Electron Correlation Effects in the Fe Dimer

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The potential energy surface of the Fe dimer is investigated on the basis of density functional theory in the generalized gradient approximation (GGA). Electron correlation effects are taken into account explicitly within the GGA+U approach. We find a value of 2.20 eV for the Coulomb repulsion parameter U to describe the Fe dimer best, yielding a $^9\Sigma_g^-$ ground state with an interatomic separation of 2.143 Å. Agreement of the associated vibrational frequency, binding energy, ionization potential, and electron affinity with experimental data as well as corresponding results calculated within a high-level ab initio approach is improved significantly compared to conventional GGA. The effect of U on calculated geometric and magnetic properties of larger Fe clusters is discussed.

1. Introduction

Magnetic transition-metal (TM) clusters are an important ingredient for a range of applications. One example is ultrahigh-density magnetic storage devices, in which the logical bits are represented by single magnetic clusters arranged on a substrate by making use of their natural self-organization.[1] Due to rapid technological advances, miniaturization has now reached a point where the particles are so small that size effects start to play an important role in determining their properties. It has been revealed, for example, that the magnetic moments of free Fe, Co, and Ni clusters are not just given by a simple interpolation between the corresponding values of the isolated atom and the bulk, but show some oscillatory behavior with cluster size.[2] Clearly, to explain these phenomena, it is inevitable to understand how the electronic structure of the clusters, which in turn strongly depends on the spatial arrangement of the atoms, evolves with particle size.

Today, this can only be achieved with the help of first-principles calculations, because a detailed examination of many properties of isolated TM clusters is a task still beyond the reach of experiments. While small magnetic clusters and even single atoms deposited on supporting substrates have already been investigated experimentally with great success,[3] it is not trivial to eliminate the influence of the substrate and obtain the properties of the corresponding isolated clusters. As they are highly reactive and sensitive to their environment, it is difficult to produce beams of size-selected clusters of sufficient intensity to determine, e.g., their electronic and magnetic structures directly. In addition, determination of the geometries of small TM clusters in the gas phase is not yet feasible in experiments. As a consequence, in the case of iron, the bond length (r_e) has only been measured for the dimer trapped in solid argon[4] and neon[5] matrixes, using the extended X-ray absorption fine structure (EXAFS) technique. Harmonic vibrational frequencies (ω_e) have been obtained for Fe$_2$, Fe$_2^-$, and Fe$_3$.[7,8] In contrast to that, dissociation energies (D_e),[9] electron affinities (EA),[7,10] and ionization potentials (IP)[11,12] have been measured to good accuracy for iron clusters containing 19, 34, and 100 atoms.

Nevertheless, although a magnetic moment of 6.5 ± 1 μ_B has been derived in a Stern−Gerlach experiment,[13] the electronic ground state has not even been determined unambiguously yet for the smallest Fe cluster, the dimer.

On the other hand, starting with the work of Harris and Jones in 1979,[14] numerous first-principles computational studies on various structural, electronic, and magnetic properties of iron clusters have been conducted.[15−20] As a detailed account of the results obtained in these studies cannot be given here, we refer the reader to the most recent articles and references therein.[18−20] Most of these works are based on density functional theory (DFT) employing the local density approximation (LDA) or different kinds of the generalized gradient approximation (GGA) for the calculation of the exchange-correlation energy, E_{xc}. It turns out that, independent of the specific implementation of DFT and the details of the computational scheme, all these studies, including the early configuration interaction (CI) calculations,[16] find a $^7\Delta_u$ ground state with a magnetic moment of 6 μ_B and a formal electronic occupation of $3d^{14}4s^2$.

However, corresponding spectroscopic properties are in rather poor agreement with experimental data. When GGA functionals are used, ω_e of Fe$_2$ is calculated to be around 400 cm^{-1}, compared to 300 cm^{-1} in experiment.[6,7] Even worse, D_e is overestimated by more than a factor of 2 (or 3, within the LDA), and the IP and the EA are off by about 10% depending on the functional used for E_{xc} and other computational details. Also, recent high-level ab initio studies based on multireference configuration interaction (MRCI) and employing great computational effort give rise to the assumption that the physics obtained in conventional DFT/GGA calculations is not correct.[21,22] In these works, a $^9\Sigma_g^-$ state with a $3d^{13}4s^3$ occupation of the molecular orbitals and a spin moment of 8 μ_B is found lowest in energy, which corresponds to the state originally proposed by Leopold et al. as the only one to be able to explain the observed photoelectron spectrum.[23] While associated vibrational frequencies agree very well with experimentally (accurately) obtained values, the bond length of ∼2.19 Å turns out to be much larger than the values obtained in the EXAFS measurements.[4,5] In addition, the failure to observe Fe$_2$ in electron spin resonance (ESR) experiments[24] is difficult to explain on the basis of a $^9\Sigma_g^-$ ground state. Whether these

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discrepancies are due to experimental uncertainties (the difference in measured bond lengths of 1.87 and 2.02 Å depending of the rare-gas host matrix, e.g., seems to be rather high), or lie in the fact that the calculations were performed at the limit of the available computational capacities, and the results could not be fully converged with respect to basis set size and level of correlation (as the authors of ref 22 have pointed out), remains to be solved. Unfortunately, the MRCI method is computationally too demanding to be, in the near future, applied to Fe clusters containing more than a handful of atoms. Consequently, if one accepts the idea that a computational procedure suitable for the investigation of larger Fe (and other TM) clusters should at least be able to capture the physics for the smallest cluster, Fe_2, an improved calculational method, preferably at the cost of DFT, seems very desirable.

In this article we show that the discrepancies between experimentally derived values for spectroscopic properties of the Fe dimer as well as corresponding results calculated within a high-level ab initio approach on the one hand, and the outcome of DFT/GGA calculations on the other hand, can be traced back to an improper description of electronic correlation effects in the latter. This originates from the fact that the Coulomb repulsion of localized electrons in partly filled d or f shells is only treated in a mean-field-like manner in conventional LDA or GGA. One way to cure this deficiency is the so-called LDA+U method (or GGA+U, when gradient corrections are taken into account), where a Hubbard-like term for the on-site Coulomb repulsion of the localized electrons is incorporated into the density functional.[25-27] This method has been applied to bulk systems and surfaces where conventional LDA gives qualitatively wrong results, leading to considerable improvement in the description of many properties of, e.g., 3d-TM oxides.[27,28] We here report results of our calculations employing the GGA+U method for the investigation of a finite, molecular system, the Fe dimer.

In section 2 we describe the computational details and discuss briefly how the on-site Coulomb interaction parameter U is introduced in the framework of DFT. Results are presented and discussed in section 3, and concluding remarks can be found in section 4.

2. Computatonal Method

Numerical Details. The calculations were performed on the basis of spin-polarized DFT[29] in combination with periodic boundary conditions and a plane-wave basis set. Exchange and correlation were treated within the GGA proposed by Perdew, Burke, and Ernzerhof (PBE),[30] together with the spin interpolation of Vosko, Wilk, and Nusair.[31] The Kohn−Sham equations were solved via iterative matrix diagonalization based on the minimization of the norm of the residual vector to each eigenstate as implemented in the Vienna ab initio Simulation Package (VASP).[32] For each Fe atom, the 3d and 4s as well as the semi-core 3p electrons were treated as valence states. The remaining electrons together with the nuclei were described by the all-electron projector augmented wave (PAW) method proposed by Blöchl[33] and adapted by Kresse and Joubert.[34] The integration over the Brillouin zone was performed by using the Γ point only and a Gaussian smearing method with a half-width of 10 meV. To investigate different magnetic states, the difference in the numbers of electrons occupying the two spin channels was kept fixed at the desired value. A noncollinear magnetization density was not taken into account.

The systems were placed in cubic supercells of 15 Å length; calculated properties involving charged species were extrapo-

TABLE 1: Properties of Fe_2, Fe_2^-, and Fe_2^+ Obtained within Conventional GGA ($U = 1.00$ eV)

system	state	r_e (Å)	ω_e (cm^{-1})	D_e (eV)	ΔE^a (eV)
Fe_2	$^7\Delta_u$	2.005	414	2.59	0.00
	$^9\Sigma_g^-$	2.144	329	2.27	0.32
	expt	2.02^b	300^{c,d}	1.18^e	
Fe_2^-	$^8\Delta_g$	2.071	378		−0.99
	expt		250^d	1.93^{d,e}	−0.90^d
Fe_2^+	$^8\Delta_u$	2.125	319		6.74
	expt			2.78^e	6.30^f

^{a} Relative energy with respect to the $^7\Delta_u$ ground state of Fe_2. ^{b} Reference 5. ^{c} Reference 6. ^{d} Reference 7. ^{e} Reference 9. ^{f} Reference 11.

lated to infinitely large supercells. The one-electron Kohn−Sham wave functions and the charge density were expanded in a plane-wave basis set with an energy cutoff of 500 eV. All calculations were carried out without imposing any symmetry constraints.

The GGA+U Approach. To improve the description of the on-site Coulomb repulsion of localized d (or f) electrons in conventional LDA, a Hubbard Hamiltonian in the unrestricted Hartree−Fock approximation is combined with the density functional in the LDA+U method.[25,26] The Coulomb interaction is characterized by a spherically averaged Hubbard parameter U describing the energy required for adding an extra d electron to a TM atom, $U = E(d^{n+1}) + E(d^{n-1}) - 2E(d^n)$, and a parameter J representing the screened exchange integral. Within the approach of Dudarev et al.,[27] which we have adopted here, the total energy only depends on the difference $U - J$

$$E_{GGA+U} = E_{GGA} + [(U - J)/2]\sum_\sigma \text{Tr}[\rho^\sigma - \rho^\sigma \rho^\sigma]$$

where ρ^σ is the on-site density matrix of the d electrons. The correction term to the GGA energy can be regarded as a penalty function which drives the on-site occupancy matrix to idempotency. As a result, unoccupied d states are shifted by $(U - J)/2$ toward higher energies, while occupied d states are moved by the same amount to lower energies. As the value of J, which is an approximation of the Stoner exchange parameter, was kept constant at $J = 1$ eV in our calculations of the Fe dimer, the strength of the single parameter U becomes the decisive quantity. For $U = 1$ eV, the conventional GGA expression for the energy is recovered, as in this case $U - J = 0$ eV. We like to mention here that the strength of the effective Coulomb interaction U in metallic bulk iron (and other 3d metals) is a topic still under debate. Steiner et al. proposed values of 1−2 eV (with $J = 0.73$ eV) deduced from experimental data,[35] while a value of $U = 2.3$ eV was found semiempirically by Olés and Stollhoff.[36] However, recent studies of correlation effects in bulk iron suggest even larger values for U comparable to corresponding values in cobalt and nickel.[37,38] In contrast to that, Cococcioni calculated $U = 2.2$ eV with a slight dependence on lattice spacing by using a constraint-DFT approach.[39]

3. Results and Discussion

Results of GGA Calculations. Before discussing the influence of electronic correlation on the potential energy surface of the Fe dimer, we first review the situation for Fe_2 as found within conventional DFT/GGA by giving a brief summary of the main results obtained in our GGA calculations. In Table 1, equilibrium distances, harmonic vibrational frequencies, dissociation energies, and total energies are listed for the neutral, the anion Fe_2^-, and the cation Fe_2^+. We note that most of these

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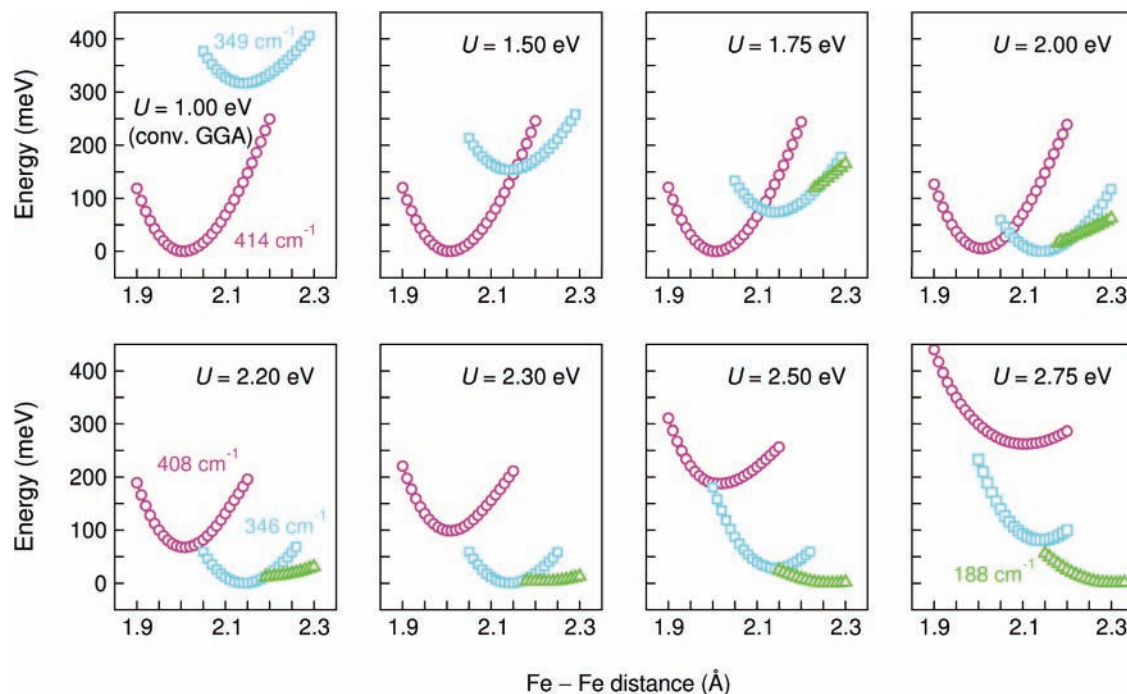
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Figure 1. Relative potential energy of the $^7\Delta_u$ (circles), $^9\Sigma_g^-$ (squares), and $^9\Delta_g$ (triangles) states of Fe_2 as a function of interatomic separation for different values of U. The curves were shifted so that $E = 0$ corresponds to the lowest energy state found for a specific value of U.

data are consistent with results of other DFT/GGA calculations. For the $^7\Delta_u$ state, e.g., Gutsev and Bauschlicher have calculated values of 2.011 Å and 397 cm^{-1} for r_e and ω_e, respectively, by employing a different GGA functional and Gaussian basis functions.[19] Chrétien and Salahub obtained corresponding values of 2.008 Å and 415 cm^{-1}.[18] For the other states, the deviations in r_e and ω_e are similar. While the same is true for the EA and IP of 0.99 and 6.74 eV, our calculated dissociation energy of 2.59 eV is considerably higher than the value of 2.18 eV obtained in ref 19.

However, the largest difference between the results presented here and those of other GGA calculations for Fe_2 concerns the energy difference ΔE between the $^7\Delta_u$ and the $^9\Sigma_g^-$ states. While values around 0.50 eV are commonly obtained by using GGA functionals and localized basis functions, we have calculated here a value of 0.32 eV. We attribute this to the use of plane waves in our study compared to Gaussian basis functions in the other works.[18,19] Small basis sets generally seem to overestimate ΔE, which can be explained by the fact that the molecular orbitals in $^9\Sigma_g^-$ are more extended and therefore need larger basis sets to be described satisfactorily. Gutsev and Bauschlicher have reported changes that occur when employing triple-ξ basis sets instead of 6-311+G*. Although they did not investigate the effect on ΔE, they find a slight increase in ω_e from 397 to 404 cm^{-1} for the $^7\Delta_u$ state, which reduces the difference from our value of 414 cm^{-1}. We therefore consider the values of ~0.50 eV for ΔE as obtained in various DFT/GGA calculations to be not converged with respect to the basis set.

Nevertheless, we find the same discrepancies compared to experimental values as reported in other DFT studies. Most strikingly, ω_e of Fe_2 and Fe_2^- is overestimated by 40% and 50%, respectively, compared to the values of 300 ± 15 and 250 ± 20 cm^{-1} obtained from photoemission data.[7] In addition, D_e of Fe_2 appears to be more than 1.4 eV too large with respect to the reference value of 1.18 eV, which was deduced from collision-induced dissociation of Fe_2^+ in combination with experimental values for the IP of Fe_2 and the Fe atom.[9] The errors in EA and IP are somewhat smaller, but still amount to

about 10%. Only the bond length agrees well with the experimental value of 2.02 Å for Fe_2 trapped in solid Ne.[5] However, although this value is generally accepted to be more reliable than the value of 1.87 Å[4] due to the smaller polarizability of the neon matrix compared to argon, the large difference between both values may be a sign that also the former value is not the true equilibrium distance of the Fe dimer. This idea is supported by results of a study performed by Jules and Lombardi.[40] Based on experimental force constants obtained from measured vibrational frequencies, they calculated values around 2.10 Å for r_e of Fe_2 by employing several empirical rules. In addition, Leopold et al. suggested a $^9\Sigma_g^-$ ground state for Fe_2 based on their photoemission spectrum.[23] This is supported by results of MRCI calculations[21,22] and raises the question of how well conventional DFT in the GGA is suited for the investigation of the Fe dimer (and possibly larger Fe clusters as well). In the next part, we discuss the effect of an explicit consideration of Coulomb repulsion as described above.

Results of GGA+U Calculations. In Figure 1 the potential energy of several states of the Fe dimer is displayed as a function of interatomic separation for different values of the Hubbard parameter U. The case $U = 1.00$ eV corresponds to conventional GGA and has been discussed in the previous section. We note that, with increasing U, the $^9\Sigma_g^-$ state with an equilibrium distance of 2.143 Å and a vibrational frequency of 346 cm^{-1} is energetically favored compared to the $^7\Delta_u$ state, and eventually becomes the ground state for $U \geq 2.00$ eV. When U is increased further, another state appears for large distances, which is identified as $^9\Delta_g$ and could not be stabilized for $U = 1.00$ eV. This state becomes lowest in energy for $U \geq 2.40$ eV. However, corresponding values for r_e and ω_e of 2.273 Å and 188 cm^{-1} obtained for $U = 2.75$ eV are way off experimental values.

To illustrate the effect of electronic correlation in terms of U, we have depicted the Kohn–Sham eigenvalues of the $^7\Delta_u$ and the $^9\Sigma_g^-$ states of Fe_2 as calculated within conventional GGA and by using $U = 2.20$ eV in Figure 2. The highest occupied level in the $^7\Delta_u$ state, which has a formal electronic occupation of $3d^{14}4s^2$, is a $3d\delta_g$ minority-spin orbital. The
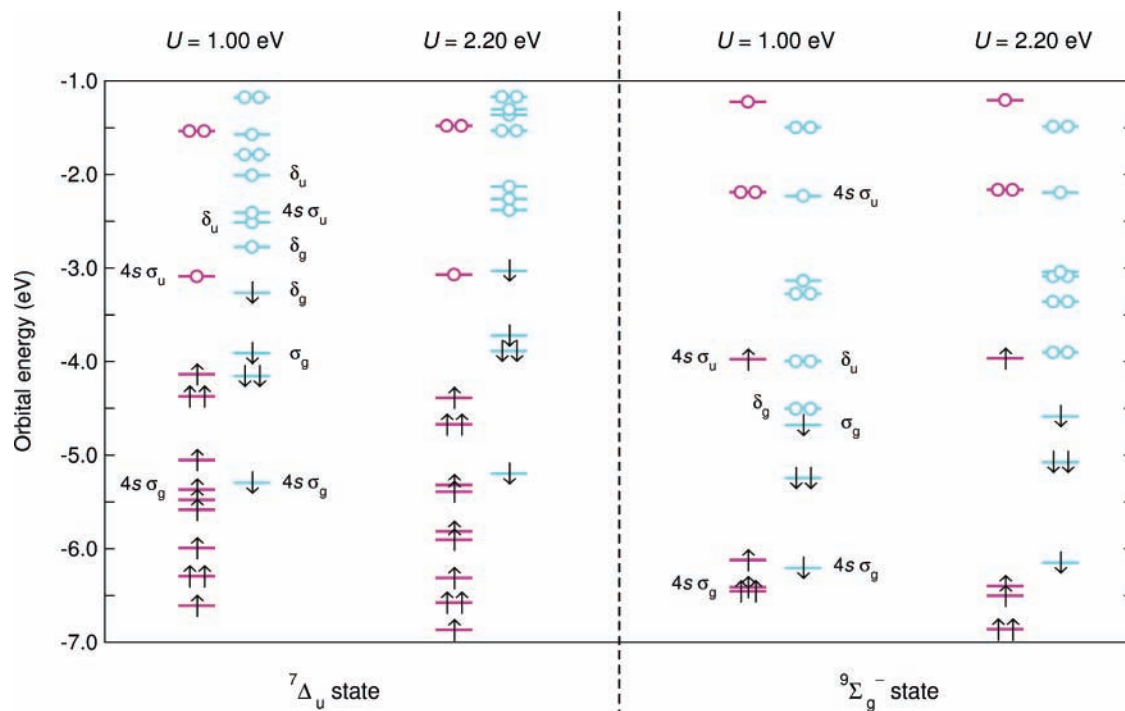
Figure 2. Kohn−Sham eigenvalues (horizontal bars) of selected states of the Fe dimer for $U = 1.00$ eV (conventional GGA) and $U = 2.20$ eV. Arrows represent electrons (of either spin), and circles denote unoccupied levels.

antibonding $4s\sigma_u$ majority-spin orbital is not occupied, which leads to a formal $4s-4s$ bond order of 1. We find that considering Coulomb repulsion explicitly has a profound influence on the electronic spectrum. Resulting from the shift of the one-electron eigenvalues, the $4s\sigma_u$ and the $3d\delta_g$ levels are nearly degenerate for $U = 2.20$ eV. As a consequence, the low-moment (6 μ_B) $^7\Delta_u$ state becomes unstable when U is increased further.

Occupation of the $4s\sigma_u$ orbital instead of the $3d\delta_g$ level yields the $^9\Sigma_g^-$ state, which is unstable within conventional GGA, as four unoccupied minority-spin 3d states are lower in energy than the occupied 4s orbital. However, with increasing U these levels are shifted toward higher energies, so that the high-moment (8 μ_B) $^9\Sigma_g^-$ state becomes the ground state for $U \geq$ 2.00 eV. The formal occupation of $3d^{13}4s^3$ is characterized by a $4s-4s$ bond order of only 1/2, leading to smaller vibrational frequency and dissociation energy compared to the $^7\Delta_u$ state.

From analogous investigations for Fe_2^- and Fe_2^+, spectroscopic properties of the Fe dimer and their dependence on the size of the parameter U were derived. Results for D_e, IP, and EA calculated with respect to the $^7\Delta_u$, $^9\Sigma_g^-$, and $^9\Delta_g$ states are shown in Figure 3. Solid lines and filled symbols mark regions where the corresponding state is the ground state. It is observed that all curves exhibit more or less linear behavior, which is expected from the linear way by which the parameter U enters the calculations. The kinks occurring at some points are due to state-crossing events. The ground state of Fe_2^+, e.g., is of $^8\Delta_u$ symmetry for $U \leq 2.00$ eV. For larger values of U, however, we obtain a state with longer bond length lowest in energy, which probably corresponds to the $^8\Delta_g$ state reported by Gutsev and Bauschlicher.[19]

For discussion, we first consider the range between $U = 1.00$ eV and $U = 2.00$ eV, where the $^7\Delta_u$ state is the ground state of Fe_2. With respect to D_e and IP, the remarkable discrepancies between the values calculated within conventional GGA and the experimental data are reduced with increasing U, while we observe a slight increase in the error of EA. For $U = 2.00$ eV,
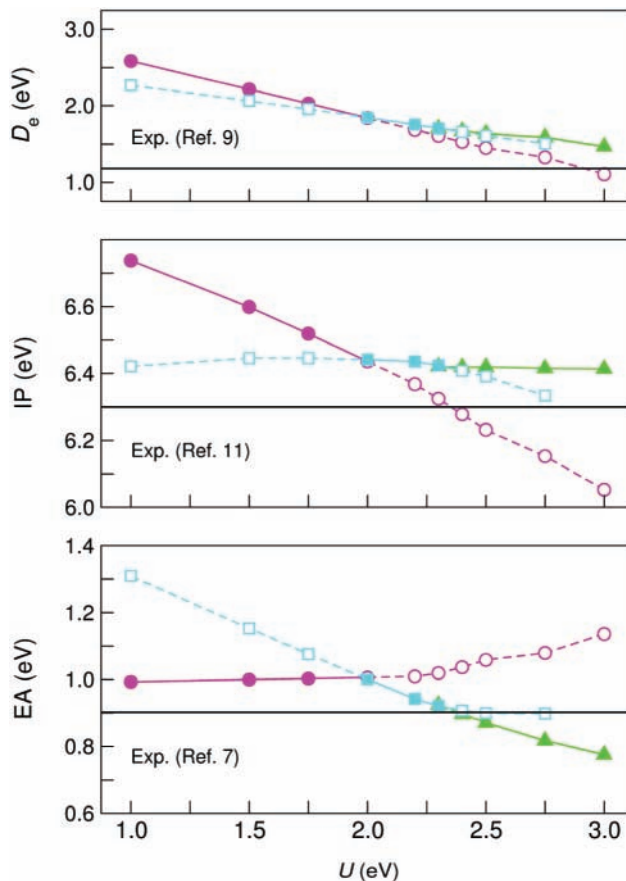

Figure 3. Dependence of D_e, IP, and EA on the size of the Hubbard parameter U. The different curves refer to different states of neutral Fe_2: $^7\Delta_u$ (circles), $^9\Sigma_g^-$ (squares), and $^9\Delta_g$ (triangles). Where lines are solid, the corresponding state is the ground state.

the errors amount to 0.66 eV for D_e, 0.14 eV for IP, and 0.10 eV for EA. These errors could be decreased further with increasing U. For instance, the IP of the $^7\Delta_u$ state reaches the

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TABLE 2: Absolute Values and Their Deviation from Experimental Data[a] for Various Properties of the Fe Dimer Calculated within Conventional GGA and by Using $U = 2.20$ eV

U (eV)	state	r_e (Å)	ω_e (cm^{-1})	D_e (eV)	IP (eV)	EA (eV)
1.00	$^7\Delta_u$	2.005	414	2.59	6.74	0.99
		−0.7%	+38.0%	+119.5%	+7.0%	+10.1%
2.20	$^9\Sigma_g^-$	2.143	346	1.75	6.44	0.94
		+6.1%	+15.3%	+48.3%	+2.2%	+4.4%

[a] For the experimental values, see Table 1.

experimental value of 6.30 eV for $U = 2.35$ eV. However, in this region the low-moment state is no longer the ground state.

Consequently, when U is increased further, a high-moment state has to be taken as reference. In doing so, we find that the EA of the $^9\Sigma_g^-$ state is a decreasing function of U. At the same time, D_e and IP stay rather constant. Keeping in mind that the $^9\Delta_g$ state with the large equilibrium distance and very low vibrational frequency is unlikely to be physically important in competing for the ground state of Fe$_2$, we arrive at errors of 0.57 eV for D_e, 0.14 eV for IP, and 0.04 eV for EA for $U = 2.20$ eV, where the $^9\Sigma_g^-$ state is lowest in energy for the neutral.

A summary of the results obtained by employing this value of U, which we consider to describe the Fe dimer best, as well as their deviation from experimental data, is given in Table 2, together with corresponding values calculated within GGA. We find that the properties of the Fe dimer calculated with $U = 2.20$ eV not only are in better general agreement with experimental findings compared to the case of conventional GGA, but also are consistent with the results of the MRCI calculations of Hübner and Sauer[21] and Bauschlicher and Ricca.[22] However, as no absolute convergence with respect to the size of the basis set and the level of correlation was achieved in these high-level ab initio studies, a direct comparison to our results should only be made with caution. When we relate our findings to other studies of electronic correlation in Fe-containing systems, we observe that we find practically the same value for U as was suggested previously for bulk iron.[36]

4. Conclusions

We have shown that explicit consideration of on-site Coulomb repulsion within the GGA+U method has a strong effect on the potential energy surface of the Fe dimer. For $U \geq 2.00$ eV, the $^9\Sigma_g^-$ state, which is located 0.32 eV above the $^7\Delta_u$ state in conventional GGA, becomes the ground state. The best agreement of corresponding spectroscopic properties with experiment and with high-level MRCI calculations is obtained for $U = 2.20$ eV. The deviations of ω_e, D_e, EA, and IP from experimental data are reduced significantly. On the basis of these results, we find that it is essential to go beyond conventional DFT/GGA and also take into account electronic correlation explicitly when investigating larger Fe clusters. Preliminary calculations have revealed that this leads, in many cases, to an enhancement of the ground-state spin magnetic moments by 2 μ_B, resulting in maximal moments of 4 μ_B per atom up to Fe$_4$. Another effect of the shift of the one-electron eigenvalues is related to cluster geometries. As the degeneracy of the electronic ground state of very symmetric isomers is often lifted within GGA+U, corresponding Jahn−Teller distortions found frequently within conventional DFT/GGA then vanish, leading to more symmetric geometries of the lowest energy isomers of Fe$_n$.

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