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Electronic States of NiFe. An *ab initio* HF-CI Study

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Ab initio Hartree–Fock and configuration interaction methods have been employed in describing the interaction between a Ni and an Fe atom. The chemical bond between the atoms is due to a $4s\sigma$ molecular orbital. The $3d$ orbitals merely cause small splittings between the potential energy curves. Equilibrium distance, dissociation energy and vibrational frequency are predicted for the ground state of the molecule.

Key words: NiFe molecule – Electronic states.

1. Introduction

The present work can be considered as part of the investigations carried out during recent years to elucidate chemical and physical properties of molecules composed of transition metal atoms [1]. Furthermore, it is a continuation of our previous work in which we determined the electronic structure of the Ni_2 [2] and the NiCu [3] molecules.

The major reasons for the great interest in these small molecules are due to the important role the molecules play as model systems in catalytic as well as chemisorptive processes.

However, our interest in the diatomic molecules composed of transition metal atoms is also connected to the fact that these molecules form building stones of metals and alloys. Through our investigations of the diatomic molecules, we hope to reach a deeper understanding of metals and alloys especially with respect to their magnetic properties.

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In the present work we have investigated the interaction between a Ni atom and an Fe atom using *ab initio* calculations.

The calculations have been carried out in the Hartree–Fock–Roothaan formalism [4] followed by limited configuration interaction (CI) treatments. The integrals were computed using the program MOLECULE [5]. The ALCHEMY [6] program system was utilized for the Hartree–Fock (HF) calculations, and finally the CI calculations were performed using ALCHEMY in conjunction with a new program for generating energy expressions [7].

2. Basis Sets and Atomic Calculations

As in our previous work, we have employed basis sets consisting of contracted Gaussian type functions (14*s*, 11*p*, 5*d*/8*s*, 6*p*, 3*d*). The basis set for the Ni atom was identical to the basis utilized in Ref. [2], and we have chosen a corresponding basis for the Fe atom.

The basis set used for the Fe atom was a modified version of the basis determined by Wachters [8] for the $^5D(3d)^6(4s)^2$ term of the Fe atom. Relative to Wachters' basis, ours was extended by the addition of two *p* functions with exponents 0.23 and 0.09, respectively. Furthermore, the exponents of the most diffuse *s* functions were altered from 0.114220 and 0.041889 to 0.26 and 0.08.

With these alterations it is possible to represent a 4*p* orbital, and altogether they provide a better description of the valence region of the molecule. We are, of course, aware of the basis sets published recently [9] which result in improved relative energies of terms originating from different electronic configurations of the atoms. However, even at the Hartree–Fock limit, the splittings between these terms are not in agreement with experiment [9]. We have chosen therefore to use basis sets corresponding to those used in our previous work in order to get results of comparable quality.

In Table 1 we have listed relative energies of the lowest lying terms resulting from different electronic configurations for both the Fe and the Ni atoms. It is noted that for both atoms the discrepancies between the experimental and the calculated energies are of the same order of magnitudes.

3. HF Calculations on NiFe

HF calculations have been carried out for several electronic configurations at the internuclear distances 4.34, 4.60, 4.80, and 6.00 a.u.

In all HF calculations performed, the electronic configuration of the Ni atom was chosen as $(3d\sigma)^2(3d\pi)^3(3d\delta)^4$. We expect that this configuration gives rise to the most realistic splittings between the potential energy curves resulting from the final CI calculations [3]. For the Fe atom, we have chosen to use partial occupation of the $3d\sigma$, the $3d\pi$ as well as the $3d\delta$ orbitals.

Table 1. Relative energies (a.u.) of low-lying terms for Ni and Fe atoms

Atom	Term	Calculated	Experimental[a]
Ni	$^3F(3d)^8(4s)^2$	0.0000	0.0000
Ni	$^3D(3d)^9(4s)^1$	0.0918	−0.0011
Ni	$^1S(3d)^{10}$	0.3458	0.0627
Fe	$^5D(3d)^6(4s)^2$	0.0000	0.0000
Fe	$^5F(3d)^7(4s)^1$	0.1071	0.0322
Fe	$^3F(3d)^8$	0.4151	0.1497

[a] Center of gravity of each multiplet has been calculated from data of C. E. Moore, Natl. Bur. Std. Circ. No. 467 (U.S. GPO, Washington D.C., 1952), Vol. 2.

In this way, we obtain orbitals which are appropriate for use in internal CI calculations allowing reorganization within the 3*d* and 4*s* shells.

In Table 2 we have presented energies and configurations of two $^3\Pi$ states and one $^5\Pi$ state. All three states are unbound relative to Ni$^3D(3d)^9(4s)^1$ + Fe$^5D(3d)^6(4s)^2$. The $^5\Pi$ state however, is bound relative to Ni$^3D(3d)^9(4s)^1$ + Fe$^5F(3d)^7(4s)^1$. Since we did not expect that a bond between the two atoms would involve Fe in the $(3d)^6(4s)^2$ configuration, we presumed orbitals from the $^5\Pi$ state to be appropriate for use in CI calculations describing low-lying states.

Population analyses of the three states show that the *d* orbitals are all well-localized. The σ orbital located on the Fe atom is however, very sensitive to the electronic configuration used in minimizing the energy. The σ orbital in the lowest-lying $^3\Pi$ state from Table 2 has turned into a hybridization between an *s* and a *p* orbital leaving only 6 *d*-electrons on the Fe atom. In the other $^3\Pi$ state from Table 2 the $3d\sigma$ orbital of the Fe atom has become strongly antibonding with an overlap population of −0.62.

Table 2. Energies of NiFe in three different states relative to an Fe atom with the $^5F(3d)^7(4s)^1$ term and a Ni atom with the $^3D(3d)^9(4s)^1$ term. The calculations were performed in the HF approximation at an internuclear distance of 4.80 a.u.

State	Configuration of the 3*d* shell of Fe[a]			Energy (eV)
	$3d\sigma$	$3d\pi$	$3d\delta$	
$^3\Pi$	1[b]	3	3	0.67
$^3\Pi$	2	4	1	3.84
$^5\Pi$	1	4	2	−0.67

[a] The configuration of the 3*d* shell of Ni is $(3d\sigma)^2(3d\pi)^3(3d\delta)^4$.

[b] In this calculation the σ orbital turned into a hybridization between an *s* and a *p* orbital.

In all calculations performed only one orbital has an appreciable overlap population. This orbital is of σ type, and it consists essentially only of the $4s$ orbitals of the two atoms.

4. Final Results and Discussion

Orbitals optimized for the $^5\Pi$ state as well as those optimized for the lowest lying $^3\Pi$ state described in Sect. 3 were utilized in CI calculations allowing full reorganization within the $3d$ shells and likewise between the $3d$ shells and the bonding $4s\sigma$ molecular orbital.

The calculations were performed in the subgroup C_{2v} of the full symmetry group $C_{\infty v}$ of the NiFe molecule. The number of configurations included within each symmetry species of C_{2v} was about 80 for the quintet states, and between 290 and 380 for the triplet and singlet states.

The potential energy curves resulting from CI calculations performed with orbitals derived from the $^3\Pi$ state are all repulsive. They only show very shallow minima at large internuclear distances. As expected, the Fe atom in the $(3d)^6(4s)^2$ configuration does not take part in the formation of a chemical bond. This result is in agreement with our previous calculations describing the interaction between two Ni atoms both in the $(3d)^8(4s)^2$ configuration [2].

Fig. 1 shows potential energy curves for a $^5\Pi$ state resulting from HF calculations, and also from CI calculations based on orbitals from the $^5\Pi$ state. Although lack of inversion symmetry in the NiFe molecule allows proper localization of the molecular orbitals in the HF approximation, it is noted that a considerable energy is gained in the CI calculations. This is, however, partly due to a change of electronic configuration of the atoms.

At the equilibrium internuclear distance, the four lowest lying states differ only in spin couplings. They all originate from the configuration $(3d\delta_{\mathrm{Ni}})^{3.00}(3d\pi_{\mathrm{Ni}})^{4.00}(3d\sigma_{\mathrm{Ni}})^{2.00}(3d\delta_{\mathrm{Fe}})^{2.46}(3d\pi_{\mathrm{Fe}})^{3.00}(3d\sigma_{\mathrm{Fe}})^{1.54}(4s\sigma)^2$. In order of increasing energy, the four lowest lying states are $^5\Pi$, $^5\Phi$, $^3\Pi$, and $^3\Phi$.

The spatial symmetry of the ground state of the NiFe molecule as determined in our calculations is in agreement with observations made by Montano [10] in his matrix isolation studies; however both the configuration and the multiplicity of the ground state differ from Montano's suggestions. Of course, the lowest lying $^5\Pi$ and $^3\Pi$ states resulting from our calculations have almost identical energies, but we do not find any bound state with the configuration proposed by Montano. The configuration of the Ni atom as part of the NiFe molecule is, however, in accordance with our previous results concerning the Ni_2 and the NiCu molecules.

Table 3 shows Mulliken population analyses of the valence orbitals of NiFe in the ground state. As was the case for Ni_2 and NiCu, the chemical bond is essentially only due to a $4s\sigma$ molecular orbital; none of the molecular orbitals arising from the $3d$ orbitals have any appreciable overlap population.

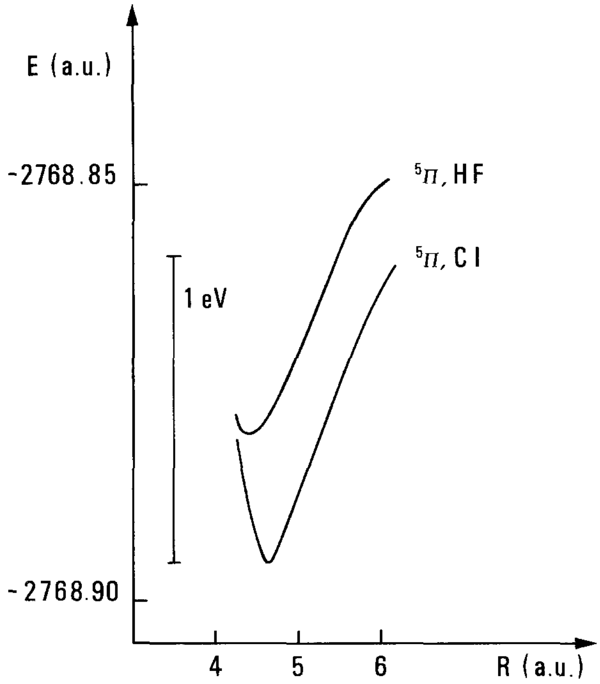

Fig. 1. Potential energy curves for NiFe in a $^5\Pi$ state calculated in the Hartree–Fock and in a limited CI approximation

Spectroscopic constants of the NiFe molecule are reported in Table 4. Since the CI wavefunctions include only molecular correlation the dissociation energies relative to $^3D(3d)^9(4s)^1$Ni + $^5F(3d)^7(4s)^1$Fe are determined as differences between the energies of the NiFe molecule at the equilibrium distance, and the sum of the HF energies of the atoms. The CI wavefunctions do not either include intraatomic correlation, and therefore the dissociation energies relative to $^3\mathrm{D}(3d)^9(4s)^1$Ni +

Table 3. Mulliken population analyses of the valence orbitals of NiFe at an internuclear distance of 4.60 a.u.

State	Orbital	Atomic population Ni	Fe	Overlap population
$^5\Pi$, CI	σ	0.50	0.93	0.57
	σ	2.01	0.04	−0.05
	σ	0.15	1.58	−0.19
	π	3.96	0.02	0.02
	π	0.03	2.94	0.03
	δ	2.98	0.02	−0.00
	δ	0.00	2.46	−0.00
Total		27.63	25.98	0.38

Table 4. Spectroscopic data for the lowest lying state of the NiFe molecule

State	Equilibrium distance (a.u.)	Dissociation energy (eV) relative to Ni$^3D(3d)^9(4s)^1$ +		Vibrational frequency (cm^{-1})
		Fe$^5F(3d)^7(4s)^1$	Fe$^5D(3d)^6(4s)^2$	
$^5\Pi$, HF	4.43	0.76	−0.12	203
$^5\Pi$, CI	4.64	1.18	0.30	467

$^5D(3d)^6(4s)^2$Fe are derived from the above-mentioned dissociation energies by adjusting for the experimental energy difference between the two terms of Fe. The vibrational frequencies have been derived using a harmonic approximation involving only the three closely spaced points at 4.34, 4.60, and 4.80 a.u. of the potential energy curves. Unfortunately, we have no experimental data for comparison.

The 39 low-lying states of NiFe at an internuclear distance of 4.60 a.u. are shown in Fig. 2. All these states are due to interaction between a Ni atom in the $^3D(3d)^9(4s)^1$ term and an Fe atom in the $^5F(3d)^7(4s)^1$ term. It is noted that all states are located within an energy range of only 0.56 eV.

Relating the dissociation energies of Table 4 to the states of Fig. 2, it seems likely that the repulsive states arising from interaction between Ni$^3D(3d)^9(4s)^1$ and Fe$^5D(3d)^6(4s)^2$ should be found in between the higher lying states of Fig. 2. However, due to lack of intraatomic correlation in the present study, it is not possible to predict these relative energies accurately.

Table 5. Energy ranges and electronic configurations for low-lying states of NiFe at the internuclear distance 4.60 a.u.

Energy range (eV)	States	*d* shell population Ni			Fe		
		δ	π	σ	δ	π	σ
0.000–0.005	$^5\Pi$, $^5\Phi$, $^3\Pi$, $^3\Phi$	3.00	4.00	2.00	2.46	3.00	1.54
0.028–0.034	$^5\Delta$, $^3\Delta$	3.00	4.00	2.00	2.24	3.76	1.00
0.033–0.041	$^5\Sigma^+$, $^5\Gamma$, $^5\Sigma^-$, $^3\Gamma$, $^3\Sigma^-$, $^3\Sigma^+$	3.00	4.00	2.00	3.00	2.00	2.00
0.106–0.138	$^5\Sigma^+$, $^5\Delta$, $^3\Sigma^+$, $^3\Delta$, $^3\Sigma^-$, $^5\Sigma^-$	4.00	3.00	2.00	2.45	3.00	1.55
0.140	$^5\Pi$	4.00	3.00	2.00	2.25	3.75	1.00
0.151	$^3\Pi$	4.00	3.00	2.00	2.90	2.20	1.90
0.157	$^3\Pi$	4.00	3.00	2.00	2.22	3.57	1.21
0.153–0.173	$^3\Phi$, $^5\Phi$, $^5\Pi$	4.00	3.00	2.00	3.00	2.00	2.00
0.231–0.238	^5H, $^5\Pi$, ^3H, $^3\Pi$	3.00	4.00	2.00	3.00	3.00	1.00
0.275	$^3\Pi$	4.00	4.00	1.00	3.00	3.00	1.00
0.279	$^5\Delta$	4.00	3.80	1.20	3.00	2.20	1.80
0.282	$^5\Pi$	4.00	4.00	1.00	2.20	3.00	1.80
0.309	$^3\Sigma^-$	4.00	4.00	1.00	2.23	3.77	1.00
0.314	$^3\Delta$	4.00	4.00	1.00	3.00	2.00	2.00
0.337	$^5\Sigma^-$	4.00	4.00	1.00	2.23	3.77	1.00
0.366–0.382	$^3\Gamma$, $^3\Delta$, $^5\Delta$, $^5\Gamma$	4.00	3.00	2.00	3.00	3.00	1.00
0.533–0.560	$^3\Phi$, $^5\Phi$	4.00	4.00	1.00	3.00	3.00	1.00

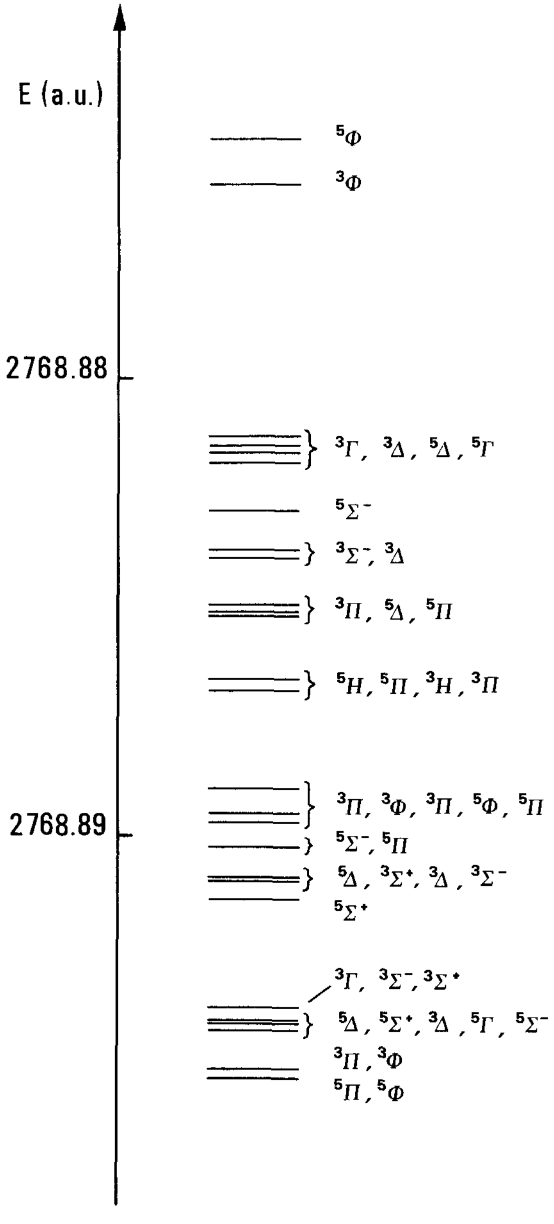

Fig. 2. Relative energies in eV of the 39 low-lying states of NiFe at an internuclear distance of 4.60 a.u. States are listed in order of increasing energy

Table 5 presents electronic configurations of all low-lying states. Most of these states are characterized by simple configurations. It is interesting to observe that for Ni, holes are found in the $3d\delta$ subshell of the 12 lowest lying states. This agrees with the configuration of the Ni atom in the low-lying states of the molecules Ni_2 and NiCu, and it verifies that formation of the chemical bond merely causes splittings of Ni $3d$ orbitals as a result of the axial symmetry.

A simple interpretation of the electronic configuration of Fe in the NiFe molecule is not possible because states of different configurations are very closely spaced, but it is noted that the Fe atom has vacancies in all of the 3*d* subshells.

It should be noted that none of the states in Fig. 2 are singlet states. While many of the quintet and triplet states have almost identical energies, the singlet states determined in the calculations are not bound at all. This is not surprising, since no singlet state can be obtained, when the doublet state of the Ni 3*d* shell interacts with the quartet state of the Fe 3*d* shell. Still, it emphasizes the importance of the state chosen for optimization of orbitals to be used in CI calculations.

In the present investigation, we have not considered spin–orbit coupling although this effect definitely causes a mixing of the closely spaced states. However, the spin-orbit coupling is probably only of minor importance with regard to the spectroscopic constants of the molecule as is the case with the NiCu molecule.

5. Conclusion

The interaction between a Ni atom and an Fe atom has been described using *ab initio* methods. HF and CI calculations have been carried out for four internuclear distances ranging from 4.34 to 6.00 a.u.

As is the case with Ni_2 and NiCu, the chemical bond in the NiFe molecule is almost solely due to a bonding $4s\sigma$ molecular orbital. The interaction between the 3*d* shells of the atoms merely cause small splittings between the potential energy curves.

The molecular ground state is $^5\Pi$, but three other states ($^5\Phi$, $^3\Pi$, and $^3\Phi$) with the same configuration are very close to the ground state in energy.

The configuration of the 3*d* shell of Ni in the low-lying states is $(3d\delta)^3(3d\pi)^4(3d\sigma)^2$. This is identical to the occupation of the Ni 3*d* shell regarded as part of the molecules Ni_2 and NiCu.

In the ground state, the configuration of the 3*d* shell of the Fe atom is $(3d\delta)^{2.5}(3d\pi)^{3.0}(3d\sigma)^{1.5}$. But for this atom, states of different configurations are located close to the ground state.

Spectroscopic data, i.e. equilibrium distance, dissociation energy, and vibrational frequency are reported for the ground state of the molecule.

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