

Theoretical study of the structure and binding of iron clusters: Fe_n ($n \leq 5$)

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The structural and electronic properties of iron clusters Fe_n ($n \leq 5$) are studied using a Gaussian orbital local (nonlocal) spin-density method. Starting from $n=2$ and 3 with localized multiple d bonds and short equilibrium bond lengths, $R_e \approx 2 \text{ \AA}$, the bonding evolves towards a metallic s pattern with longer R_e 's and higher atomic magnetic moments. Ferromagnetic ground states are highly favored with the gain in magnetic energy promoting the close-packed structure (for $n=3-4$) or distortions into more open structures (for $n=5$).

Transition-metal (TM) cluster properties of ferromagnetic elements present a challenge to state-of-the-art experimental and theoretical techniques. For example, recent beam experiments have found a complex magnetic behavior of size-selected iron and cobalt clusters,^{1,2} not anticipated previously.³ The clusters deflect toward increasing magnetic field with effective magnetic moments μ_{eff} per atom far below the bulk moments. This was identified as superparamagnetism by Khanna and Linderth,⁴ where each cluster has a large magnetic moment, equal to the ferromagnetic alignment $n\mu$ of the n atomic moments in the cluster. With this model and with the cluster temperature-dependent results of Bucher, Douglas, and Bloomfield,² it was found that the true moment μ of small Co_n clusters, of $2.08\mu_B$, is indeed enhanced (by about 20%) over the bulk value⁴ whereas for Fe_n a lower bound of $2.2\mu_B$ (Ref. 4) for the true μ was established. As a measure of the binding of these highly polarized valence electrons, the ionization potentials (IP's) of Fe_n ($n \leq 25$), determined by Rohlfiing *et al.*,⁵ start to decrease nonmonotonically from the atomic IP toward the bulk work function as n increases. Lastly, the collision-induced dissociation of Fe_n^+ ($n=2-19$) has been studied.⁶ In this way, and using the known adiabatic IP's,⁵ were determined the bond dissociation energies (BDE's) of ionic and neutral iron clusters. The trends exhibited by these size-dependent properties imply complicated electronic structures, unique, nonbulklike, in which the spin-polarization effects may play an important role⁵ and indicate a nontrivial evolution from insulating (more localized electrons) to metallic behavior (more itinerant electrons).

Cluster properties may also depend sensitively on the geometry. But experimental bond lengths (R_e) and bond angles for TM clusters are scarce.⁷

On the theoretical side, it is only very recently that modern techniques have proven their ability to determine the lowest-energy structures of relatively large clusters. Particularly, s and sp valence electron systems have been well studied.⁸ Due to the complexity of the TM atomic forces, which arise from the complex TM-TM exchange-correlation interactions, calculations on TM clusters commonly are done with the constraints of *frozen* bond

lengths and/or bond angles, usually equal to the bulk values.⁹

Density-functional-theory- (DFT) based methods, developed only recently,¹¹ have proven their ability to handle structural relaxation in TM clusters. Using the local spin-density approximation (LSDA) of DFT, Chen *et al.*¹⁰ have determined the structural and magnetic properties of neutral Fe_n , $n \leq 4$. However, the LSDA substantially overestimates the BDE's and D_e 's of TM clusters.

Here we report the results of all-electron calculations, using DFT local and nonlocal exchange-correlation potentials, for neutral (Fe_n) and charged (Fe_n^+) iron clusters up to $n=5$. We demonstrate the power of these methods for the analysis of the binding of electrons and atoms and of the bond strengths within the cluster (IP's, D_e 's, and BDE's).

We have used the code deMon:¹¹ a linear combination of Gaussian-type orbitals DFT-based method. The LSDA was included as in Vosko, Wilk, and Nusair¹² while the nonlocal spin density (abbreviated here simply as NL, for "nonlocal") gradient-type corrections were those of Perdew and Wang for exchange,¹³ and Perdew for correlation.¹⁴ For each Fe atom the $3d^7 4s^1$ orbital basis set of Ref. 15 was used.

Without imposed symmetry constraints, and by means of the Broyden-Fletcher-Goldfarb-Shanno algorithm,¹⁶ the geometries were optimized by minimizing the norm of the gradient, 10^{-4} a.u. threshold. All R_e 's and bond angles were simultaneously refined. Several candidates were tried in each case so as to locate different minima on the potential energy surface. Mulliken analyses were done to obtain the atomic charges, per spin.

The ground states (structures $2a$, $3a$, $4a$, and $5a$ in Fig. 1) of Fe_n ($n \leq 5$) are ferromagnetic, with a high number of nearest-neighbor bonds (NNB) and with average magnetic moments μ enhanced over the bulk value, $2.2\mu_B$, by 22–45%. (Though convergence difficulties were found, due to near degeneracy at the Fermi level, all clusters were converged to integral spin-orbital occupation numbers; see Ref. 11 for more computational details.) Additionally, for a given cluster (for example, $5a$) there is an uneven distribution of atomic moments, which depends

ized, mainly between these sites. The change in R_{12} indicates an antibonding behavior of E_F in Fe_5 . Our IP values mimic the experimental pattern and are nearer to this than the ΔSCF ones. The biggest discrepancy is for Fe_2 ; here the NL IP is ≈ 0.7 eV higher, while the ΔSCF one is ≈ 1 eV lower. For Fe_5 , DFT and ΔSCF overestimate, by 0.57 and 0.45 eV. For $n=3$ and 4, our agreement with experiment is excellent. The ΔSCF calculations⁹ revealed d -like E_F for $n=2-5$. We have found E_F 's of d -type for $n=2,3$ and of s -type for $n=4,5$. The changes in the electronic structure, from the unoptimized to the fully relaxed (structural and electronic) geometries, with the most noticeable ones in the compositions of the Fermi levels, stress the importance of geometry optimization on iron cluster properties. Even in this small range, $n \leq 5$, theory and experiment show an overall decrease of the IP's, as needed to converge towards the bulk work function.

The calculated BDE's for Fe_n and Fe_n^+ are shown on Fig. 3. We have used $\text{Fe}_n(\text{Fe}_n^+) \rightarrow \text{Fe}_{n-1}(\text{Fe}_{n-1}^+) + \text{Fe}$,

TABLE I. Molecular parameters D_e , R_e , and ω_e of Fe_n ($n \leq 5$) clusters in their calculated ground states.

	Fe_2	Fe_3	Fe_4	Fe_5
	D_e (eV)			
LSDA ^a	4.38	8.26	13.08	17.93
LSDA ^b	4.05	7.81	12.29	
NL ^c	3.24	5.99	9.83	13.89
NL-NS ^d	2.08	4.23	7.48	10.98
CI ^e	-1.29			
Expt.	1.14, ^f 1.30 ^g			
	R_e (Å)			
LSDA	1.96	2.10	2.22	2.22-2.32 ^h
LSDA ^b	1.98	2.04	2.25	
NL	2.00	2.10	2.22	2.23-2.31 ^h
CI ^e	2.02			
Expt.	1.87, ⁱ 2.02 ^j			
	ω_e (cm^{-1})			
LSDA	497			
LSDA ^b	418			
NL	474			
CI ^e	448.5			
Expt. ^k	299.6			

^aLocal spin-density results for the structures 2a, 3a, 4a, and 5a of Fig. 1; with respect to spherical 5D Fe atoms.

^bLocal spin-density results from Ref. 10.

^cNonlocal spin-density results with respect to spherical 5D Fe atoms.

^dNonlocal spin-density results with respect to nonspherical (NS) 5D Fe atoms.

^eCI results from Ref. 19, the D_e value is with respect to 5D Fe atoms.

^fFrom Ref. 6.

^gFrom Ref. 21(a).

^hOnly the range of the shortest distances is indicated, see Fig. 1.

ⁱFrom Ref. 18.

^jFrom Ref. 17.

^kFrom Ref. 21(b).

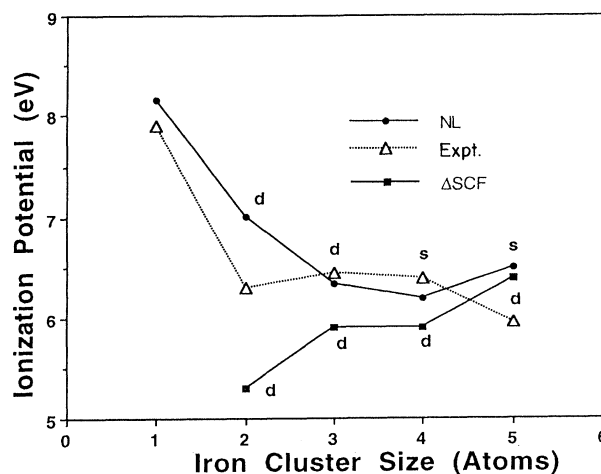


FIG. 2. Adiabatic NL ionization potentials of Fe_n ($n \leq 5$) (solid circles) along with the experimental values from Ref. 5 (open triangles) and with the ΔSCF *ab initio* results (solid squares) for unoptimized geometries from Ref. 9. The orbital type of the Fermi level is indicated.

in all cases, and employed NL total energies for the fully relaxed Fe_n , Fe_{n-1} , Fe_n^+ , and Fe_{n-1}^+ , and for the non-spherical Fe atom. Our results reproduce the main trends of neutrals and cations.⁶ We believe that a significant part of the discrepancy may be traced to the errors in describing the iron atom discussed above.

For Fe_2 our errors are of 0.78 and of 0.94 eV when compared with the observed values, 1.30 (Ref. 21) and 1.14 eV.⁶ From Fe_2 to Fe_3 our increase is of 0.08, while experimentally⁶ it is of 0.68 eV; this gives an error of 0.34 eV for the BDE of Fe_3 . From Fe_3 to Fe_4 our increase is of 1.1 eV, and this is the biggest (this may be explained and in fact is expected due to the 2D \rightarrow 3D transition,

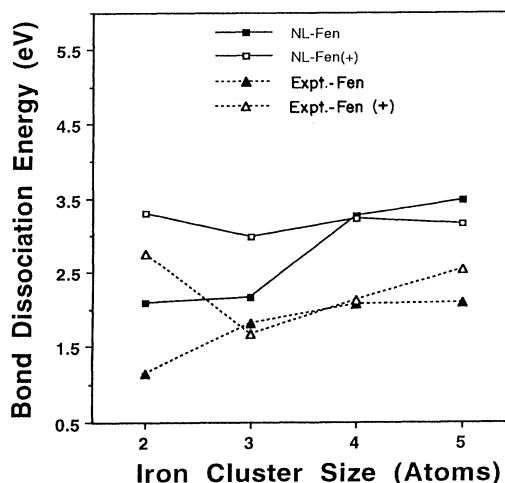


FIG. 3. The NL bond dissociation energies for neutral atoms, Fe_n (solid squares), and cations, Fe_n^+ (open squares), up to $n=5$. Also shown are the experimental results for neutrals (solid triangles) and cations (open triangles) from Ref. 6.

which produces a saturation in the number of NNB); however Lian, Su, and Armentrout⁶ have found an increase of only 0.24 eV. From Fe₄ to Fe₅, our increase is of 0.22 eV, that of Lian, Su, and Armentrout is 0.02 eV.⁶ Summarizing for Fe_n: the BDE's increase with increasing *n*. While the calculations show a big jump from *n*=3 to *n*=4, the experimental values, which are kinetically controlled, show this jump from *n*=2 to *n*=3. Thermodynamic determinations of this property would be of clear interest.

Experiment and theory agree that Fe₂⁺ is much more stable than Fe₂. In Fe₂ the *d* electrons are piled up in the internuclear region, due to the multiple *d*-bond formation, whereas the 4*s*σ_g MO is pushed out from that region as if it were antibonding.¹⁹ In Fe₂⁺, the suppression of the *d*δ⁺ electron restores 4*s*σ_g into the bonding region: there is an increase of the 3*dz*² electrons (along the molecular *z* axis) in 4*s*σ which indicates a *d*-bonding enhancement in Fe₂⁺. This σ bond is stronger than the π or δ bonds.

Fe₃⁺ is 0.82 eV more stable than Fe₃. After correcting by the underestimation in the total energy of Fe₂⁺ as inferred from the overestimation in the IP of Fe₂ (through Fe₃⁺ → Fe₂⁺ + Fe), it is found that Fe₃⁺ is 0.08 eV more stable than Fe₃. Experimentally this is reversed by 0.15 eV.⁶ But there is agreement in that Fe₂⁺ (Fe₃) is more stable than Fe₃⁺ (Fe₂). Fe₂ and Fe₃ have similar electronic structures; also in Fe₃⁺ there is an increase of *d* electrons. In Fe₂, Fe₂⁺, Fe₃, and Fe₃⁺, there are similar bonding schemes, mainly of *d*-type. This is also implied by the sharp photoionization thresholds.^{5,6}

There is agreement that Fe₄⁺ is as stable as Fe₄, see Fig. 3. In Fe₄, structure 4*a*, the E_F is *s*-like, highly delocalized throughout the cluster, showing typical nonlocalized weak metallic bonding. We expect similar electronic structures for *n* > 5, where there is little difference in the BDE's of Fe_n and Fe_n⁺.⁶

Fe₅⁺ is 0.32 eV less stable than Fe₅. After correcting by the total energy of Fe₅⁺ (as above for Fe₃⁺), Fe₅⁺ is 0.25 eV more stable than Fe₅. This is also so experimentally, by 0.45 eV.⁶ In Fe₅, E_F is *s*-like. But this MO instead of being delocalized, is localized on sites 1 and 2 of 5*a*. This, and the distortions from the most compact geometry of Fe₅, are two of the main features which account for the lack of equal BDE's for Fe₅ and Fe₅⁺.

In conclusion, the Gaussian DFT code deMon has allowed an unprecedented level of analysis of the properties of small TM clusters. The main features of the observed trends (*μ*'s, IP's, D_e's, and BDE's) have been accounted for and insight has been achieved as to how the structural, electronic, and magnetic parameters are involved in the stability of these clusters. The two forces, chemical and magnetic, drive the iron clusters towards ferromagnetic ground states with a maximization in the chemical bond formation.

These computations, though demanding, have all been done on general use Silicon Graphics 4D/280 and FPS 511 servers, over the last year. Extensions into the 10–15 TM-atom size range, fully optimized, should be feasible. This will open possibilities for the study of far more interesting models for reactions involving TM's than has heretofore been possible.

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