

Structure and magnetism in iron clusters

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Abstract

We present a general overview about existing experimental and theoretical works on structural and magnetic properties of small iron clusters in order to get a deeper understanding of the quantum effects which govern the dependence of their physical and chemical properties in the nanometer range. We find that experimental information on structure and morphology of the clusters is very limited, while there is a considerable amount of studies related to magnetic and electronic properties. Calculations based on first principles have been performed by a number of groups using different approaches to describe exchange and correlation effects. There is, however, serious disagreement among them regarding important cluster properties like magnetic moments and ground state geometries even of the smallest possible entities. We show that this can be partly traced back to the degree of symmetry imposed during the calculations, because it turns out that especially the magnetic moments are strongly dependent on cluster geometry. From our calculations we find that energetic ground states are characterized by distorted shapes for all cluster sizes considered. It is concluded that in order to obtain reliable values for the ground state properties of iron clusters, one has to consider regions of the potential energy surfaces belonging to unsymmetrical arrangements of the atoms and to allow for full relaxation of the atoms during the simulation.

Keywords: *Ab initio* calculations, Distorted iron structures, Magnetism

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1. INTRODUCTION

When spatial dimensions of their building blocks fall into the nanometer regime, many physical and chemical properties of materials not only change significantly compared to their corresponding bulk values, but are also strongly dependent on particle size and morphology. This is related to quantum effects, which become pronounced for particle sizes in the nanometer range, and is one of the reasons why nanostructured materials are often considered to be the key for future technologies [1,2]. The strong size dependence of many properties opens up the possibility to design new materials with unique properties, tailored to fit the specific needs in the desired application. A prominent example for this is the optical band gap, which in some materials can be tuned directly by changing grain sizes. Thereby it becomes possible to build devices which emit light from every desired part of the visible spectrum [3].

Another physical quantity which is strongly size dependent is the magnetic moment per atom of magnetic particles. In free atoms, the orbital magnetic moments and spin multiplicities are maximized according to Hund's rules. In contrast to that, delocalization of the electrons and formation of bands in combination with the crystal field lead to nearly totally quenched orbital moments and strongly diminished spin magnetic moments in transition metal (TM) bulk systems, leaving only iron, cobalt and nickel ferromagnetic (FM). It now turns out that in the corresponding nanoparticles, total magnetic moments and also the ratio of spin and orbital moment are not given by a simple interpolation between the limiting values of the free atom and the infinite bulk system. One rather observes an oscillatory behavior with peaks for certain sizes of the clusters [4]. A number of possible explanations have been proposed, but a detailed understanding of this phenomenon is still missing.

One of the most important technical applications for magnetic nanoparticles are ultrahigh-density magnetic storage devices, in which each bit is represented by exactly one magnetic nanoparticle. During the production process one can make use of the natural self-organization of the particles to obtain large-scale regular arrangements on a substrate [5]. While this already works for particles with dimensions around 10 nm [6], the fabrication of such arrays containing even smaller particles with sizes of only a few nanometers still represents a major coalescence problem [7]. Add to that, with decreasing size of the magnetic moments it becomes

more and more difficult to read and write information, and also the stability of the magnetic moments of the particles at finite temperature is reduced dramatically as the so called paramagnetic limit (a certain, temperature-dependent particle size) is reached. One is therefore interested in materials with a large magnetic anisotropy, like, e.g., FePt [8,9]. Experimentally, structural and magnetic properties of very small objects are in many cases difficult or even impossible to measure. The questions of the evolution of magnetism in TM clusters with particle size and their geometric structures are therefore still widely unanswered and represent a very interesting and challenging topic for research.

Due to recent technological advances and the development of highly elaborated experimental techniques it has become possible nowadays to investigate certain properties of TM clusters directly [4,10-33]. In scanning tunneling microscopes, e.g., various properties of extremely small clusters deposited on metal surfaces down to single adatoms can be studied [21,31]. Orbital and spin magnetic moments of supported clusters have been measured using the X-ray magnetic circular dichroism (XMCD) technique [28,32,33]. Free clusters have been subject to investigations of the dependence of magnetic moments on cluster size and temperature using a Stern-Gerlach magnet in combination with a time-of-flight mass spectrometer (TOFMS) [4,14,17,20,22,26]. Vibrational frequencies of free magnetic clusters have been measured by resonance Raman spectroscopy [11,23], while bond lengths of small clusters down to the dimer were obtained by trapping the metal atoms in inert gas matrices and performing extended X-ray absorption fine structure (EXAFS) measurements [10,12]. But a systematic investigation of structural, electronic and magnetic properties of small, size selected TM clusters still represents a major challenge for experimentalists. It is therefore not surprising that up to day there are only a few non-theoretical works concerning these properties of small gas phase clusters.

On the other hand, during the last two decades the development of accurate and numerically very efficient theoretical methods based on the first principles has gone hand in hand with a massive increase in computer capacities making it now possible to study such atomic systems in detail with *ab initio* methods. The number of publications related especially to cluster geometry and magnetic properties of both unsupported [13,34-67] and deposited [68,69] magnetic clusters has therefore increased quickly since the early 80's. Calculations based on model Hamiltonians

have also been performed [70,71]. Recently, studies on TM particles containing up to about 1000 atoms have appeared which are based on an efficient self-consistent tight-binding method [72-80] or the use of model potentials, especially the embedded atom method (EAM) [81-83].

In this article we give an overview on the current standing of experimental and theoretical research concerning small Fe clusters. As far as theoretical works are concerned, we will limit ourselves to results of former *ab initio* calculations. We will only discuss properties of free, gas-phase clusters, but a brief introduction into the topic of clusters deposited on supporting substrates will also be given. Results from our own calculations regarding structural and magnetic properties of Fe clusters containing up to 15 atoms are presented afterwards, together with a possible explanation of the origin of the large differences between results of former calculations.

2. EXPERIMENTAL DATA

At present, experimental information about structural properties of unsupported Fe clusters is very limited. To our knowledge, the bond length has only been obtained for the dimer [10,12] with sufficient accuracy, while vibrational frequencies have been obtained for the dimer and the trimer [11,23]. Concerning the latter, the degree of distortion of the cluster has been subject to a recent Raman spectroscopic study [23] but is still not yet known exactly. Ground state geometries of larger clusters have not been obtained at all experimentally.

The situation is slightly different for the determination of other physical and chemical properties of the clusters by which the underlying geometrical structure might be inferred. For example, the ionization potential (IP) and the electron affinity (EA) of Fe clusters containing up to 100 and 34 atoms, respectively, have been measured [13,15,16,19,24]. Using collision induced dissociation with xenon, fragmentation energies of positively charged clusters up to Fe_{19}^+ were determined [18]. In combination with the information about the IPs this data was used to calculate bond dissociation energies of the corresponding neutrals [27]. Already in 1985, Cox *et al.* have measured the magnetic moments of Fe clusters containing between 2 and 17 atoms [14]. They found that all clusters were paramagnetic with a linear increase of the total moment with the number of atoms. Magnetic moments of free Fe particles

from a molecular beam in the size range of 25 to 700 atoms have been measured in Stern-Gerlach experiments by Billas *et al.* [4]. In the latter study, also the temperature dependence of the magnetic moments was investigated. Specific heat measurements were performed recently for Fe clusters containing 130 to 400 atoms [26]. Using this information in combination with theoretical investigations, the geometric structure or at least the shape of the clusters can sometimes be deduced.

In the following we first discuss experimental results with respect to properties related to geometric structure of the smallest possible clusters. After that, we take the magnetic moment per atom as an example for a size-dependent observable and follow its evolution with particle size.

2.1 Fe dimer

We start our discussion with the Fe dimer, for which some direct experimental information on atomic separation from rare gas matrix isolation studies is available. Purdum *et al.* have performed EXAFS measurements on Fe highly diluted in a neon matrix [12]. They obtain an Fe—Fe distance of 2.02 ± 0.02 Å for the lowest Fe concentration of 0.4 at.% and attribute this to an average over the bond lengths of the dimer, the trimer and the tetramer which they consider to be the dominant cluster sizes at this low concentration. In later works, this distance has always been taken to be the bond length R_e of the Fe₂ dimer. In an earlier study, Montano and Shenoy have trapped Fe atoms in an argon matrix at a very low concentration of 0.1 at.% and calculated an Fe—Fe distance of 1.87 ± 0.13 Å which they attribute to the bond length in Fe₂ [10]. It is generally believed that the value of 2.02 Å resembles the true Fe₂ bond length more closely because of the smaller polarizability of the neon matrix. Nevertheless, the strong reduction of R_e compared to the bulk nearest-neighbor distance of 2.48 Å is evident.

From resonance Raman spectroscopic measurements on Fe isolated in solid argon, Moskovits and DiLella obtained a vibrational frequency of 299.6 cm⁻¹ and a force constant of 1.48 mdyn/Å for the Fe dimer [11]. By applying several empirical rules that describe correlations between force constants, bond orders and bond lengths, Jules and Lombardi derived from this value bond lengths of 2.12 Å and 2.06 Å, respectively [84].

We are aware of only one experimental study where the IP of Fe₂ has been measured [13]. From laser photoionization experiments, the authors obtain a value of 6.30 eV. Combining this value with the measured fragmentation energy of Fe₂⁺, Lian *et al.* have derived a value of 1.14 ± 0.10 eV for the bond dissociation energy of Fe₂ [18]. A revised value of 1.18 eV has been given recently by Armentrout [27]. A smaller value of 0.78 ± 0.17 eV has been obtained by Shim and Gingerich already in 1982 from mass spectrometric experiments in combination with Hartree Fock (HF) calculations [36].

From photoelectron spectroscopic (PES) measurements, Leopold and Lineberger obtain a value of 0.902 ± 0.008 eV for the electron affinity of Fe₂ [30]. The simplicity of the observed spectra is in contrast to the result of the HF study of Shim and Gingerich [36], where a large number of low-lying, nonbonding 3*d* states and a single bond of almost pure 4*s*—4*s* character between the Fe atoms is predicted. Leopold and Lineberger therefore conclude that the 3*d* electrons in Fe₂ are delocalized and contribute considerably to the bonding in the dimer, resulting in a bond order greater than one. But we like to point out that the ground state electronic structure of the Fe dimer has not yet been determined experimentally. The only reliable available information stems from computational studies based on first principles (see Sec. 3.1.1).

The magnetic moment of the Fe dimer was measured to be 6.1 ± 1.0 μ_B in a TOFMS in combination with a Stern-Gerlach apparatus by Cox *et al.* [14]. This corresponds to a value of 3.05 μ_B per atom.

2.2 Fe trimer

To our knowledge, there are no direct experimental results concerning the bond lengths in the Fe trimer, except for the observation that they are substantially contracted compared to the atomic separation in bulk iron [12]. But in a recent study based on Raman spectroscopy, Haslett *et al.* find that Fe₃ is a Jahn-Teller distorted, triangular molecule of *D*_{3*h*} parentage [23]. Although they have obtained a vibrational frequency of 249 cm⁻¹ at a temperature of 20 K, which they attribute to the symmetric stretch mode, they could not reveal the whole vibronic structure of the cluster as the bands in the spectrum were much too broad. Furthermore, the observed spectrum

was too complex to fit to a simple quadratic Jahn-Teller model. The authors conclude that this may originate from spin-orbit effects.

The electronic structure of Fe₃ has been examined in a recent PES study [19]. The authors obtain a value of 1.47 ± 0.08 eV for the adiabatic electron affinity. A revised value of 1.43 ± 0.06 eV has recently been given by Wang *et al.* from similar experiments [24]. The obtained spectrum is more complicated than the corresponding spectrum for the dimer. The first two peaks were assigned to energy levels obtained from extended Hückel molecular orbital calculations for an equilateral triangle with bond lengths of 2.1 Å and correspond to a 3*d* like and a strongly bonding 4*s* like state. The remaining part of the spectrum could not be resolved. From the calculations, the authors report a value of 2.67 μ_B per atom (a total moment of 8 μ_B). A similar magnetic moment has been obtained experimentally by Cox *et al.* [14]. They give a value of 8.1 ± 1.0 μ_B, which corresponds to 2.7 μ_B per atom.

The fragmentation energy of the Fe trimer is considerably larger than that of the dimer. Lian *et al.* report a value of 1.82 ± 0.13 eV for the dissociation into Fe₂ and atomic Fe [14]. A revised value of 1.91 eV has been proposed recently by Armentrout [27].

2.3 Larger clusters

For free Fe clusters larger than the trimer there is no direct experimental information about their morphology available. But by comparing results from first-principles calculations regarding, e.g., electronic structure, to corresponding experimental observations, the underlying cluster geometries might be inferred and interesting physical properties might be revealed. So experimental data concerning IPs, EAs, dissociation and fragmentation energies and magnetic moments provide invaluable information for the determination of ground state geometries – and thereby also related properties – from *ab initio* calculations.

2.3.1 Ionization potentials

Rohlfing *et al.* have measured IPs for Fe clusters containing up to six atoms in threshold photoionization experiments [13]. They provide the only available values for Fe₂ and Fe₃. Yang and Knickelbein have obtained IPs for Fe₆ to Fe₉₀ by using a similar technique [16]. They observe that the IPs decrease rapidly but

nonmonotonically with cluster size up to about Fe₂₀. For larger clusters, the IP evolves more slowly and smoothly. By measuring the coverage-dependent IP of Fe clusters covered with ammonia and extrapolating to bare clusters, Parks *et al.* have found IPs for Fe₄ to Fe₁₀₀ [15]. As pointed out by the authors, a major advantage of their experimental technique is its simplicity. Connected to this are error bars which are slightly larger than those of the other studies, but all measured values are consistent. In Table I we give the resulting IPs for up to Fe₁₀.

Table I. Experimental IPs of Fe clusters up to Fe₁₀ in eV. Uncertainties of the last digits are given in parentheses.

Fe ₂	Fe ₃	Fe ₄	Fe ₅	Fe ₆	Fe ₇	Fe ₈	Fe ₉	Fe ₁₀	Ref.
6.30(1)	6.45(5)	6.4(1)	5.95(5)	5.9(1)					[13]
			6.20	5.96	5.76	5.48	5.50	5.41	[16]
		6.78(36)	6.30(12)	6.26(16)	5.97(39)	5.97(39)	5.44(14)	5.44(14)	[15]

2.3.2 Electron affinities

The EA of the Fe dimer has been obtained to be 0.902 ± 0.008 eV (see Sec. 2.1) by Leopold and Lineberger in a PES measurement [30]. In laser photodetachment experiments, Wang *et al.* have obtained EAs for Fe clusters containing up to 24 atoms starting with the trimer [19]. They find a nonmonotonic behaviour of EA with cluster size. In a recent publication, the size range has been extended up to Fe₃₄, and revised values were given for the smaller clusters [24]. Results for EA up to Fe₁₀ are given in Table II.

Table II. Experimental EA's of Fe clusters up to Fe₁₀ in eV. Uncertainties of the last digits are given in parentheses.

Fe ₂	Fe ₃	Fe ₄	Fe ₅	Fe ₆	Fe ₇	Fe ₈	Fe ₉	Fe ₁₀	Ref.
0.902(8)									[30]
	1.47(8)	1.72(8)	1.81(8)	1.51(8)	1.39(8)	1.66(8)	1.75(8)	1.85(8)	[19]
	1.43(6)	1.78(6)	1.84(6)	1.58(6)					[24]

2.3.3 Fragmentation energies

Lian et al have measured bond dissociation energies (D_e) of charged Fe_n^+ clusters by collision-induced dissociation with xenon [18]. By combining these data with information about the IPs of Fe_n and Fe_{n-1} according to the formula

$$D_e(Fe_n) = D_e(Fe_{n-1}) + IP(Fe_n) - IP(Fe_{n-1}),$$

fragmentation energies of the type $Fe_n \rightarrow Fe_{n-1} + Fe$ of the corresponding neutrals were obtained. Revised values were given by Armentrout in a recent publication [27]. They are displayed in Table III together with the values for the charged clusters, again for clusters containing up to 10 atoms. It becomes clear from the numbers that the thermodynamic stability of the clusters increases with their size. Except for Fe_2 , the fragmentation energies of the neutral clusters are slightly smaller but similar to those of the corresponding cations and vary nonmonotonically with cluster size.

Table III. Experimental fragmentation energies of charged and neutral Fe clusters up to Fe_{10} in eV.

N	2	3	4	5	6	7	8	9	10	Ref.
$Fe_n^+ \rightarrow Fe_{n-1}^+ + Fe$	2.78	1.75	2.24	2.69	3.26	3.32	2.61	2.91	2.94	[27]
$Fe_n \rightarrow Fe_{n-1} + Fe$	1.18	1.91	2.19	2.25	3.17	3.12	2.33	2.92	2.86	[27]

2.4 Evolution of the magnetic moments with cluster size

In Stern-Gerlach experiments Billas *et al.* obtained the magnetic moment m per atom as a function of the number of atoms per cluster [4]. From the figure in the corresponding publication it is obvious that the moments of all clusters are higher than the bulk value of $2.2 \mu_B$, but well below the moment of $4 \mu_B$ of the free atom. Up to a size of about 120 atoms, m shows large oscillations around a mean value of about $3 \mu_B$. There are certain cluster sizes which exhibit relatively large moments, and others, where the moment is smaller than that of clusters of similar size. These peaks occur for cluster sizes of 55, 110, 325, and 625 atoms and might be due to the strong dependence of m on geometrical structure and thereby related to a successive icosahedral shell filling of the clusters. The transition from around $3 \mu_B$ for smaller clusters to about the bulk value for large clusters has been qualitatively explained to be related to a change in electronic structure from fully polarized majority $3d$ bands for small clusters to partly filled bands as in the bulk for larger

clusters. But the authors point out that, as the experiments were performed at a temperature $T = 120$ K, the measured values for m are only lower limits for the moments as T goes to zero.

3. FIRST-PRINCIPLES CALCULATIONS

In contrast to the sparseness of experimental results, there are quite a number of theoretical works on Fe clusters [34-45,48-50,54-59,62-67,69-71,73,75]. At present, most of them are based on first-principles calculations [34-45,48-50,54-59,62-67,69], but we observe an increasing number of studies using the tight binding approximation, which seems to be especially suitable for larger clusters and has been applied to systems containing up to about 1000 atoms with success [70,71,73,75]. Apart from a few calculations on single clusters of larger size [66], systematic first-principles calculations have only been performed for Fe clusters containing less than 20 atoms. Most of them are based on density functional theory (DFT) [85,86] in the local density approximation (LDA) or the generalized gradient approximation (GGA) for the calculation of the exchange and correlation energy, but there are also a number of works based on Hartree Fock (HF) in combination with configuration interaction (CI) or even multireference CI.

Because of the uncertainty concerning the correct cluster geometries, in most studies some sort of relaxation of the atoms has been performed. But as it turns out, the potential energy surfaces of Fe clusters exhibit a complicated structure with a large number of local minima which are often very close in energy, but separated by considerable energy barriers. Things are even more complicated by the fact that often different local minima on the potential energy surface belong to different values of the total spin. This has to be kept in mind when calculations, where the spin multiplicity is a constant, are performed. It also turns out that the electronic structure of Fe clusters is far from being simple. Near the Fermi energy, the clusters exhibit a large number of nearly degenerate states, which gives rise to Jahn-Teller like distortions and requires a good description of exchange and correlation effects to obtain the correct ground states. We start our discussion with reviewing results from former *ab initio* calculations concerning the smallest clusters before we present results of our own calculations and turn our attention to the evolution of magnetic moments with cluster size.

3.1 Geometries and related properties of small clusters

3.1.1 Fe₂

For a long time, the only Fe cluster that could be treated in first principles calculations was the dimer. The first non-empirical calculation on Fe₂ was performed already in 1979 by Harris and Jones [34]. By using DFT and the LDA, they obtain an equilibrium bond length (R_e) of 2.09 Å and a ${}^7\Delta_u$ electronic ground state, which corresponds to a magnetic moment of 3.0 μ_B per atom. In agreement with a subsequent calculation based on the X_α method [13], the bond is characterized as a formal triple bond consisting of one $s-s$ and two $d-d$ bonds and has a strength (D_e) of 3.45 eV, which is about three times larger than the available experimental values.

In contrast to that, Shim and Gingerich obtain a single $4s-4s$ bond and essentially nonbonding $3d$ cores from HF based CI calculations [36]. Related to this, a very high density of 112 electronic states within 0.5 eV from the ${}^7\Delta_u$ ground state, arising from weak interactions between the localized $3d$ electrons, is predicted. But there is no experimental evidence for this finding, the PES spectrum of Fe₂ being very simple and showing only two states in an energy range of 1 eV [30]. The calculated bond length of 2.40 Å is closer to the nearest neighbor distance of 2.48 Å in bulk iron, but a rather large overestimation of the experimental value for Fe₂ of around 2.0 Å. The associated bond dissociation energy of 0.78 eV is probably too small. The reason for this is that the ground state of Fe₂ is not described well by a single configuration. By using multireference CI, Tomonari and Tatewaki have obtained an equilibrium bond length of 2.02 Å and show that the bond is made up of one and a half $d-d$ and one $s-s$ bond [37]. The band structure of the Fe dimer has been subject to a subsequent study [38]. An IP of 5.3 eV has been obtained, which is in rather good agreement with the experimental value of 6.3 eV. A study based on CI with quadruple excitations yields modified values of $R_e = 2.06$ Å and $D_e = 1.57$ eV and confirms the ${}^7\Delta_u$ symmetry of the ground state, thereby yielding magnetic moments of 3.0 μ_B per atom [43]. In contrast to that, the most recent MRCI calculation predicts a ${}^9\Sigma_g^-$ ground state [65].

Up to day, starting with the first study of Harris and Jones in 1979, there have been a considerable number of both all-electron and pseudopotential DFT-based works related to Fe₂ (and Fe clusters in general), employing the LDA and many different GGA functionals [30-32,34-36,41-43,47-67,69]. In these studies, numerous different

aspects of structural, electronic and magnetic properties have been investigated to a great extent; a detailed discussion of all the results cannot be given here. We will instead focus on some key properties and refer the reader to the corresponding literature.

The use of the LDA yields an equilibrium bond length of 1.93 – 1.97 Å for the FM ground state with a magnetic moment of 3.0 μ_B per atom. A paramagnetic solution with $S = 0$ is obtained for $R_e = 1.70 - 1.88$ Å. The corresponding dissociation energies are 3.81 – 5.16 eV and 1.64 – 2.6 eV, respectively [40,45,50,56,57,58], and depend strongly on the details of the calculational scheme. There seems to be no stable AF solution in LDA. In calculations taking a noncollinear magnetization density into account, a collinear ground state for FM Fe₂ is obtained [50,57].

The inclusion of gradient corrections (often denoted as nonlocal terms) into the density functional yields slightly larger bond lengths of 1.98 – 2.03 Å and reduced dissociation energies between 2.30 and 3.54 eV. Analysis of the bond order confirms the existence of a triple bond, showing that in metal-metal bonds the bond order is not necessarily a good indicator for the bond strength [49]. Harmonic vibrational frequencies are overestimated, according to the binding energies. Calculated values range from 393 cm⁻¹ to 474 cm⁻¹ [44,56,64,67], compared to the experimental value of 299 cm⁻¹ [11]. A spin multiplicity of seven for the ground state is obtained in nearly all calculations. This corresponds to a total magnetic moment of 6.0 μ_B , or a magnetic moment per atom of 3.0 μ_B . Only in one recent publication a different value of 3.32 μ_B per atom is reported [69].

A detailed discussion of the electronic structure of the small Fe clusters, including the dimer, has been given recently by Gutsev [62], Chrétien and Salahub [64] and Gutsev and Bauschlicher [67]. In contrast to LDA, there are AF states found in GGA calculations which are, for some spin multiplicities, lower in energy than a FM or NM solution. From these works it also becomes clear that there are many electronic states close in energy and with similar properties. This accounts for the fact that results for some calculated properties differ to a great extent when different first principles methods are used. The performance of many DFT methods including hybrid functionals in the calculation of TM dimer properties has recently been investigated in detail [55,56]. The authors find that the accuracy of the results is

strongly dependent on the functional employed, with the pure GGA functionals performing considerably better than the hybrid methods and LDA.

Castro and Salahub have calculated the ionization energy and the electron affinity of the Fe dimer to be 7.21 and 0.95 eV using LDA and 7.00 and 1.31 eV using GGA [44]. Revised values of 7.14 and 1.17 eV for GGA are given by the authors in a very recent publication [64], which are already in rather good agreement with the available experimental data of 6.30 and 0.90 eV. By employing a different functional to calculate the exchange and correlation energy, the agreement can even be improved to within the uncertainty of the experimental values, as was shown by Gutsev and Bauschlicher. They obtain values of 6.68 and 0.94 eV, respectively [67].

3.1.2 Fe₃

The Fe trimer has also been subject to a considerable amount of theoretical work. It is the smallest Fe cluster for which different geometric arrangements of the atoms belonging to different symmetry groups are possible. In the first *ab initio* study on Fe₃, Rohlfing *et al.* obtained an equilateral triangle with bond lengths of 2.00 Å and a FM ground state with 2.67 μ_B per atom using the X_α method [13]. Tatewaki *et al.* have performed HF calculations for Fe₃ with a fixed triangular geometry (all bond lengths were kept at the bulk nearest neighbor distance of 2.48 Å) and calculated an IP of 5.9 eV by considering an atomic correlation correction. But the authors point out that relaxation of the atoms and the inclusion of correlation effects is inevitable for a further discussion.

In all subsequent studies at least some sort of geometry optimization was performed. But it turns out that the potential energy surface of the Fe trimer has a complex structure with many local minima which are close in energy. In particular, final geometries obtained in relaxation processes are dependent on starting structures which themselves are therefore not unimportant. This might be the reason why in nearly all DFT studies an equilateral triangle has been proposed as the ground state structure, no matter whether LDA or GGA functionals were used [40,44,45,34-36,57,58]. Only recently, the ground state of the Fe trimer has been assigned to be an acute-angled, isosceles triangle (C_{2v} symmetry) for most GGA functionals, with one short bond of 2.10 – 2.15 Å and two longer bonds of about 2.30 Å [54,64,67]. The ground state in LDA calculations is indeed an equilateral triangle with side

lengths of about 2.11 – 2.14 Å depending on the method of calculation. Taking this as a starting structure for a geometry optimization in a GGA calculation presumably leads again to an optimized structure of the same symmetry, which might explain the earlier findings. The bent geometry is, however, in agreement with a recent Raman spectroscopic study of matrix-isolated, mass-selected Fe₃ [23]. The calculated harmonic vibrational frequencies are of the order of 60 cm⁻¹ (antisymmetric stretching mode) and 230 cm⁻¹ (symmetric stretching mode) for all low-lying states with a spin multiplicity of 11, not allowing one to prefer one state over the other as ground state for Fe₃ [64,67].

As specified, the exact symmetry of the electronic ground state of the Fe trimer is still a matter of discussion. The ¹¹A₁ and ¹¹A₂ states are nearly degenerate, and it is pointed out that higher levels of theory are needed to determine the true ground state of Fe₃. For a very detailed, comprehensive overview see Ref. 64 and 67. The ground state magnetic moment of the Fe trimer is 8 μ_B using the LDA and 10 μ_B in GGA calculations, corresponding to 2.67 μ_B per atom. Solutions with AF or NM spin arrangements are much higher in energy. An unusually high magnetic moment of 3.49 μ_B per atom was found by Šljivančanin and Pasquarello [69], but the authors did not specify the geometric parameters of their structure.

Another geometry, which has been studied to some extent, is the linear chain. In their LDA calculations, Chen *et al.* [40] and Castro and Salahub [44] have found this structure to lie about 0.8 eV per atom above the triangular ground state. The total magnetic moment is 6 μ_B, while the bond lengths are with 1.9 Å even shorter than in the dimer. A linear, asymmetric isomer with a total moment of 8 μ_B was found by Ballone and Jones at about 0.7 eV per atom above the ground state [45]. By allowing for noncollinear magnetic structures in an unconstrained approach where the magnetization density is treated as a vector observable, stable solutions with interesting arrangements of the spins for the linear chain Fe trimer were found. While Oda *et al.* find a noncollinear AF-like state with a finite moment of 1.27 μ_B for the central atom by using LDA [50], Hobbs *et al.* obtain a fully collinear AF solution by using LDA, but a noncollinear state in GGA [57]. In both cases, though, the noncollinear states are located well above the triangular ground state.

3.1.3 Fe₄

The tetramer is the smallest Fe cluster that can have a three-dimensional geometric structure. The first calculations of Chen *et al.* [40] and Castro and Salahub [44] have found regular tetrahedrons with bond lengths of 2.25 Å and 2.22 Å, respectively, and a magnetic moment of 12 μ_B , to be the ground state structure in both LDA and GGA. Other geometries with lower dimensionality like a square and a linear chain have also been considered but turned out to be much higher in energy. Allowing for relaxation by performing molecular dynamics simulations based on the LDA, Ballone and Jones found the tetrahedron to be unstable against a distortion towards a lower symmetry [45]. This butterfly structure still resembles the perfect tetrahedron and is characterized by two short bonds (2.17 Å) and four longer bonds (2.43 Å). A similar structure with C_{2v} symmetry has also been obtained in all-electron GGA calculations [48,49]. The authors were able to show that the distortion is due to a maximization in directional bonding, the bond orders of 1.4 of the short bonds (2.16 Å) being considerably higher than the corresponding values of 1.1 of the longer bonds (2.26 Å), and originates from a threefold-degenerate electronic ground state in the perfect tetrahedron according to the Jahn-Teller theorem. In subsequent studies, this geometry has been found again, in plane-wave pseudopotential calculations [50,58] as well as in all-electron calculations with Gaussian basis sets [63].

A different ground state was found by Hobbs *et al.* by employing a GGA functional [57]. They obtain a geometry of C_{2v} symmetry with four short bonds (2.23 Å) and two longer bonds (2.55 Å). Although they use a fully unconstrained approach to noncollinear magnetism, the authors find a collinear magnetic ground state with a total magnetic moment of 14 μ_B . This result is supported by Gutsev [62] and Gutsev and Bauschlicher [67] in recent publications. They have considered all possible spin multiplicities and investigated the effect of using different GGA and LDA functionals. They find that GGA functionals all yield 14 μ_B ground states slightly below the 12 μ_B solutions, with geometries similar to the one found by Hobbs *et al.*, while LDA gives the structure with two short and four long bonds and a total magnetic moment of 12 μ_B .

An overview of all states found by employing a certain GGA functional has been given by Chrétien and Salahub [64]. They have found a large number of low-lying states in a small energy range from the ground state and conclude that a definitive assignment of the ground state of Fe₄ is at the moment not yet possible.

In contrast to that, it seems to be confirmed that the ground state of Fe_4^+ is the regular tetrahedron. The threefold degenerate orbital is occupied by one 4s-like electron in neutral Fe_4 of T_d symmetry, so upon ionization the perfect tetrahedron can be stabilized [48,49]. Interestingly, the total magnetic moment of Fe_4^+ is found to be $11 \mu_B$, violating the empirical rule that the multiplicity of the neutral is one smaller or greater than the multiplicity of the corresponding anion or cation [64,67]. But the energy difference to the next state with $13 \mu_B$ appears to be rather large, supporting the assignment of the found state as the ground state. The calculated IP's of 6.20 eV [64] and 5.71 eV [67] show some deviation from the experimental values of 6.4 and 6.78 eV.

The situation is different for the anion, Fe_4^- . While a definitive assignment of the geometry with lowest energy is not a trivial task (4 states were found within the first 60 meV [64]), the multiplicity of 16 corresponding to a total magnetic moment of $15 \mu_B$ has been confirmed. The EA of 1.76 eV [67] calculated by using a functional form of the exchange-correlation energy proposed by Perdew and Wang in 1991 [89] is in excellent agreement with experiment, while the values obtained by a different functional [64] and the LDA [44] show larger deviations.

3.1.4 Fe_5

Concerning the ground state geometry of this cluster, there is a considerable number of different results. Whereas in some cases the square pyramid (C_{4v} symmetry) has been proposed [38], most calculational schemes seem to favor the trigonal bipyramid or derived structures.

The calculations of Castro and Salahub on the Fe pentamer suggest as the most stable isomer a distortion of the D_{3h} trigonal bipyramid with a multiplicity of 17 corresponding to magnetic moments of $3.2 \mu_B$ per atom [44]. In LDA, this state is nearly degenerate with the perfect D_{3h} structure and a multiplicity of 15, whereas it is located 50 meV per atom lower when gradient corrections are added. This might be the reason why in many subsequent publications the ideal trigonal bipyramid has often been found as the ground state of Fe_5 . For example, Ballone and Jones find a D_{3h} structure with diagonals and bases of 2.20 Å and 2.31 Å, respectively, and a total magnetic moment of $14 \mu_B$ [38], whereas O. Diéguez et al. obtain slightly longer bonds and $16 \mu_B$ [58].

An analysis of the bond orders in Fe_5 reveals that there are mainly single bonds (related to bond lengths of about 2.2 Å), but also bonds with even lower order (related to distances between 2.3 Å and 2.6 Å). This decrease in bond orders when going from Fe_2 to Fe_5 (and further) is balanced by an increase in coordination number and is responsible for the fact that the magnetic moments per atom stay rather constant as cluster size increases. It will be shown later that this trend continues up to about Fe_8 .

An interesting topic which currently attracts considerable interest is the possibility of noncollinear arrangements of the magnetic moments. The Fe pentamer is the only Fe cluster for which a noncollinear magnetic ground state has been proposed [50,57,66]. From LDA-based, ultrasoft pseudopotential calculations, Oda *et al.* have found a state with trigonal bipyramidal geometry and a total magnetic moment of 14.57 μ_B , to be the ground state of Fe_5 . The moments of the basal atoms are in parallel, but the moments of the two apical atoms are tilted by approximately 30° in opposite directions. The authors propose a FM interaction between nearest neighbors, and an AF interaction between next-nearest neighbors, to be responsible for this. Hobbs *et al.* were able to stabilize this structure for the perfect trigonal bipyramid by using LDA as well as GGA [57]. The corresponding collinear states we found to be 32 meV and 14 meV per atom, respectively, higher in energy. The canting of the spins results in increase of the total magnetic moment from 14 μ_B to 14.5 μ_B in the LDA calculation. In contrast to that, the moment is substantially reduced from 18 μ_B to 15.9 μ_B when using GGA.

Gutsev and Bauschlicher have optimized the structure of Fe_5 for different multiplicities in all-electron calculations based on GGA [67]. They confirm the finding that the ground state of Fe_5 is given by a distorted structure. Due to the lack in experimental data, a comparison of their calculated frequencies with measured values is not possible. But the calculated EA of 1.84 eV is in perfect agreement with the experimental values, as well as the IP of 6.04 eV (see Sec. 2.3).

3.1.6 Fe_6

In contrast to the pentamer, there are only few results from ab initio calculations for Fe_6 . The first ab initio study on Fe_6 was performed by Ballone and Jones. They have found a capped trigonal bipyramid (C_1 symmetry) as the lowest energy structure, 20

meV per atom below the compressed octahedron (D_{4h} symmetry). For both geometries, the magnetic moments were $3.33 \mu_B$ per atom.

The opposite order of states was obtained by Castro [49]. The compressed octahedron with C_{2h} symmetry and also $3.33 \mu_B$ per atom was found to be the ground state, at both LDA and GGA level of theory. The bond lengths vary from 2.24 to 2.61 Å, with bond orders between 1.2 and 0.5. So the trend towards smaller bond orders but higher coordination numbers with increasing cluster size is continued with Fe_6 . Separated by only 45 meV per atom from this state the authors find the capped trigonal bipyramid. A similar result was obtained by Diéguez *et al.* [58]. They also find the two structures nearly degenerate in energy.

Gutsev and Bauschlicher have calculated harmonic vibrational frequencies and fragmentation energies as well as the IP and the EA of Fe_6 [67]. The agreement of the latter two with experimental values is very good, with 6.15 eV and 1.61 eV, respectively. The fragmentation energy of 3.74 eV is 0.57 eV larger than in experiment, but the trend towards higher thermodynamic stability with increasing cluster size is recovered. There are no experimental frequencies available to compare with. Interestingly, the authors find that there is no drastic change in cluster geometry when going from the neutral cluster to the anion or the cation, with all bond lengths in the range of 2.32 to 2.72 Å.

3.1.6 Fe_7

Results from DFT calculations on the Fe heptamer were first reported by Ballone and Jones in 1995 [45]. They have obtained the regular pentagonal bipyramid (D_{5h} symmetry) with a magnetic moment of $3.14 \mu_B$ per atom as the lowest energy structure for Fe_7 by using the LDA in combination with norm-conserving pseudopotentials and corrections to account for effects of the core electrons on the spin polarization. The corresponding atomic distances are 2.20 and 2.21 Å between nearest neighbors, and 2.37 Å between the apical atoms. Separated in energy by 0.11 eV from the ground state the authors have found as another stable isomer an incomplete stellated tetrahedron (C_s symmetry), followed by a skewed structure of nearly C_2 symmetry and a capped octahedron (C_s), which are located another 0.03 eV per atom higher. In spite of the fact that these isomers have geometries quite different from the D_{5h} ground state structure, with inter-nuclear separations of nearest

neighbor Fe atoms between 2.16 and 2.37 Å, they possess the same total magnetic moment of 22 μ_B .

The pentagonal bipyramid with $m = 3.14 \mu_B$ per atom is also reported to be the ground state of Fe₇ in the LDA study of Diéguez *et al.* [58]. Although the authors have applied a similar computational scheme, their computed bond lengths are somewhat larger (2.24 Å between nearest neighbors and 2.41 Å between apical atoms). In this study, the capped octahedron has been found to be located in energy only 0.03 eV above the ground state.

A rather different result has been reported by Castro already in 1997 [49]. From a DFT-based all-electron calculation using the GGA (in the form PP86), he also found a capped octahedron (C_3) to be a stable isomer. But in energy 0.23 eV lower is the distorted pentagonal bipyramid of C_1 symmetry, which is also the energetic ground state. As pointed out above, the origin of this distortion is the existence of a degenerate electronic state in the corresponding ideal structure. The interatomic separations are in the range of 2.21 to 2.29 Å, but there are also some distances between neighboring atoms which are as large as 2.50 Å. An analysis of the bond orders therefore mainly yields values of around 1.0 (single bonds), but there are also bonds with a strength of about 0.5. The effect the increase in coordination compared to smaller Fe clusters has on the magnetic moment is therefore balanced by a decrease in bonding, resulting again in a total moment of 22 μ_B . An analysis of the DOS reveals, that the contribution from the 4s and the 4p states to the magnetic moment are not negligible, being around 0.14 μ_B per atom. In addition, the Fermi level is of 4sp type, which enhances the trend of metallic-like bonding in the cluster.

That the undistorted nature of the ground state is not due to the use of the LDA has been shown by Bobadova-Parvanova *et al.* [63]. These authors used a cluster configuration search algorithm to find candidates of ground state structures combined with tight-binding calculations based on DFT (DFTB). The ten lowest energy structures were then further optimized at LDA level. The calculations yield a distortion of the pentagonal bipyramid of D_{5h} symmetry to an optimal structure of Fe₇ of C_1 symmetry with a magnetic moments of 3.14 μ_B per atom [63], in agreement with the result of Castro [49]. The pentagonal bipyramid turned out to be not even a minimum, having three imaginary vibrational frequencies.

3.1.6 Fe₈ to Fe₁₅

We are aware of only one first-principles study on Fe₈ and Fe₉. By using the LDA, Diéguez *et al.* obtain magnetic moments of 3.0 and 2.89 μ_B per atom, respectively, and a bidisphenoid and a tricapped trigonal prism as ground state geometries [58]. The lowest energy state is separated by a rather large barrier of 70 meV per atom from the next state in Fe₈, while for Fe₉ the first two states are within 20 meV per atom.

For Fe₁₀, a symmetric shape was found with LDA as a result of refining the ten lowest energy structures obtained with the DFTB method [63]. This method has the advantage that larger cluster sizes can be treated because of lower computational costs. The optimum structure corresponds to a hollow, cage-type geometry with a symmetry axis going through the apex atoms and magnetic moments of 2.80 μ_B per atom. This symmetric D_{4d} structure seems to be non-degenerate and no Jahn-Teller distortion is expected. We would however like to point out that these LDA results are in contrast to GGA calculations undertaken by our group, which yield a distorted cluster as ground state for Fe₁₀.

For the larger cluster sizes, Fe₁₁, Fe₁₂, and Fe₁₃, the LDA calculation of Diéguez *et al.* suggests icosahedral geometries, with magnetic moments of 2.73, 2.67 and 2.62 μ_B per atom, respectively. Interestingly, for Fe₁₃ an AF alignment of the spins has been found, with a small moment of -0.24 μ_B for the central atom of the icosahedron. The GGA calculations performed by ourselves show again that the clusters possess distorted geometries with FM spin structures. Of particular interest is here that the many-atom clusters allow for the investigation of hollow clusters by omitting atoms in or near the center of the cluster.

3.2 Magnetic moments

As has been pointed out above, it turns out that results for some of the calculated properties of Fe clusters differ to a great extent from one publication to the next. As an example, we will take the magnetic moment m per atom. In Fig. 1, m as obtained from different calculations based on DFT is shown. Blue curves represent results from LDA calculations, magenta curves mark studies employing GGA functionals. Results from the most recent publications of Gutsev and Bauschlicher [67] and

Chrétien and Salahub [64] are not included, as they are in principle identical to the ones of Hobbs *et al.* [57] and have already been discussed extensively in the preceding chapters.

It is obvious that m varies from cluster to cluster, with an upper bound of $4 \mu_B$ of the free atom, and a lower bound of $2.2 \mu_B$ of bulk iron. The maximum of $3.6 \mu_B$ per atom is reached for Fe_5 in the GGA calculation of Šljivančanin *et al.* [69]. Incorporating gradient corrections into the calculations generally leads to higher values for the magnetic moments. But we also note the differences between results obtained by different LDA (and GGA) calculations. Whereas, e.g., Castro *et al.* [49] have obtained a magnetic moment of $2.67 \mu_B$ per atom for Fe_3 , Hobbs *et al.* find a value of $3.33 \mu_B$ per atom, and Šljivančanin *et al.* even $3.49 \mu_B$ per atom.

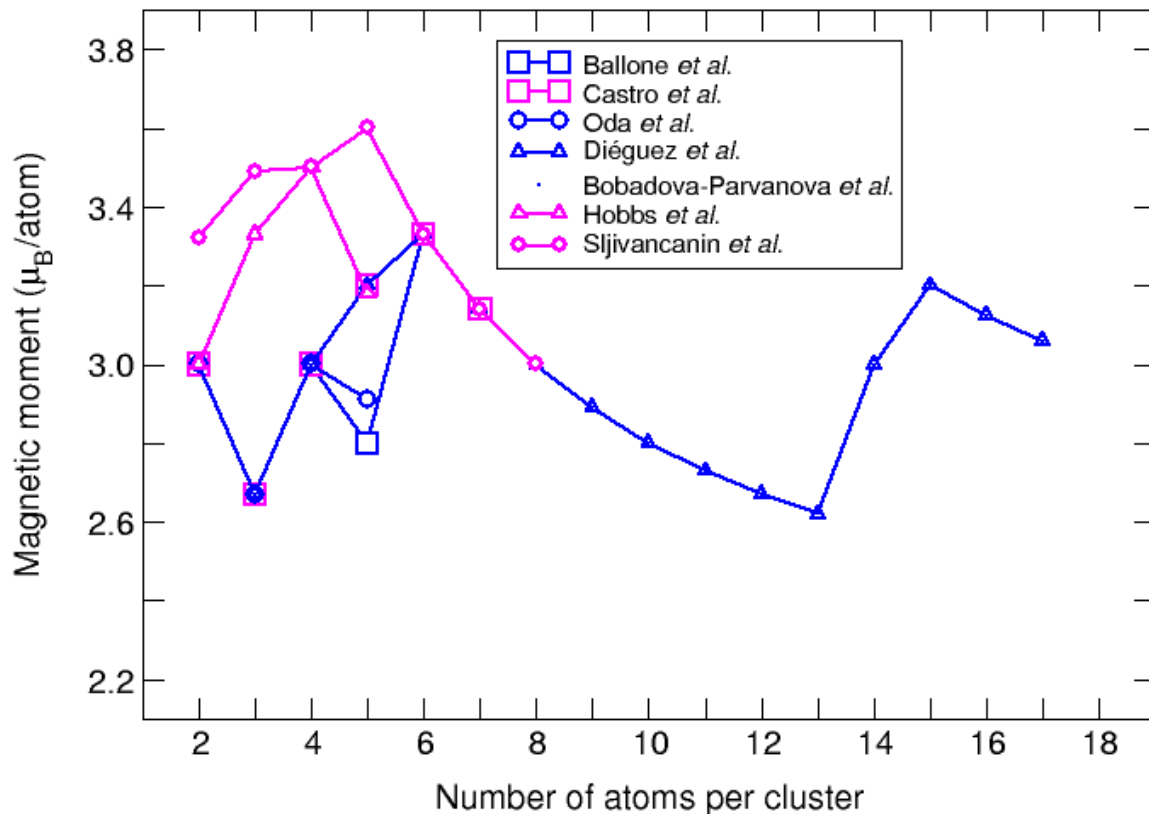


Fig. 1: Dependence of the magnetic moments per atom in Fe clusters on cluster size as obtained in former *ab initio* calculations. Blue lines correspond to LDA, magenta lines to GGA calculations.

To understand the origin of these differences one has to look more closely to the details behind the simulations. As pointed out in the previous section, the assignment of a ground state for a particular cluster is not trivial and strongly depends on the geometric structures considered. In the following we present results of our own ab initio calculations regarding structural, electronic and magnetic properties of Fe clusters.

4. OWN CALCULATIONS

We have performed total energy calculations in the framework of DFT allowing for full relaxation of the atoms without imposing any symmetry constraints. A number of eight valence electrons was taken into account for each Fe atom, the remaining core electrons together with the nuclei were described by pseudopotentials following the projector augmented wave (PAW) method as implemented in the Vienna ab initio simulation package (VASP) [87,88]. For the exchange correlation functional we chose a form proposed by Perdew and Wang in 1991 [89]. As the calculations were performed with periodic boundary conditions, the electronic wavefunctions were expanded in a plane wave basis set. The corresponding energy cutoff was kept fixed at a value of 335 eV throughout the calculations. For the supercell we have chosen a cube with sides 12 Å to ensure that the interaction of the clusters with their images is negligible. The integration over the irreducible part of the Brillouin zone was performed using the Γ -point only. Convergence criteria were set to very small values of 10^{-7} eV during the self-consistency cycles and 10^{-6} eV for the ionic movements (corresponding to very tight convergence in other program packages). We also allowed for a fully non-collinear magnetization density by treating it as a vector observable in an unconstrained approach as described by in the recent publication by Hobbs *et al.* [57].

In Fig. 2 the ground state geometries for Fe clusters containing up to 15 atoms as obtained from our calculations are depicted. They are the result of extensive searches for global energy minima without imposing any symmetry constraints. It becomes clear already by looking at the pictures that the clusters do not possess the highest possible symmetry but are to some degree distorted.

The geometries we have found for the ground state structures are in general agreement with the corresponding results of Gutsev and Bauschlicher [67] and Chrétien and Salahub [64] for the small clusters up to Fe_6 . Like Castro [49], we also find the distorted pentagonal bipyramid for Fe_7 . Comparison of the results for larger cluster sizes is difficult because no similar calculations based on GGA exist. Nevertheless, our calculations seem to show that the metallic-like bonding in the iron clusters with the appearance of degenerate states at the Fermi level causes Jahn-Teller distortions for the larger clusters as well.

The resulting magnetic moments per atom are shown in Fig. 3, together with the results of former calculations from Fig. 1. We note that our results are consistent with most of the former GGA calculations, with two exceptions. Lower values were obtained by Castro *et al.* [49] for Fe_3 and Fe_4 , but this has already been explained to

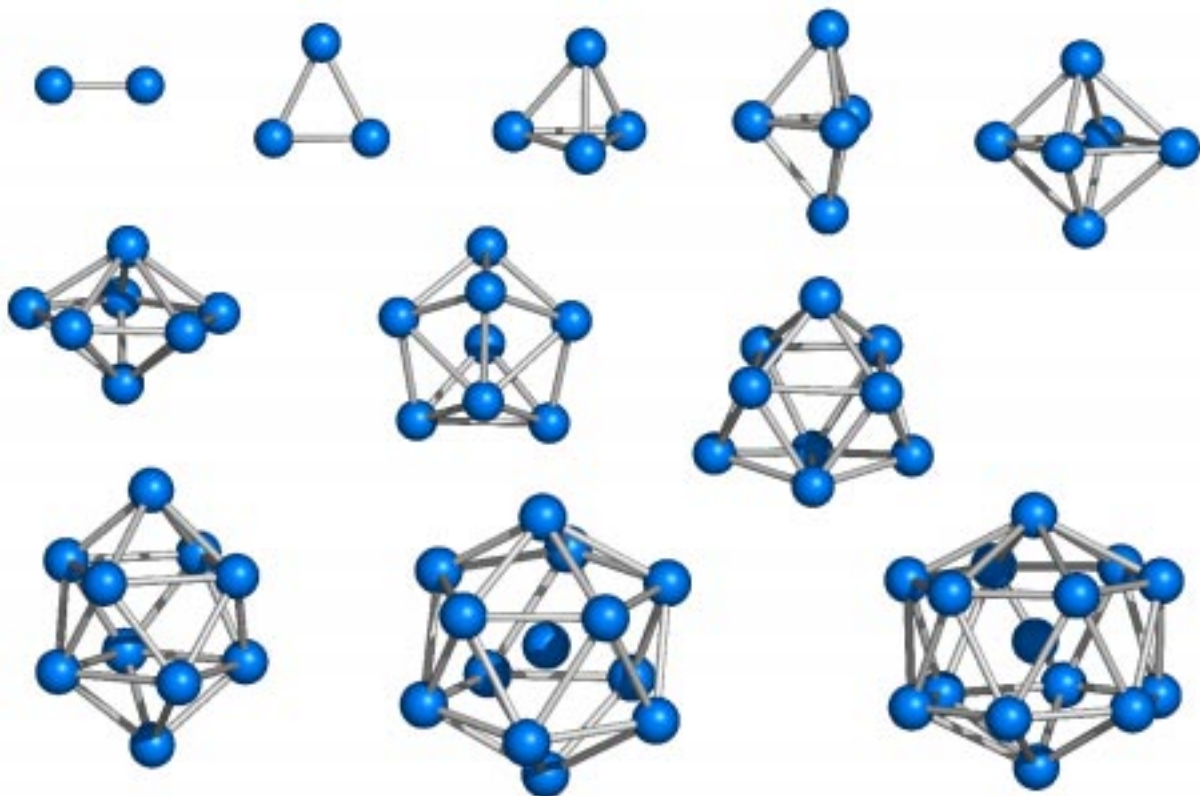


Fig. 2: Ground state geometries of Fe clusters containing between 2 and 15 atoms as obtained from our DFT/GGA calculations. All structures exhibit some degree of distortion from the regular shape.

be due to certain limitations in the calculational scheme [64]. The values of Šljivančanin *et al.* [69] are generally higher than our values. We interpret this to be due to the fact that these authors did not take into account complete relaxation of the atoms. We will take the intriguing scenario of symmetry and relaxation as well as non-collinear versus collinear magnetism in the Fe pentamer as an example to investigate the interrelation of atomic and magnetic degrees of freedom.

We have performed geometry optimization for the Fe₅ cluster in the framework of DFT in the GGA starting from different initial geometries. We have allowed for noncollinear arrangements of the magnetic moments and did not impose any symmetry constraints. The energetic relationships are shown schematically in Fig. 4. The high-symmetry structure (trigonal bipyramid) is energetically relatively unfavorable. The energy can be lowered by a canting of the magnetic moments of the apical atoms, as has been found earlier [50,57]. But a geometric, Jahn-Teller like

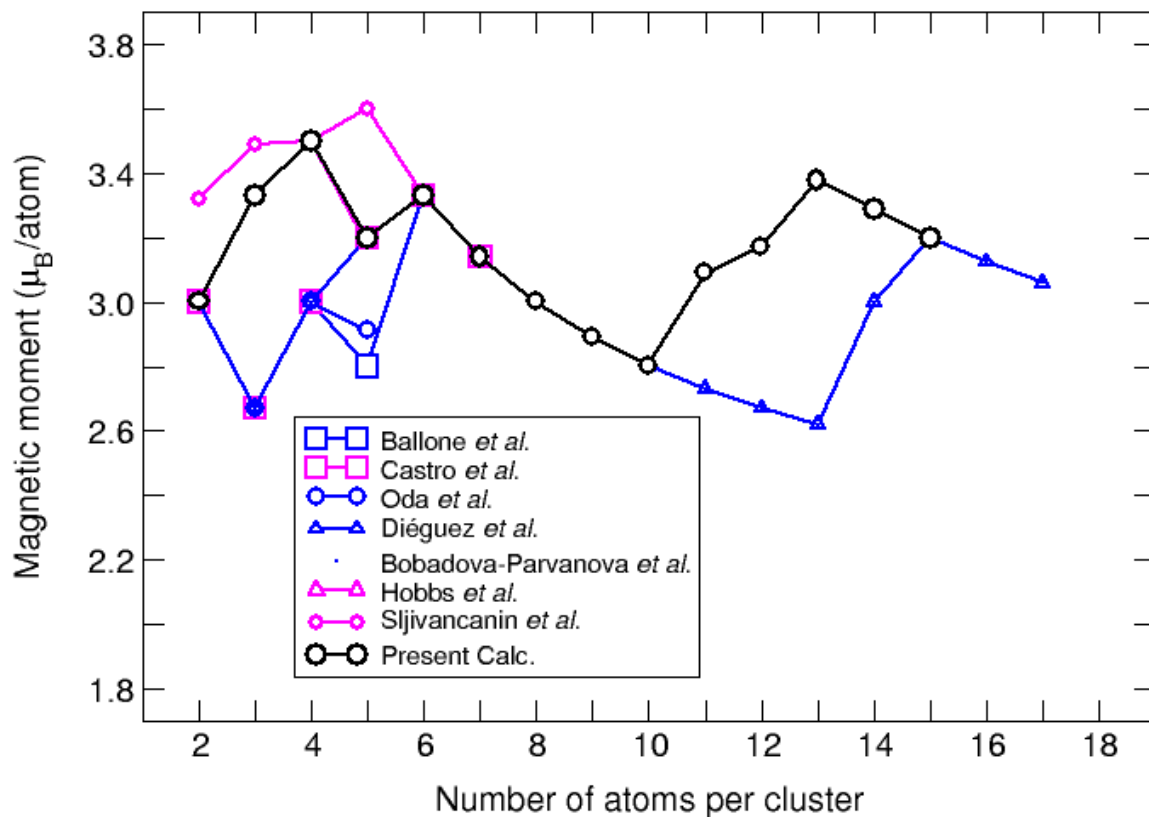


Fig. 3: Comparison of the magnetic moments obtained in the present calculation (black) with available data from other *ab initio* calculations (blue: LDA, magenta: GGA).

distortion to a lower symmetry reduces the total energy even more and results again in a perfect collinear spin structure. This example shows how subtle geometry and details of the spin arrangement interfere in the small iron clusters.

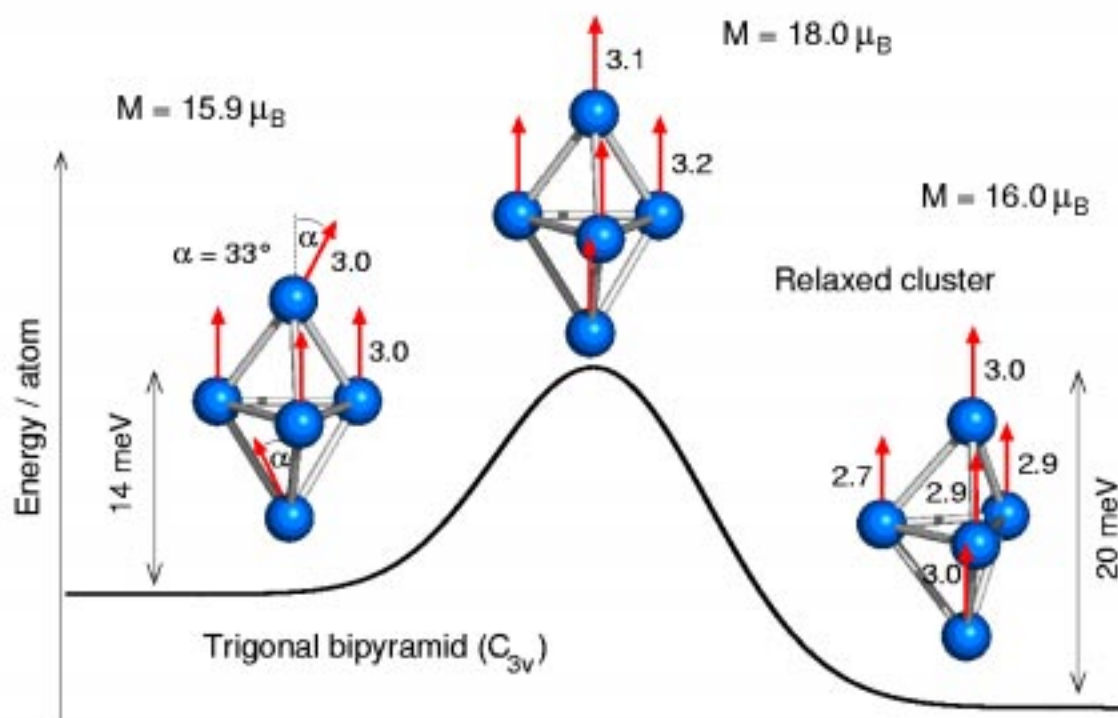


Fig. 4: Schematic sketch of the energetic and magnetic relationships between different local minima on the potential energy surface of the Fe_5 cluster. Magnetic moments are represented by red arrows, whose lengths correspond to the absolute values of the moments.

5. SUPPORTED FE CLUSTERS

In contrast to calculations regarding free clusters, only very few has been reported about small Fe clusters deposited on a supporting substrate. In a recent publication, Šljivančanin *et al.* have found from their *ab initio* calculations that, upon deposition, the magnetic moments of small clusters up to Fe_6 are very much reduced compared

to the values of the gas phase clusters [69]. In contrast to that, the geometrical structure of the clusters is nearly preserved. The authors explain this effect by intracluster charge rearrangements due to the interaction of Fe states with O $2p$ states from the MgO surface.

The calculations have been performed in the framework of DFT and the GGA. Therefore it is surprising that the magnetic moments of the free clusters found by the authors are much higher than in other, similar DFT calculations. As there is no direct information about the precise geometric structures of the unsupported clusters given, and because the authors point out that they took as starting geometries the final structures given by Diéguez *et al.* as a result of their LDA calculation [58], we assume that the observed effect is not so much related to the adsorption of the clusters on the substrate, but rather to an overestimation of the moments of the free clusters due to an insufficient relaxation process, as pointed out in Sec. 4. But to resolve this question, further calculations are required, possibly with revised functional forms for exchange and correlation.

From experimental side, the number of studies related to properties of supported clusters is increasing, due to advances in experimental techniques. By using XMCD, Lau *et al.* have recently obtained spin and orbital magnetic moments of small Fe clusters up to Fe₉ deposited on Ni/Cu(001) surfaces and were able to show that their ratio varies considerably with cluster size. This effect was explained by the presence of enhanced orbital moments in the clusters.

6. CONCLUSION

We have given an overview about structural and magnetic properties of Fe clusters as found in experiments and calculations based on first-principles methods. We have found that corresponding results obtained in the literature are not consistent and seem to depend strongly on the details of the simulation method, e.g., on the form of the exchange correlation functional employed in DFT calculations. We have also shown that in order to obtain reliable values for magnetic moments of the clusters, it is important to take into account relaxation of the atoms. Ground state geometries of small Fe clusters were found to be distorted and characterized by a collinear, FM arrangement of the spin moments. To obtain a detailed picture of the dependence of

magnetic moments on cluster size, and in order to reach the experimentally accessible size regime, further calculations are required.

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