the reported binding energy for the dimer is closest to the experimental and theoretical value available. Furthermore, we find that the decay behavior of the binding energy curve indicates that the obtained cluster structures are the ground states.

The calculated fragmentation energy, second-order energy difference, and HOMO-LUMO energy gap revealed that the Fe$_7$, Fe$_8$ and Fe$_9$ clusters are more stable than other cluster sizes.

Compared to experimental and theoretical data, all of our VIP and VEA results are sometimes underestimated and sometimes overstated. The Fe$_2$ cluster corresponds to the most stable structure in the chemical hardness analysis.

The calculated magnetic properties of the lowest energy Fe$_n$ clusters exhibited a total magnetic torque of (3.00 - 3.354) µ$_B$, except for the Fe$_{10}$ cluster, which takes the value 3.385 µ$_B$. To our knowledge, the physicochemical properties of iron groups have not yet been calculated with the SIESTA code. Therefore, the results obtained from this fundamental work will be useful to guide future experiments, particularly in the fabrication of new nanocatalysts.

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ФІЗИКО-ХІМІЧНІ ХАРАКТЕРИСТИКИ КЛАСТЕРА Feₙ (n = 2–10) ЗА ТЕОРІЄЮ ФУНКЦІОНАЛУ ГУСТИНИ

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У цій роботі ми представляємо теоретичне дослідження геометрії рівноваги та енергетичних, електронних і магнітних властивостей Fen (n = 2–10) на основі теорії функціоналу густини (DFT). Результати отримані з використанням обох узагальнених градієнтних наближень відповідно до схеми, описаної Perdew-Burke-Ernzerhof (GGA-PBE). Більш стабільні отримані структури порівняно з іншими ізомерами раніше не були знайдені. Результати, розраховані як розрахована енергія фрагментації та різниця енергій другого порядку, показують, що кластери Fen(n = 7,8,9) більш стабільні, ніж кластери інших розмірів. Крім того, розраховані магнітні властивості найбільш стабільних кластерів демонструють різний магнітний момент між значеннями 3,00 мкБ і 3,35 мкБ, за винятком кластера Fe10, який приймає верхнє значення 3,38 мкБ. Ці результати важливі для експертів-експериментаторів, які активно розробляють нові системи нанокаталізу у фізичній та хімічній областях.
Ключові слова: *кластери заліза; відносна стабільність; теорія функціоналу густини; енергія зв'язку; магнітні властивості*