VOLUME 47, NUMBER 16

15 APRIL 1993-II

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

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(Received 11 November 1992)

The structural and electronic properties of iron clusters Fe_n $(n \le 5)$ 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, $R_e \simeq 2$ Å, 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 $\mu_{\rm eff}$ per atom far below the bulk moments. This was identified as superparamagnetism by Khanna and Linderoth,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 $(n \le 25)$, determined by Rohlfing 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 exchangecorrelation 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 $3d^74s^1$ 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 $(n \le 5)$ 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

10 956



FIG. 1. The lowest-energy structures of Fe_n $(n \le 5)$. Ground states are 2a, 3a, 4a, and 5a for n=2, 3, 4, and 5, respectively. Also indicated are the LSDA and NL (values in parentheses) relative energy of the isomers (in eV/atom), the multiplicity 2S + 1, the spin per atom (in bohr magnetons), and the LSDA and NL (values in parentheses) equilibrium bond lengths.

on the chemical environment. In 2a-4a the R_e 's are much shorter than the shortest distance in the bulk, 2.48 Å, whereas in 5a there are various short values, close to that of 4a, along with R_e 's close to, but bigger than, 2.48 Å.

The LSDA R_e of Fe₂ is 1.96 Å. The NL R_e , 2.00 Å, is nearer to the value determined in the less polarizable neon matrix, 2.02 Å, ¹⁷ which should more closely resemble the R_e of Fe₂, than that measured in an argon host, 1.85 Å.¹⁸ The spin-polarized configuration of Fe₂, $\{1\sigma 1\pi^2 1\delta^2 2\sigma 1\delta^{*2} 1\pi^{*2} 1\sigma^*\}^{\dagger}\{1\sigma 1\pi^2 2\sigma 1\delta_{E_F}\}^{\downarrow}$, is consistent with a ⁷ Δ_u molecular state, places the Fermi level E_F at the minority $d\delta^{\downarrow}$ weakly bonding molecular orbital (MO), and indicates formally a double d and a single (from $2\sigma^{\uparrow\downarrow}$) s bond. Tomonari and Tatewaki¹⁹ have found a large d contribution to the bonding in the ⁷ Δ_u state of Fe₂.

LSDA indicates a C_{3v} geometry for Fe₃, with $R_e = 2.10$ Å and with a total spin S equal to 4. The linear combination of atomic orbitals-LSDA (Ref. 10) and the selfconsistent field (SCF)-X α -SW (Ref. 5) (where SW denotes scattered wave) calculations have found 3a with $R_e = 2.04$ (Ref. 10) and 2.00 Å, ⁵ and with S = 4. The farinfrared spectra suggest that Fe₃ is bent.²⁰ In fact, 3b is 2.16 eV higher.

For Fe₄, the three-dimensional (3D) structure 4*a* was found to be of lowest energy with $R_e = 2.22$ Å, S = 6, and

a high number of NNB. The 2D geometry 4b is higher than 4a, by 1.94 eV at NL and by 1.5 eV at LSDA, with shorter R_e , 2.03 Å (LSDA), a lower magnetization, S=4, and a lower number of NNB. Similarly, Chen *et al.*¹⁰ have found 4b (with $R_e = 2.05$ Å, S=4) 1.12 eV over 4a (with $R_e = 2.25$ Å, S=6).

For Fe₅, the distorted trigonal bipyramid 5*a* was found to be the one of lowest energy. This may be regarded as an attempt of the system to maximize the number of NNB. The trigonal bipyramid 5*b* is energetically quasidegenerate with 5*a*, at LSDA. After an NL relaxation 5*b* is 0.25 eV higher than 5*a*. The total spin of 5*b* is equal to 7, while its state with S=8 is 0.13 eV higher. Although the difference is small, this is the reverse order from that of 5*a* where the state with S=7 is 0.01 eV higher than the one with S=8.

The structure 5*a* is a Jahn-Teller distortion of the S=8 state of 5*b*, which has a degenerate electronic state (there is one electron in the twofold-degenerate *s*-like MO at the top of the majority-spin manifold), and is therefore unstable. The result is the stabilization of the higher spin state, S=8, in the more open structure 5*a*. This was the reverse for Fe₄ and Fe₃ where the stability of the compact structures was enhanced by the magnetic energy, as shown above and as pointed out previously.¹⁰

The D_e of Fe₂-Fe₅ at different levels of calculation are shown in Table I. Our results for LSDA are close to those of Chen et al. up to n=4 (Ref. 10) (the discrepancy, 0.2-0.3 eV/atom, may be due to a different configuration for the atom; it is not stated in Ref. 10 whether the experimental or the LSD ground state was chosen, or to differences in the computational details). Compared with the experimental D_e of Fe₂, 1.30 (Ref. 21) and 1.14 eV,⁶ LSDA overestimates this property by more than three times. The NL corrections improve substantially, $\simeq 1$ eV, the estimation of D_e . Further, removal of the constraint of a spherical atomic charge density²² produces a deeper atomic energy if a NL SCF calculation is done, which in turn improves the estimation of D_{e} . In this way, the D_e for Fe₂, 2.08 eV, is overestimated by about 0.7 eV. Configuration interaction (CI) techniques give $R_e = 2.02$ Å and $\omega = 448.5$ cm⁻¹, but Fe₂ is unbound with respect to ground-state iron atoms.¹⁹ The nonspherical NL treatment of the atom is the best one can currently do. Higher accuracy will require a better understanding of open-shell multiplets in terms of DFT.

The calculated NL adiabatic IP's for the Fe_n $(n \le 5)$ ground-state structures are shown in Fig. 2, together with the experimental⁵ and the symmetry-broken \triangle SCF *ab initio* results done for bulk fragments.⁹ The structural relaxations were of +0.09, +0.05, and -0.002 Å for Fe₂⁺, Fe₃⁺, and Fe₄⁺, respectively. This means that for Fe₂ the $1\delta_{E_F}^{\downarrow}$ MO (from which the electron was ionized) is not as weakly bonding as expected; it behaves as a bonding orbital whereas in Fe₃ and in Fe₄ the electrons at E_F behave as weakly bonding or as nonbonding. In Fe₃ a d^{\downarrow} electron was ionized while in Fe₄ a delocalized s^{\uparrow} electron was removed. In Fe₅⁺ the relaxations range from +0.002 to +0.076 Å except for one of -0.116 Å, between sites 1 and 2 of 5a. Here, an s^{\uparrow} electron was ion-

9

ized, mainly between these sites. The change in R_{12} indicates an antibonding behavior of E_F in Fe₅. Our IP values mimic the experimental pattern and are nearer to this than the Δ SCF ones. The biggest discrepancy is for Fe₂; here the NL IP is $\simeq 0.7$ eV higher, while the Δ SCF one is $\simeq 1$ eV lower. For Fe₅, DFT and Δ SCF overestimate, by 0.57 and 0.45 eV. For n=3 and 4, our agreement with experiment is excellent. The Δ SCF 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 $\operatorname{Fe}_n(\operatorname{Fe}_n^+) \rightarrow \operatorname{Fe}_{n-1}(\operatorname{Fe}_{n-1}^+) + \operatorname{Fe}_n$.

TABLE I. Molecular parameters D_e , R_e , and ω_e of Fe_n $(n \le 5)$ 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°	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	5		
		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
CIe	2.02			
Expt.	1.87, ⁱ 2.02 [.]	Ì		
		$\omega_e \ (\mathrm{cm}^{-1})$		
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.

[°]Nonlocal spin-density results with respect to spherical ${}^{5}D$ 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).

(eV) NL Ionization Potential Expt. ∆SCF 6 d d 5 3 4 5 2 0 1 Iron Cluster Size (Atoms)

FIG. 2. Adiabatic NL ionization potentials of Fe_n $(n \le 5)$ (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 Fe₂ 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 Fe₂ to Fe₃ 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 Fe₃. From Fe₃ to Fe₄ 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.

10 958

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=3to 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 Fe_2^+ 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 $4s\sigma_g$ MO is pushed out from that region as if it were antibonding.¹⁹ In Fe₂⁺, the suppression of the $d\delta^{\downarrow}$ electron restores $4s\sigma_g$ into the bonding region: there is an increase of the $3dz^2$ electrons (along the molecular *z* axis) in $4s\sigma$ which indicates a *d*-bonding enhancement in Fe₂⁺. This σ bond is stronger than the π or δ bonds.

 Fe_3^+ is 0.82 eV more stable than Fe_3 . After correcting by the underestimation in the total energy of Fe_2^+ as inferred from the overestimation in the IP of Fe_2 (through $Fe_3^+ \rightarrow Fe_2^+ + Fe$), it is found that Fe_3^+ is 0.08 eV more stable than Fe_3 . Experimentally this is reversed by 0.15 eV.⁶ But there is agreement in that Fe_2^+ (Fe₃) is more stable than Fe_3^+ (Fe₂). Fe_2 and Fe_3 have similar electronic structures; also in Fe_3^+ there is an increase of *d* electrons. In Fe_2 , Fe_2^+ , Fe_3 , and Fe_3^+ , there are similar bonding schemes, mainly of *d*-type. This is also implied by the sharp photoionization thresholds.^{5,6}

There is agreement that Fe_4^+ is as stable as Fe_4 , 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 Fe_5^+ is 0.32 eV less stable than Fe_5 . After correcting by the total energy of Fe_5^+ (as above for Fe_3^+), Fe_5^+ is 0.25 eV more stable than Fe_5 . This is also so experimentally, by 0.45 eV.⁶ In Fe_5 , 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 Fe_5 , are two of the main features which account for the lack of equal BDE's for Fe_5 and Fe_5^+ .

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.

Valuable discussions with Leif Goodwin and a critical reading of the manuscript by Dr. M. E. Casida are gratefully acknowledged. Support from NSERC and the Canadian Network of Centres of Excellence in Molecular and Interfacial Dynamics is gratefully acknowledged, as is the provision of computing resources by the Services Informatiques de l'Université de Montréal. M.C. acknowledges partial financial support from Dirección General de Asuntos del Personal Académico, Universidad Nacional Autónoma de México.

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