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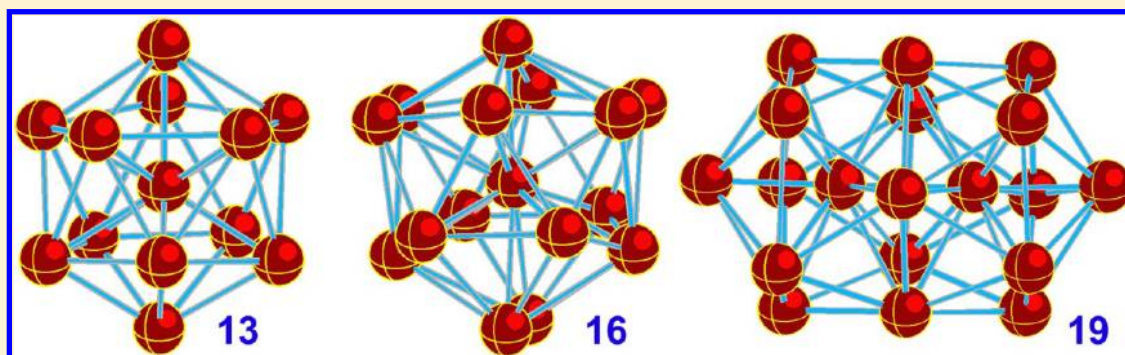


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Structure and Properties of Fe_n , Fe_n^- , and Fe_n^+ Clusters, $n = 7-20$ G. L. Gutsev,^{*,†} C. A. Weatherford,[†] P. Jena,[‡] E. Johnson,[§] and B. R. Ramachandran[⊥][†]Department of Physics and [§]School of the Environment, Florida A&M University, Tallahassee, Florida 32307, United States[‡]Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284, United States[⊥]College of Engineering & Science, Louisiana Tech University, Ruston, Louisiana 71272, United States

ABSTRACT: The electronic and geometrical structures of the Fe_n , Fe_n^- , and Fe_n^+ series ($n = 7-20$) are studied using all-electron density functional theory with the generalized gradient approximation. Equilibria of the geometrical configurations of the lowest total energy states in all three series are found to be similar except for Fe_9^- , Fe_9^+ , Fe_{10}^- , Fe_{10}^+ , Fe_{15}^- , and Fe_{19}^+ . Our computed ionization energies of the neutrals, vertical electron detachment energies, and energies of Fe atom abstraction are in good agreement with experiment. It is found that the one-electron model corresponding to the change in the total magnetic moment of $\pm 1.0\mu_B$ due to either attachment or detachment of an electron is valid in most cases. The exceptions are Fe_4^+ , Fe_{10}^- , Fe_{10}^+ , Fe_{12}^- , Fe_{13}^+ , and Fe_{14}^+ , where the change in the total magnetic moment is $+3\mu_B$ (Fe_{10}^- and Fe_{12}^-), $-3\mu_B$ (Fe_4^+ , Fe_{11}^+ , and Fe_{14}^+), and $-9\mu_B$ (Fe_{13}^+). The reason for an anomalously large quenching of the total spin magnetic moment in Fe_{13}^+ is explained. Our computed total spin magnetic moments per atom match the recent experimental values within the experimental uncertainty bars.

1. INTRODUCTION

Iron clusters have been intensively studied by a number of experimental techniques. Electron detachment energies (EDEs) were measured^{1,2} using laser photodetachment spectroscopy for the singly negatively charged Fe_n^- clusters ($n \leq 34$), and the ionization energies (IEs) were obtained³⁻⁵ using photoionization of the neutral Fe_n clusters ($n \leq 100$). The measured EDEs slowly increase as n increases, whereas the IEs decrease up to $n = 32$ and oscillate at around 5.0 eV for larger n values. The IE of the largest Fe_{100} cluster measured is 4.98 eV, which has to be compared to the bulk iron work function of 4.5 eV.

Fragmentation energies of mass-selected Fe_n^+ clusters were obtained for $n = 2, 3$, and 6 using photofragmentation⁶ and for $n = 2-19$ using collision-induced dissociation.^{7,8} Armentrout et al.^{7,9} also estimated the IE of neutral clusters and deduced binding energies for the neutral clusters in the same $n = 2-19$ range. Within the experimental uncertainty bars, the neutral $D_0(\text{Fe}_{n-1}-\text{Fe})$ and cationic $D_0(\text{Fe}_{n-1}^+-\text{Fe})$ dissociation energies are the same for a given n . The largest binding energy is found in the Fe_{13} and Fe_{13}^+ clusters. Experimental structural data on iron species are rather scarce. The Fe–Fe bond length was measured for the Fe_2 dimers trapped in argon ($r_e = 1.87 \pm 0.13 \text{ \AA}$)¹⁰ and neon ($r_e = 2.02 \pm 0.02 \text{ \AA}$)¹¹ matrixes. Vibrational frequencies were obtained for gas-phase Fe_2 ,¹² and Fe_2^- ,¹³ and for matrix-

isolated Fe_3 .¹⁴ The geometry of a neutral Fe_{17} cluster was obtained¹⁵ in a salt.

The magnetic behavior of iron clusters is rather complicated,¹⁶ as revealed by the molecular beam deflection (Stern–Gerlach) measurements for iron clusters composed from 25 to ~ 700 atoms in the 80–1000 K temperature range. All clusters are found to be ferromagnetic, and the magnetic moment per atom approaches the bulk limit of $2.15\mu_B$ (Bohr magneton) from the larger value side as the cluster size increases. In a recent paper,¹⁷ it was further noted that there are low-spin ferrimagnetic states of Fe_n in the $20 \leq n \leq 200$ range along with the high-spin ferromagnetic states found previously. The total magnetic moments of these low-spin states are $\sim n\mu_B$, whereas the total magnetic moments of the high-spin states are $\sim 3n\mu_B$.

For smaller iron clusters with $n = 10-25$, Knickelbein¹⁸ performed Stern–Gerlach deflection experiments and found that the magnetic moments show large oscillations for $n < 15$, while they are close to $3\mu_B$ for the larger clusters, in agreement with the result of Billas et al.¹⁹ A separation of the total magnetic moment into its spin and orbital constituents was recently done²⁰ for Fe_n^+

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clusters ($n = 2-20$) using X-ray magnetic circular dichroism (XMCD) spectroscopy. It was found that the orbital magnetic moment amounts to 8–15% of the total magnetic moment, that is, the major contribution comes from the spin magnetic moment. A smaller orbital contribution of $0.08\mu_B$ to the total magnetic moment per atom of $3.05\mu_B$ was theoretically predicted²¹ for neutral Fe_{13} .

Theoretical simulations have been mainly performed for small iron clusters using density functional theory (DFT) with the local spin density approximation (LSDA) as well as with generalized gradient approximation (GGA) methods, often combined with effective core potentials (ECPs). Special attention was paid to the Fe_2 dimer,^{22–34} whose ground state is still under debate.³⁵ All-electron DFT-GGA computations have been done for iron clusters with $n = 2-8, 10, 13$, and 19 .^{36–46} The DFT-GGA-ECP calculations were performed for neutral clusters with $n = 2-8$,⁴⁷ $2-13$,^{48,49} 6 ,⁵⁰ and 13 .^{51–53} The LSDA computations^{54–56} were performed for Fe_n with $n = 2-7$ and 13 , while the LSDA-ECP computations were performed⁵⁷ in the $2 \leq n \leq 17$ range. These LSDA-ECP results were used in a tight-binding parametrization followed by the DFT-TB computations of iron clusters with sizes up to $n = 32$ ⁵⁸ and $53-57$.⁵⁹ Molecular dynamics simulations were performed⁶⁰ for Fe_n , $n = 4-36$. Negatively charged Fe_n^- clusters with $n = 3-6$ were considered by Li et al.,⁶¹ whereas both positively and negatively singly charged iron clusters $\text{Fe}_n^{+/0/-}$ were the subject of several papers with different n ranges, namely, $n = 2-4$,⁶² $2-5$,⁶³ $2-6$,⁶⁴ and $2-10$.⁶⁵ We note that the DFT functional used in ref 65 is the OPBE functional⁶⁶ obtained by combining the OPTX exchange⁶⁷ with the PBE correlation.⁶⁸

Noncollinearity of local spin magnetic moments in iron clusters was the subject of several papers. Oda et al.⁶⁹ found noncollinear magnetic moments for Fe_3 and Fe_5 in the series Fe_n with $n = 2-5$, but Hobbs et al.⁷⁰ and Cheng et al.⁷¹ have not found any stable noncollinear state for Fe_3 . Recently, Khanna et al.⁷² have studied noncollinear effects in neutral Fe_n and anionic Fe_n^- clusters with $n = 2-8$ and concluded that “while our studies predict collinear ground states for most clusters, we do find noncollinear states energetically close to the ground states in most cases.” Rollmann et al.⁷³ performed computations of Fe_n in a wider $2 \leq n \leq 15$ range, imposing no symmetry constraints, and found that geometric distortions do restore the collinearity of the local spin magnetic moments in all cases considered. The same conclusion was arrived at in the spin-polarized DFT-TB computations of Fe_5 and Fe_{13} .⁷⁴ Therefore, one can anticipate that noncollinear effects are small for larger iron clusters considered in the present work as well.

The aim of this work is to extend our previous study⁶⁴ of the neutral and singly positively and negatively charged Fe_n clusters with $n = 2-6$ to n values up to 20 using the same all-electron DFT-GGA approach. We compute the vertical and adiabatic ionization energies of the neutral species and the vertical and adiabatic energies of an extra electron detachment from the anionic species and compare them to experiment. Our computed binding energies of an Fe atom in the neutral and cationic clusters are also compared to experiment. Special attention is paid to the dependence of magnetic properties on the charge. In particular, we explain the origin of an anomalously small spin magnetic moment per atom in Fe_{13}^+ observed in the recent XMCD experiments.²⁰ Finally, we compute the second total energy differences and compare them with “magic” numbers found experimentally from the abundance spectra.

2. DETAILS OF COMPUTATIONS

As in our previous work,⁶⁴ the Becke–Perdew–Wang exchange–correlation functional (BPW91)^{75,76} and the 6-311+G* (15s11p6d1f/10s7p4d1f) basis sets⁷⁷ were used in the present calculations, which were started using Gaussian 03⁷⁸ and finished using Gaussian 09.⁷⁹ The performance of several commonly used functionals was tested in our previous work,⁶⁴ where the BPW91 approach was found to be the most stable approach in the harmonic frequency computations of several closely spaced states of the neutral and charged Fe_3 and Fe_4 clusters. Gaussian 09 contains a number of recently developed functionals, including the improved PW91 and PBE functionals and their long-range corrected modifications. The quality of different new exchange–correlation functionals has now been intensively tested using different databases,⁸⁰ and the PW91 method was found to have a good performance with respect to that of the new exchange–correlation functionals.⁸¹

As concerns the basis set choice, we found that the 6-311+G* basis set is adequate for a reliable reproduction of the experimental electron attachment and detachment energies for Fe_n and Fe_n^- , respectively, for $n = 2-6$. An extension of this basis with polarization and diffuse functions [the 6-311+G(3df) basis] or the use of the def2-TZVP basis set,⁸² which contains a significantly larger number of primitive functions, was tested for neutral Fe_{12} and Fe_{13} . No significant changes in the results of computations compared to those obtained using the 6-311+G* basis set was observed. Preliminary optimizations of trial configurations of larger clusters were performed using a smaller 6-311G* basis set, followed by optimizations using the 6-311+G* basis set. For each cluster, we tested several geometric configurations, including those obtained in the previous work. Each geometry optimization was followed by harmonic vibrational frequency computations in order to confirm the stationary character of the state obtained. If an optimization arrived at a transition state, optimizations following the imaginary vibrational frequency modes were performed until all imaginary frequencies were eliminated.

We compute the adiabatic electron affinity (EA_{ad}) of a neutral as

$$\text{EA}_{\text{ad}}(\text{Fe}_n) = E_{\text{tot}}^{\text{el}}(\text{Fe}_n) + \text{ZPVE}(\text{Fe}_n) - [E_{\text{tot}}^{\text{el}}(\text{Fe}_n^-) + \text{ZPVE}(\text{Fe}_n^-)] \quad (1)$$

where $E_{\text{tot}}^{\text{el}}(\text{Fe}_n)$ and $E_{\text{tot}}^{\text{el}}(\text{Fe}_n^-)$ are the total electronic energies of the lowest-energy states of Fe_n and Fe_n^- and ZPVE is the zero-point vibrational energy computed in the harmonic approximation. The adiabatic ionization energy (IE_{ad}) is computed in a similar way

$$\text{IE}_{\text{ad}}(\text{Fe}_n) = E_{\text{tot}}^{\text{el}}(\text{Fe}_n^+) + \text{ZPVE}(\text{Fe}_n^+) - [E_{\text{tot}}^{\text{el}}(\text{Fe}_n) + \text{ZPVE}(\text{Fe}_n)] \quad (2)$$

The vertical ionization energies (VIE_{\pm} 's) were computed for two possible one-electron detachment channels corresponding to the cation states whose spin multiplicities differ from the spin multiplicity of the neutral parent by ± 1 at the geometry of the neutral lowest total energy state.

$$\text{VIE}_{\pm}(\text{Fe}_n) = E_{\text{tot}}^{\text{el}}(\text{Fe}_n^+, (2S + 1) \pm 1) - E_{\text{tot}}^{\text{el}}(\text{Fe}_n, 2S + 1) \quad (3)$$

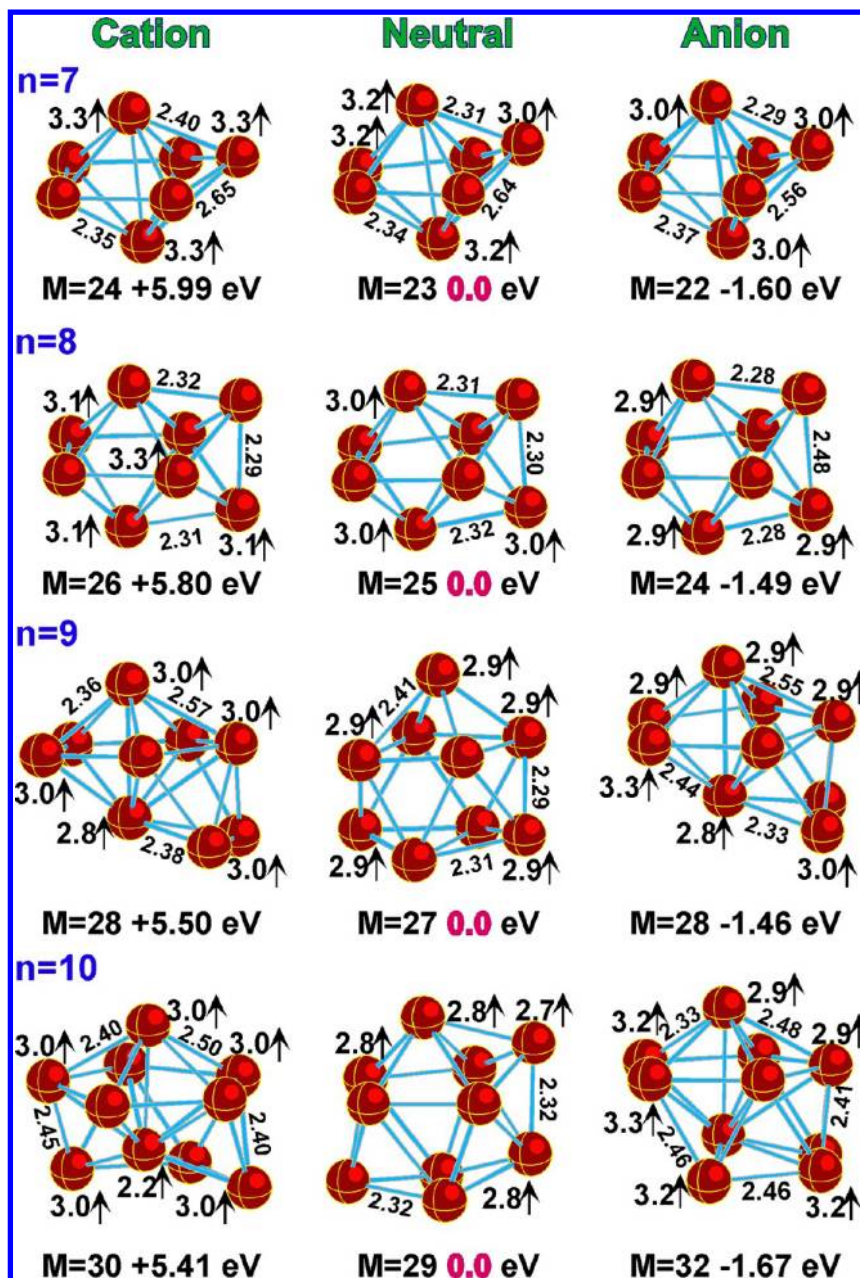


Figure 1. Geometrical configurations corresponding to the lowest total energy states of Fe_n^+ , Fe_n , and Fe_n^- for $n = 7-10$. M denotes the multiplicity $2S + 1$. Bond lengths are in Å.

The vertical electron detachment energies (VDE_±'s) of an anion were computed at the geometry of the anion lowest total energy state.

$$\text{VDE}_{\pm}(\text{Fe}_n^-) = E_{\text{tot}}^{\text{el}}(\text{Fe}_n, 2S + 1) - E_{\text{tot}}^{\text{el}}(\text{Fe}_n^-, (2S + 1) \pm 1) \quad (4)$$

The energy (D_0) of an Fe atom abstraction from Fe_{n+1} is computed as

$$D_0(\text{Fe}_n - \text{Fe}) = E_{\text{tot}}^{\text{el}}(\text{Fe}_n) + \text{ZPVE}(\text{Fe}_n) + E_{\text{tot}}(\text{Fe}) - [E_{\text{tot}}^{\text{el}}(\text{Fe}_{n+1}) + \text{ZPVE}(\text{Fe}_{n+1})] \quad (5)$$

Atomization energies (E_{atom}) of an Fe_n cluster are computed as

$$E_{\text{atom}}(n) = \frac{[E_{\text{tot}}^{\text{el}}(\text{Fe}_n) + \text{ZPVE}(\text{Fe}_n) - nE_{\text{tot}}(\text{Fe})]}{n} \quad (6)$$

Local spin magnetic moments on atoms, which are identified with the excess spin densities on atoms, are obtained using the natural atomic orbital (NAO)⁸³ population analysis. The NAO populations were also used for analyzing the bonding patterns in Fe_{13}^- .

3. RESULTS AND DISCUSSION

First, we present the lowest total energy structures found for Fe_n^+ , Fe_n , and Fe_n^- ($n = 7-20$), followed by comparison of our computed ionization and dissociation energies with experiment. Next, we discuss the behavior of the spin magnetic moment per atom and compare the computed total spin magnetic moments per atom with experiment. We explain an anomalous behavior of

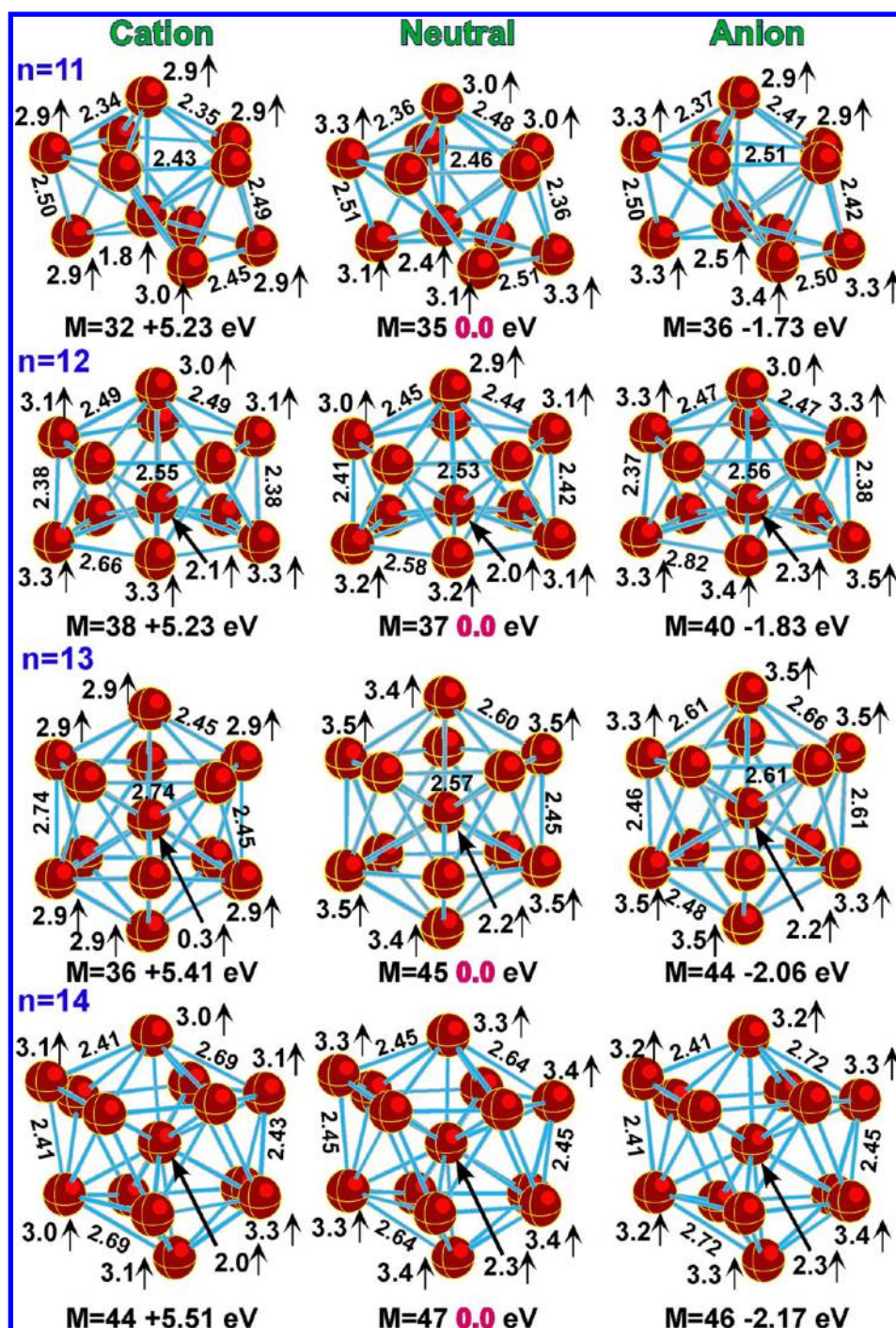


Figure 2. Geometrical configurations corresponding to the lowest total energy states of Fe_n^+ , Fe_n , and Fe_n^- for $n = 11-14$.

the total spin magnetic moment of the Fe_{13}^+ cation found in experiment. It is shown that the binding energies of Fe atoms are rather independent of the charge for a given n . Finally, we compute the second-order differences in total energy.

Geometrical Configurations. The geometrical structures obtained for the lowest total energy states of Fe_n^+ , Fe_n , and Fe_n^- ($n = 7-20$) are presented in Figures 1–4, where each state is specified by its spin multiplicity $M = 2S + 1$. The neutral geometrical configurations found are similar to those from the previous work,^{57,58} except for Fe_{17} , whose lowest total energy state geometrical configuration found in this work is similar to that found in a salt.¹⁵ The corresponding state is lower in total

energy by 0.12 eV than the state possessing the geometrical configuration from the previous work. The structure patterns in the lowest total energy states in the neutral Fe_n series can be described as follows. From $n = 7$ to 12, the structures are formed by stripping off atoms from a slightly distorted icosahedral Fe_{13} cluster; for $n = 14$, a six-member ring replaces a five-member ring; for $n = 15$, the second six-member ring replaces the second five-member ring; from $n = 16$ to 19, the structures contain two six-member rings and caps consisting of 1–4 atoms. The second core atom appears in the geometrical structure of the lowest total energy state of Fe_{20} , which consists of two five-member rings and one six-member ring in the middle capped by two single atoms.

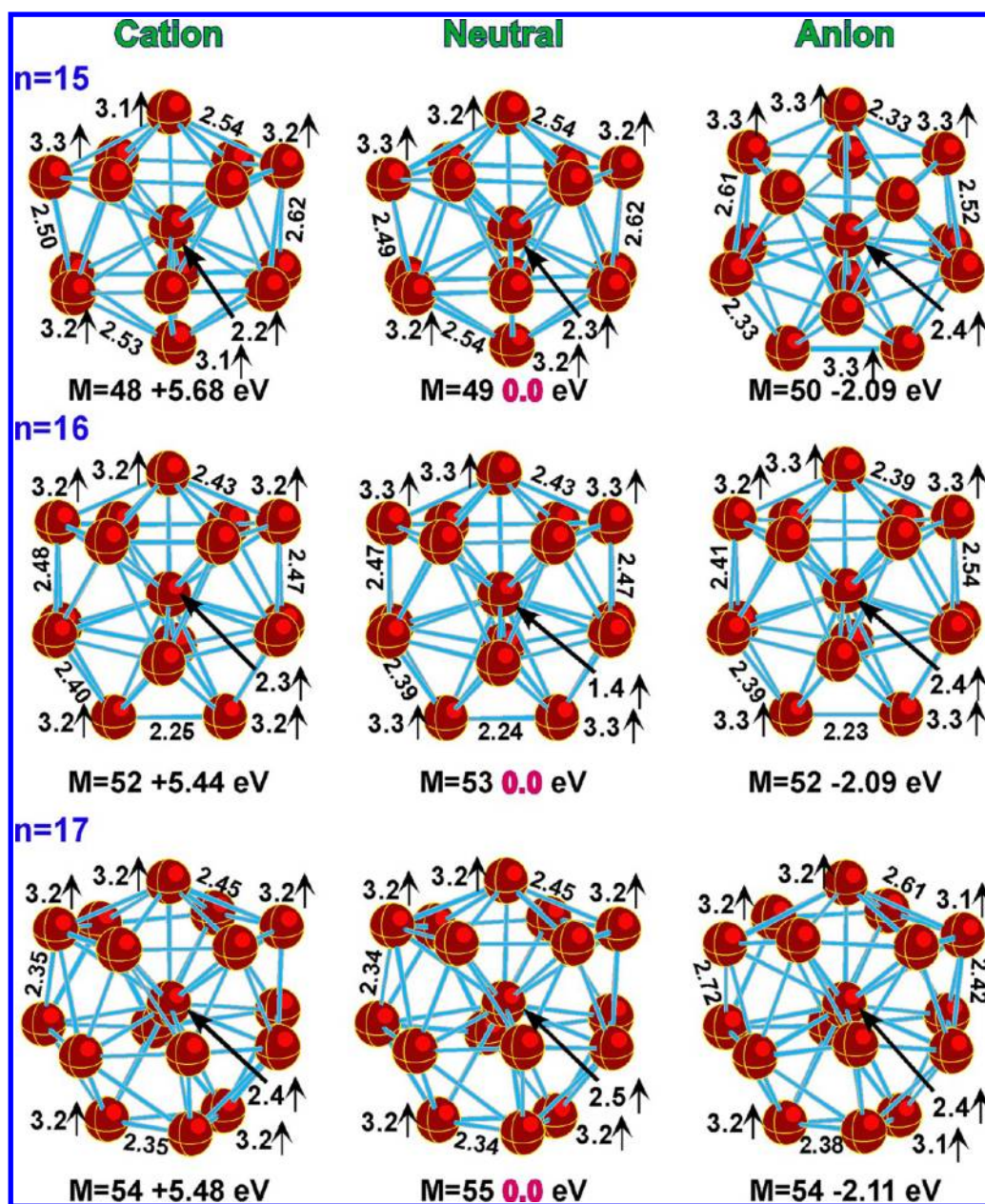


Figure 3. Geometrical configurations corresponding to the lowest total energy states of Fe_n^+ , Fe_n , and Fe_n^- for $n = 15$ –17.

The geometrical configurations of the lowest states in the Fe_n^+ and Fe_n^- series are similar to those of the corresponding neutral clusters, except for a few cases. In the cation series, the geometrical configurations of Fe_9^+ , Fe_{10}^+ , and Fe_{19}^+ are different from the geometrical configurations of the corresponding neutrals. In the anion series, the difference between geometries is observed for Fe_9^- , Fe_{10}^- , and Fe_{15}^- . In all other cases, the attachment/detachment of an electron to/from a neutral cluster does not lead to a significant change in the bond lengths. This can be seen from the comparison of the bond lengths given in Figures 1–4. Typically, the bond length changes are smaller than 0.05 Å. Occasionally, some bond length changes reach 0.2 Å.

IEs and Electron Affinities. Table 1 presents the vertical and adiabatic ionization energies of the neutral Fe_n clusters computed according to eqs 2 and 3 together with experimental data. As is seen, the adiabatic and vertical ionization energies are quite close to each other, except for $n = 9, 10, 13$, and 19. The reason for the difference between the adiabatic and vertical ionization energies

for $n = 9, 10$, and 19 can be related to the difference in the geometrical configurations of the corresponding neutrals and cations, whereas the Fe_{13} and Fe_{13}^+ pair presents a case where the electron detachment leads to an anomalous lowering of the total spin magnetic moment. In nearly all cases, our computed adiabatic ionization energies do match the corresponding experimental values within the experimental uncertainty bars. The OPBE values⁶⁵ appear to be underestimated, especially for the Fe_{10} cluster.

The EA_{ad} 's of the neutrals computed according to eq 1 and the VDE_{\pm} 's of an extra electron from the Fe_n^- anions computed according to eq 4 are presented in Table 2 and compared to the experimental values obtained using laser photodetachment spectroscopy.^{1,2} The experimental data correspond to the VDE_{\pm} and possess quite narrow uncertainty bars. As is seen from Table 2, our differences between the smallest VDE_{\pm} 's and the experimental values are within 0.2 eV for each n . The OPBE values⁶⁵ are in less satisfactory agreement. On the basis of

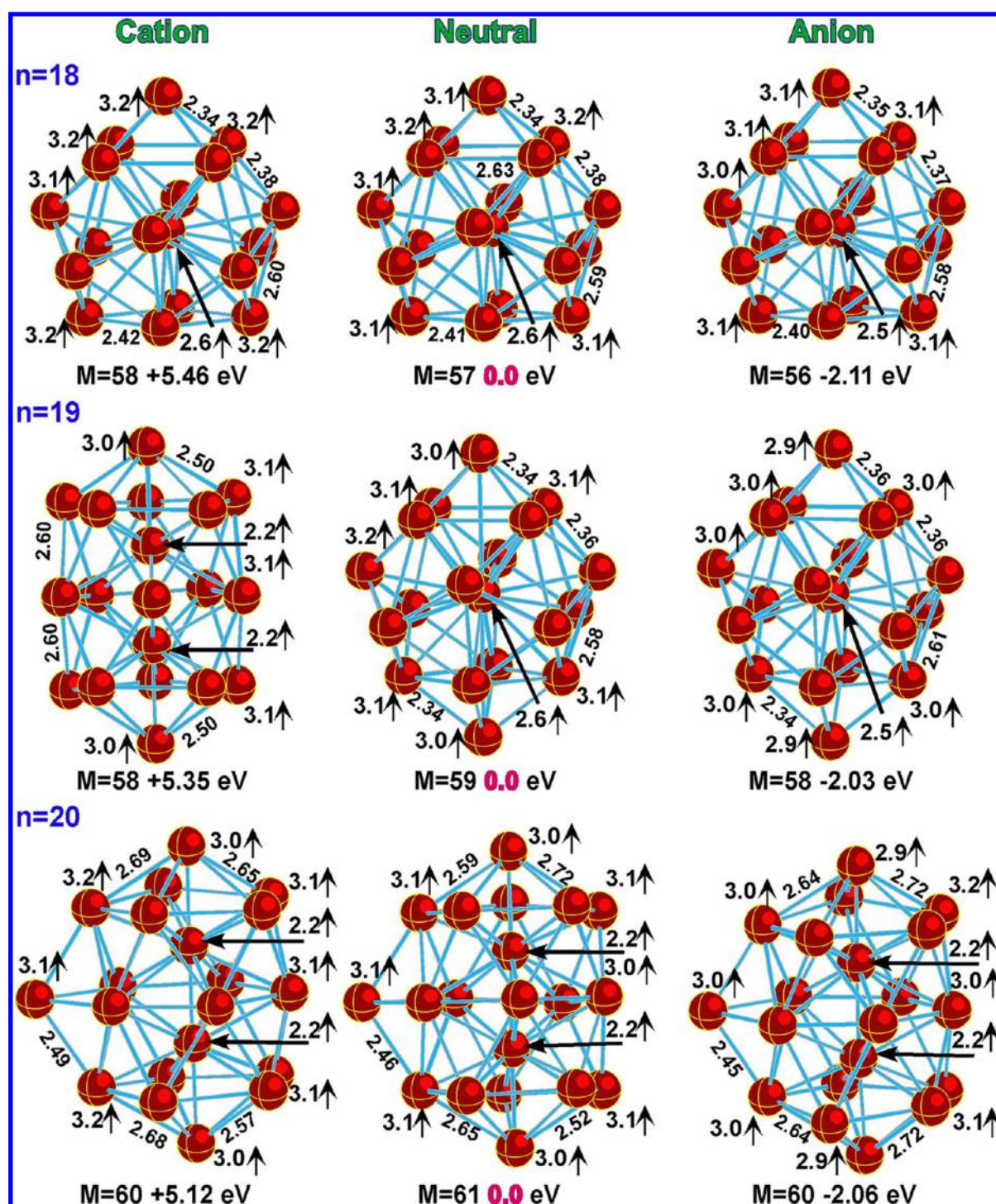


Figure 4. Geometrical configurations corresponding to the lowest total energy states of Fe_n^+ , Fe_n , and Fe_n^- for $n = 18$ –20.

comparison of our computed values to experiment, one can conclude that the BPW91 method is quite reliable in computations of neutral and charged iron clusters.

Spin Magnetic Moments. The total magnetic moment is defined in the Russell–Saunders scheme as $\mu = (2S + L)\mu_B$, where μ_B is the Bohr magneton and L and S are the total angular and spin moments, respectively. The total spin magnetic moment, $M = 2S\mu_B$, is computed as $[n_\alpha - n_\beta]\mu_B$, where n_α and n_β are the numbers of the majority spin and minority spin electrons, respectively. The local spin magnetic moments on

atoms are considered to be equal to the excess spin densities obtained using the NAO populations.

Figure 5 compares our total spin magnetic moments per atom with the values obtained previously in the DFT-ECP⁵⁷ and DFT-TB⁵⁸ computations. The all-electron DFT-GGA values for $n = 2$ –6 were previously computed⁶⁴ at the same BPW91/6-311+G* level. The DFT-TB values match the DFT-ECP values, except for $n = 5$, which can be due to the fact that tight-binding parameters were calibrated using the DFT-ECP results. Our computed values match the DFT-ECP values only for $n = 2, 7, 8, 9, 10$, and 15. The largest difference of $0.8\mu_B$ is found for $n = 13$, where the

Table 1. Computed VIE_{\pm} 's and IE_{ad} 's of Neutral Iron Clusters along with Experimental Data^a

	Fe ₇	Fe ₈	Fe ₉	Fe ₁₀	Fe ₁₁	Fe ₁₂	Fe ₁₃
$M = 2S + 1$	23	25	27	29	35	37	45
VIE_{+}	6.09	5.95	5.69	5.68	5.78	5.33	5.89
VIE_{-}	6.14	6.32	6.03	5.92	5.33	5.27	5.62
IE_{ad}	5.99	5.80	5.49	5.19	5.23	5.23	5.41
IE_{ad}^b	5.41	5.20	4.66	4.20			
exptl ^c	5.76 ± 0.05	5.48 ± 0.05	5.50 ± 0.05	5.41 ± 0.05	5.45 ± 0.05	5.52 ± 0.05	5.61 ± 0.05
exptl ^d	5.97 ± 0.39	5.97 ± 0.39	5.44 ± 0.14	5.44 ± 0.14	5.42 ± 0.16	5.42 ± 0.16	5.76 ± 0.18
	Fe ₁₄	Fe ₁₅	Fe ₁₆	Fe ₁₇	Fe ₁₈	Fe ₁₉	Fe ₂₀
$M = 2S + 1$	47	49	53	55	57	59	61
VIE_{+}	5.92	5.81	5.81	5.67	5.51	5.63	5.22
VIE_{-}	5.63	5.68	5.44	5.48	5.51	5.51	5.18
IE_{ad}	5.51	5.68	5.44	5.48	5.46	5.35	5.12
exptl ^c	5.70 ± 0.05	5.56 ± 0.05	5.63 ± 0.05	5.50 ± 0.05	5.40 ± 0.05	5.18 ± 0.05	
exptl ^d	5.80 ± 0.19	5.40 ± 0.18	5.64 ± 0.06	5.57 ± 0.13	5.40 ± 0.18	5.12 ± 0.15	5.12 ± 0.15

^aAll values are in eV. ^bOPBE/TZV results from ref 65. ^cExperimental values from ref 4. ^dExperimental values from ref 5.

Table 2. Computed VDE_{\pm} 's of the Fe_n^{-} Anions and EA_{ad} 's along with the Experimental Data^a

	Fe ₇ ⁻	Fe ₈ ⁻	Fe ₉ ⁻	Fe ₁₀ ⁻	Fe ₁₁ ⁻	Fe ₁₂ ⁻	Fe ₁₃ ⁻
$M = 2S + 1$	22	24	28	32	36	40	44
VDE_{+}	1.73	1.73	1.70	1.84	2.12	2.33	2.22
VDE_{-}	2.08	2.13	1.50	1.74	1.76	1.87	2.12
EA_{ad}	1.60	1.49	1.46	1.67	1.73	1.83	2.06
EA_{ad}^b	1.00	0.92	1.01	1.39			
exptl ^c	1.39 ± 0.08	1.66 ± 0.08	1.75 ± 0.08	1.85 ± 0.08	2.00 ± 0.08	2.12 ± 0.08	2.20 ± 0.08
exptl ^d	1.50 ± 0.06	1.76 ± 0.06	1.80 ± 0.06	1.90 ± 0.06	2.03 ± 0.06	2.14 ± 0.06	2.24 ± 0.06
	Fe ₁₄ ⁻	Fe ₁₅ ⁻	Fe ₁₆ ⁻	Fe ₁₇ ⁻	Fe ₁₈ ⁻	Fe ₁₉ ⁻	Fe ₂₀ ⁻
$M = 2S + 1$	46	50	52	54	56	58	60
VDE_{+}	2.29	2.52	2.20	2.18	2.16	2.13	2.03
VDE_{-}	2.22	2.10	2.23	2.34	2.39	2.40	2.28
EA_{ad}	2.17	2.09	2.09	2.11	2.14	2.03	1.99
exptl ^b	2.23 ± 0.08	2.25 ± 0.08	2.01 ± 0.08	2.06 ± 0.08	2.14 ± 0.08	2.01 ± 0.08	2.01 ± 0.08
exptl ^c	2.26 ± 0.06	2.28 ± 0.06	2.09 ± 0.06	2.16 ± 0.06	2.22 ± 0.06	2.11 ± 0.06	2.10 ± 0.06

^aAll values are in eV. ^bOPBE/TZV results from ref 65. ^cExperimental values from ref 1. ^dExperimental values from ref 2.

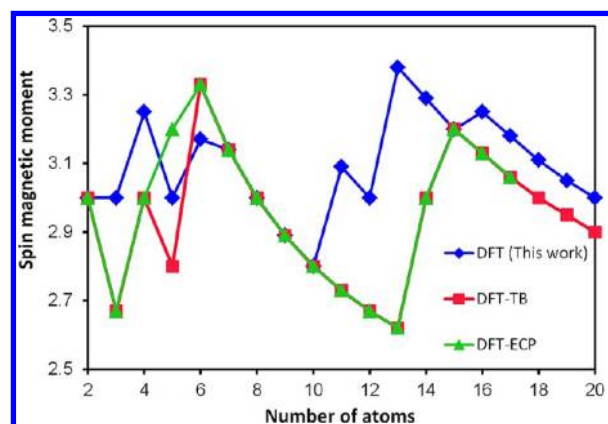


Figure 5. Comparison of the total spin magnetic moment per atom obtained in the present work (DFT), that in ref 58 (DFT-TB), and that in ref 57 (DFT-ECP). The computations were performed for $n = 2-17$.

BPW91/6-311+G* value is the maximal value in the series, whereas the DFT-ECP value is the minimal one. Note that our spin multiplicity value $2S + 1 = 45$ for the lowest total energy state of Fe_{13} is the same as that found previously in the all-electron DFT calculations³⁹ and the semicore DFT calculations.⁵²

The dependence of the total spin magnetic moment per atom on the cluster charge is shown in Figure 6. According to the one-electron model, the magnetic moment of a singly charged cluster, whether it is positively or negatively charged, should differ from its neutral by $\pm 1.0\mu_B$. This is assuming that the geometric structure and the electron energy levels do not change significantly when the electron is either detached or attached.

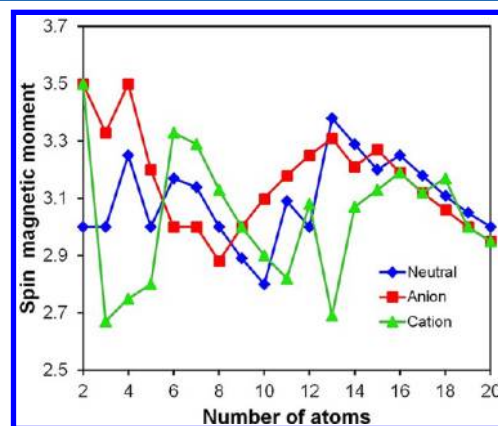


Figure 6. Total spin magnetic moment per atom in $Fe_n^{0/-/+1}$.

Table 3. SMMs and TMMs per Atom of the Fe_n^+ Cations^a

	Fe_7^+	Fe_8^+	Fe_9^+	Fe_{10}^+	Fe_{11}^+	Fe_{12}^+	Fe_{13}^+
SMM ^b	3.29	3.13	3.00	2.90	2.82	3.08	2.69
SMM ^c	3.13 ± 0.46	3.19 ± 0.46	2.76 ± 0.38	3.44 ± 0.46	3.30 ± 0.42	3.41 ± 0.50	2.44 ± 0.38
TMM ^c	3.42 ± 0.50	3.45 ± 0.46	3.35 ± 0.38	3.63 ± 0.48	3.48 ± 0.46	3.50 ± 0.51	2.63 ± 0.41
TMM ^d				4.6	4.8	5.4	2.45
	Fe_{14}^+	Fe_{15}^+	Fe_{16}^+	Fe_{17}^+	Fe_{18}^+	Fe_{19}^+	Fe_{20}^+
SMM ^b	3.07	3.13	3.19	3.12	3.17	3.0	2.95
SMM ^c	3.49 ± 0.49	3.7 ± 0.49	3.56 ± 0.48	3.15 ± 0.42	3.47 ± 0.46	3.34 ± 0.43	3.45 ± 0.45
TMM ^c	3.62 ± 0.50	3.88 ± 0.51	3.68 ± 0.49	3.55 ± 0.47	3.59 ± 0.47	3.61 ± 0.47	3.89 ± 0.50
TMM ^d	3.5	2.7	2.9	2.8	3.0	2.8	2.7

^aAll values are in Bohr magnetons (μ_B). ^bThis work. ^cXMCDs values from ref 20. ^dStern–Gerlach values from ref 18 for the neutral Fe_n clusters,

Table 4. NAO Populations in the Lowest Total Energy States of Fe_{13} and Fe_{13}^{+a}

	spin majority	POP	spin minority	POP	total	POP
Fe_{13} , $2S = 4\mu_B$						
1 $\text{Fe}_{\text{center}}$	$3d^{4.93}4s^{0.44}4p^{0.04}4d^{0.13}$	5.54	$3d^{2.68}4s^{0.47}4p^{0.09}4d^{0.05}$	3.29	$3d^{7.61}4s^{0.91}4p^{0.13}4d^{0.18}$	8.83
2 Fe_{apex}	$3d^{4.96}4s^{0.63}4p^{0.04}$	5.63	$3d^{1.93}4s^{0.30}4p^{0.03}$	2.26	$3d^{6.89}4s^{0.93}4p^{0.07}$	7.89
10 Fe_{ring}	$3d^{4.96}4s^{0.69}4p^{0.04}$	5.69	$3d^{1.88}4s^{0.30}4p^{0.03}$	2.21	$3d^{6.84}4s^{0.98}4p^{0.07}$	7.90
Fe_{13}^+ , $2S = 3.5\mu_B$						
1 $\text{Fe}_{\text{center}}$	$3d^{4.19}4s^{0.25}4p^{1.04}4d^{0.02}$	5.49	$3d^{3.88}4s^{0.27}4p^{1.05}4d^{0.03}$	5.23	$3d^{8.07}4s^{0.52}4p^{2.09}4d^{0.06}$	10.74
2 Fe_{apex}	$3d^{4.92}4s^{0.20}4p^{0.16}$	5.28	$3d^{2.07}4s^{0.17}4p^{0.15}$	2.39	$3d^{7.00}4s^{0.37}4p^{0.31}$	7.68
10 Fe_{ring}	$3d^{4.92}4s^{0.20}4p^{0.16}$	5.28	$3d^{2.07}4s^{0.17}4p^{0.15}$	2.39	$3d^{7.00}4s^{0.37}4p^{0.31}$	7.68
Δ		−4.85		+4.0		+0.8

^aPOP denotes the total NAO population. Small contributions from excited AOs are omitted. Δ is the difference between the total occupation from the top and bottom parts of the corresponding column.

A reduction in the magnetic moment occurs when the electron is removed from the majority spin orbital, while an enhancement in the moment occurs when the electron is removed from the minority spin orbital. Among iron clusters considered in this work, only Fe_{10}^+ and Fe_{12}^+ in the anion series as well as Fe_4^+ , Fe_{11}^+ , Fe_{13}^+ , and Fe_{14}^+ in the cation series do not obey this one-electron rule. The corresponding differences are $+3\mu_B$ (Fe_{10}^-), $+3\mu_B$ (Fe_{12}^-), $-3\mu_B$ (Fe_4^+), $-3\mu_B$ (Fe_{11}^+), $-9\mu_B$ (Fe_{13}^+), and $-3\mu_B$ (Fe_{14}^+).

The dramatic decrease in the total spin magnetic moment found for the Fe_{13}^+ cation is in agreement with the results of recent XMCD measurements.²⁰ Table 3 compares our total spin magnetic moments per atom to the XMCD data in the whole measurement range. As is seen, an anomalous quenching of the total magnetic moment is observed only for Fe_{13}^+ , whose total magnetic moment is $2.63 \pm 0.41\mu_B$, whereas the neighbors Fe_{12}^+ and Fe_{14}^+ possess the total magnetic moments of $3.34 \pm 0.43\mu_B$ and $3.62 \pm 0.50\mu_B$, respectively. Our total spin magnetic moment per atom computed for Fe_{13}^+ is $2.69\mu_B$ agrees well with the experimental value of $2.44 \pm 0.38\mu_B$. Generally, our computed spin magnetic moments per atom match the experimental values within the experimental uncertainty bars. Because the orbital magnetic moment contribution to the total magnetic moment is small according to the XMCD data in Table 3, one can consider the total spin magnetic moment to be a good approximation to the total magnetic moment in iron clusters. Both our computed values for the total spin magnetic moment and the XMCD values for the total magnetic moment are different from the Stern–Gerlach values of Knickelbein¹⁸ for smaller n (see Table 3), whereas there is good agreement for larger n .

In order to gain insight into the anomalous behavior of the total spin magnetic moment in Fe_{13}^+ , we analyze the NAO populations in the lowest total energy states of Fe_{13} and Fe_{13}^+ presented in Figure 4. The majority and minority spin

populations together with the total valence populations of Fe_{13} and Fe_{13}^+ are shown in Table 4. The total populations in the neutral Fe_{13} cluster correspond to the promotion of a 4s electron into the spin minority 3d shell in the ground-state $3d^64s^2$ electronic configuration of an Fe atom, except for the central atom, whose population is higher due to the contributions from the shell atoms (see the last column in Table 4). In the Fe_{13}^+ cation, the 4s AOs are depleted because of their promotion not only into the minority spin 3d shells but also into the vacant 4p states. The net difference of 0.8 e between the sums of the total occupations in Fe_{13} and Fe_{13}^+ differs from 1.0 e because of neglecting small contributions from excited AOs. Comparing the majority and minority spin populations, one can notice that the promotion of the majority spin 4s electrons into 4p vacant orbitals leads to a difference of -4.85 e between the cation and neutral majority spin populations (-0.15 e is lost because of neglecting small contributions from excited AOs). The difference between the total minority spin populations of Fe_{13}^+ and Fe_{13} is $+4.0$ e; that is, the net change in the excess spin densities is $9\mu_B$.

It is natural to wonder why such a $4s \rightarrow 4p$ promotion leads to the dramatic decrease in the total spin magnetic moment of Fe_{13}^+ . The answer is related to high T_h symmetry of the cation wave function. The bonding molecular orbitals belonging to the T_{1u} representation of the T_h point group are composed of 4p orbitals and can accommodate six electrons. In order to fill these bonding orbitals, the majority spin 4s electrons have to be promoted into the minority spin 4p states. This process leads to the quenching of the total spin magnetic moment and is responsible for the exceptionally low value of the total magnetic moment in the Fe_{13}^+ cation.

Thermodynamic Stability. The energies corresponding to the abstraction of one Fe atom from the neutral and charged iron clusters are computed according to eq 5 and are presented in Table 5 together with experimental data. Generally, our values

Table 5. Comparison of an Fe Atom Abstraction Energy [$D_0(\text{Fe}_n-\text{Fe})$] to Experiment and Atomization Energy per Atom (E_{atom})^a

	Fe ₇	Fe ₈	Fe ₉	Fe ₁₀	Fe ₁₁	Fe ₁₂	Fe ₁₃
$M = 2S + 1$	23	25	27	29	35	37	45
$D_0(\text{Fe}_n-\text{Fe})$	3.48	3.27	2.99	3.20	3.38	3.57	3.79
exptl ^b	3.12 ± 0.15	2.33 ± 0.15	2.92 ± 0.15	2.86 ± 0.15	3.22 ± 0.15	3.52 ± 0.15	4.32 ± 0.15
E_{atom}	2.58	2.67	2.70	2.75	2.81	2.87	2.94
	Fe ₁₄	Fe ₁₅	Fe ₁₆	Fe ₁₇	Fe ₁₈	Fe ₁₉	Fe ₂₀
$M = 2S + 1$	47	49	53	55	57	59	61
$D_0(\text{Fe}_n-\text{Fe})$	3.48	4.38	3.51	3.50	3.36	3.45	3.24
exptl ^b	3.01 ± 0.15	3.76 ± 0.15	3.38 ± 0.15	3.21 ± 0.15	3.13 ± 0.15	3.65 ± 0.15	
E_{ato}	2.98	3.08	3.10	3.13	3.14	3.16	3.16

^aAll values are in eV. ^bExperimental values from ref 9.

differ by not more than 0.4 eV from the experimental values if the corresponding uncertainty bar values are accounted for, except for the Fe₈ cluster, where the discrepancy is 0.79 eV. Also, the experiment predicts Fe₁₃ to be the most stable species with respect to an Fe atom abstraction. However, we found that Fe₁₅ is the most stable cluster in the series. The atomization energies computed according to eq 6 show a slow growth as n increases. The binding energy per atom of 3.16 eV in the largest Fe₂₀ cluster is still substantially smaller than the bulk iron cohesive energy of 4.39 eV.⁸⁴ Comparison of the energy of Fe atom abstraction in the neutral and charged Fe_{*n*} clusters is presented in Figure 7. As is seen, the energy of Fe atom abstraction is nearly independent of the charge for a given n .

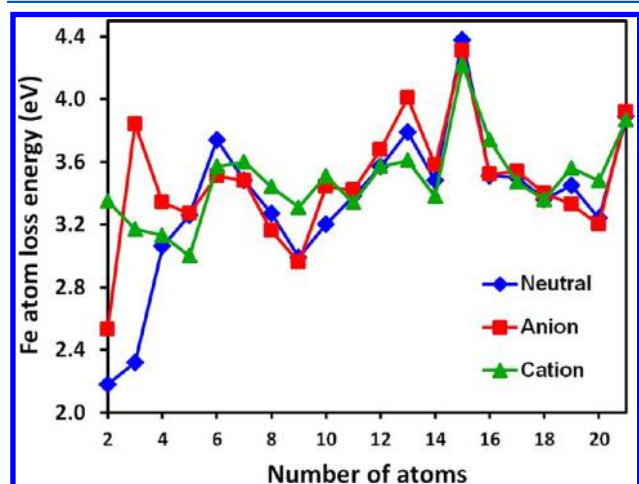


Figure 7. Fe atom abstraction energies of the $\text{Fe}_n^{0/-1/+1} \rightarrow \text{Fe}_{n-1}^{0/-1/+1} + \text{Fe}$ channels.

In order to estimate the relative stabilities of the neutral and charged iron clusters, we use the conventional formula for the second total energy differences $\Delta_2 E_{\text{tot}}(n) = E_{\text{tot}}(n+1) - 2E_{\text{tot}}(n) + E_{\text{tot}}(n-1)$. One can rewrite this formula as

$$\begin{aligned} \Delta_2 E_{\text{tot}}(n) &= [E_{\text{tot}}(n+1) - E_{\text{tot}}(n) - E_{\text{tot}}(1)] \\ &\quad - [E_{\text{tot}}(n) - E_{\text{tot}}(n-1) - E_{\text{tot}}(1)] \\ &= D_0(\text{Fe}_{n+1}) - D_0(\text{Fe}_n) \end{aligned} \quad (7)$$

The results of computations using this equation are displayed in Figure 8 for the neutral and charged iron clusters. Except for small n values, the behavior of the $\Delta_2 E_{\text{tot}}(n)$ function for the neutral, anionic, and cationic iron clusters is similar. We note that Fe clusters containing 7, 13, 15, and 19 atoms are among the most stable ones, which agrees with experimental data on the

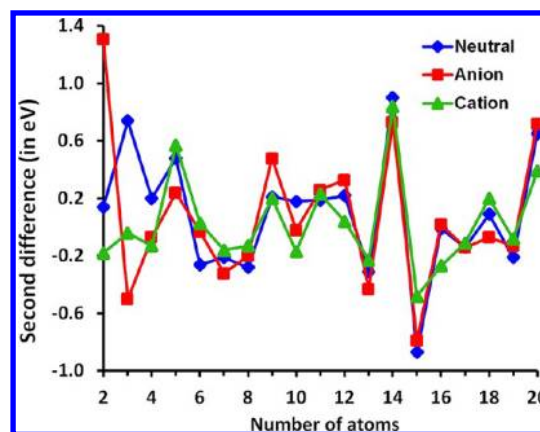


Figure 8. Second-order differences of the $\text{Fe}_n^{0/-1/+1}$ total energies.

intensity distribution in the mass spectra.⁸⁵ These numbers match our values. However, the theory also predicts one more magic number $n = 10$, which is lacking in the abundance spectrum. On the whole, one can anticipate that the thermodynamics of neutral and charged iron clusters can be satisfactorily described at the level of theory used in this work.

4. SUMMARY

The all-electron density functional theory computations with the generalized gradient approximation are performed for the Fe_n , Fe_n^- , and Fe_n^+ series for $n = 7-20$. It is found that the geometrical configurations of only Fe_9^- , Fe_9^+ , Fe_{10}^- , Fe_{10}^+ , Fe_{15}^- , and Fe_{19}^+ are different from those of the corresponding neutrals. In all other cases, the anion and cation lowest total energy states possess the same geometrical configurations as their neutral parents, and the detachment or attachment of an electron does not result in large changes in the bond lengths.

Our computed IEs of the neutrals and the VDE_{\pm} 's of the anions are in quantitative agreement with experiment. It was found that the energy of Fe atom abstraction from a neutral or charged iron cluster is nearly independent of the charge. Agreement of the computed energies of Fe atom abstraction with experiment is satisfactory, except for Fe₈, where the difference is 0.79 eV. The theoretical magic numbers computed from the second total energy differences agree with all experimentally observed magic numbers.

Our systematic study of the evolution of the magnetic properties in the iron clusters showed that the one-electron model where an electron detaches or attaches from/to a molecular orbital with the corresponding change in the total magnetic moment of $\pm 1.0\mu_B$ is valid in most cases. The exceptions are Fe_4^+ , Fe_{10}^- , Fe_{11}^+ , Fe_{12}^+ , Fe_{13}^+ , and Fe_{14}^+ , where the

change in the total magnetic moment is different, namely, $+3\mu_B$ (Fe_{10}^- and Fe_{12}^-), $-3\mu_B$ (Fe_4^+ , Fe_{11}^+ , and Fe_{14}^+), and $-9\mu_B$ (Fe_{13}^+). The reason for an anomalously large quenching of the total spin magnetic moment in Fe_{13}^+ is related with high T_h symmetry of this cation. The T_{1u} set of molecular orbitals is composed of 4p orbitals, which are occupied by six electrons promoted from the majority spin 4s electrons. The majority spin electron detachment and promotion of majority spin electrons into the minority spin 4p orbitals result in the net change of $9\mu_B$ in the total magnetic moment. Our computed total spin magnetic moments per atom match the experimental values within the experimental uncertainty bars.

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Notes

The authors declare no competing financial interest.

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