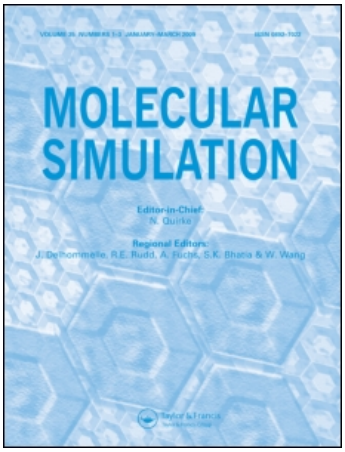

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Ab initio calculation of magnetism in Fe, Co and Ni

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A simple dimer cluster model combined with density functional B3LYP/6-311G(d,p) *ab initio* calculations is employed to describe the magnetic ordering in Fe, Co and Ni. The proposed adjacent spin-pair model reproduces the observed reduction of the Bohr magneton in the 3d metal series, and is in agreement with the Stoner theory and the multidisciplinary ideas of Pauling regarding electronic, magnetic and chemical bond properties in 3d transition metals.

Keywords: molecular simulation; magnetism; quantum chemistry

1. Introduction

During the last decades, our group have reported diversified multidisciplinary research using molecular simulation to elucidate problems including metal-containing systems [1–10]. In particular, a complete quantitative treatment of the magnetic behaviour in Fe, Co and Ni remains problematic since 3d electrons are neither completely localised on single centres nor entirely delocalised. In the localised electron model, the d electrons are strongly bound to individual atoms, whereas due to direct exchange interaction between adjacent atoms with parallel spins there is a decrease in the energy of the system [11–13]. In the itinerant d electron model, the complexity of the electronic configuration of the valence levels has made more difficult a better comprehension of the mechanisms yielding magnetism in the transition metals. Zener's [14] indirect exchange model for magnetism of transition metals contain both localised and itinerant character, whereas spin coupling between the incomplete d shells and the conduction electrons leads to ferromagnetic alignment of d spins. Stearns [15] attributed the origin of ferromagnetism to the indirect coupling between the predominantly localised d-like electrons and the smaller number of itinerant d-like electrons. This model suggests that about 5% of the 3d electrons are in itinerant bands and 95% are in d bands, which are sufficiently narrow such that they may be considered as localised, yielding scaling rules for contributions to hyperfine fields. Following Stearns, Mota and Coutinho Filho [16] introduced a two d-band model, where one band is narrow and degenerate representing the quasi-localised electrons, whereas the other band is wide containing few itinerant electrons, and the reported results for magnetism of Fe are in fairly good agreement with low- as well as high-temperature experimental data. Pauling [17] made a great contribution to the comprehension of ferromagnetism by elaborating a theory based on the supposition that in most transition metal atoms (Cr, Mn, Fe, Co and Ni), there exist as much as six conduction electrons. The value of 5.78 was designated as the metallic valence for Fe, which is the result of subtracting 2.22 electrons from the eight electrons in $3d^64s^2$ configuration. This value, 2.22, represents the number of unpaired electrons and also the saturation value of the magnetic moment of iron. Pauling's resonating valence bond (RVB) theory of metals assumes that hybrids of 3d, 4s and 4p orbitals combine with orbitals of other atoms in the crystal, yielding bonding orbitals occupied by electron pairs. The number of covalent bonds resonating among the available interatomic positions increase from one to nearly six in the sequence K, Ca, Sc, Ti, V, Cr; remains nearly constant from Cr to Ni; and begins to decrease with Cu. The remaining d orbitals, with very small interatomic overlap, are occupied by non-bonding electrons that are mainly responsible for the ferro- and paramagnetic properties of metals. RVB provides a surprisingly good qualitative explanation of many properties of transition metals (including those of the palladium and platinum groups), such as interatomic distances, characteristic temperatures, hardness, compressibility and coefficients of thermal expansion, accounting, satisfactorily as well, for the observed values of the atomic saturation magnetic moments of the ferromagnetic elements iron, cobalt, nickel and their alloys. Based on Pauling's ideas of occupation and bonding of valence orbitals, resonance of covalent bonds and conduction band metallic orbitals, we developed a diatomic molecular cluster model that gives a correct quantitative description of the electronic, magnetic, hyperfine interactions, as well

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as chemical bond properties of ferromagnetic iron [18]. In the present work, we extend this model to describe the magnetism in Fe, Co and Ni. It is shown that our adjacent electron spin-pair molecular model leads to a good agreement with experiments and supports the ideas of Stoner and Pauling regarding magnetism in transition metals.

2. The dimer cluster model

In spite of the sophisticated theoretical techniques now available, the properties of bulk Fe, Co and Ni are not well understood from first principle calculations and the discrepancies regarding magnetism in 3d transition metals are still not completely elucidated. For example, the attempt to determine magnetic properties and band structure by using large clusters leads to serious difficulties in defining the correct magnetic state. Atomic clusters represent an important class of reduced dimensionality systems and have produced some unexpected results bearing on magnetic ordering in small systems. In fact, transition metal clusters containing up to 100 atoms have been shown to exhibit novel magnetic behaviour including non-bulk-like magnetic ordering and unusually large magnetic moments [19]. The evolution of magnetism from the atom to the bulk constitutes a fundamental problem of basic and applied physics, and its correct description is important for understanding magnetism at the nanoscale level. In addition to the spin state definition problem, the quality of the calculations is critically dependent on the cluster size. We herewith avoid these types of complex problems. Since small atomic systems can be described in detail by using sophisticated molecular orbital calculations, let us start with a metal dimer to model the magnetic metals. Such a molecular model was previously applied to describe ferromagnetic iron and revealed the aspects of magnetism that at first sight it would appear not to be possible with the model [18]. The M_2 cluster is, of course, an extreme limit of a cluster model, but it has much relevance to the bulk systems. For example, small-angle scattering data for bulk iron indicate the existence of spin clusters implying short-range order well into the paramagnetic region [20]. The fact that one can easily define spin states in dimers, which are physically meaningful, constitutes another good reason to consider that they can be used as substitutes for much larger clusters. The present results are surprisingly good and call attention to how one might better understand magnetism in the 3d transition metals by using this simple model.

The dimers are calculated by employing the B3LYP/6-311G(d,p) density functional theory (DFT) via the Gaussian program [21]. The B3LYP hybrid density functional is constructed using the correlation functional of Lee, Yang and Parr (LYP) combined with the exchange functionals by Becke: the three-parameter Hartree–Fock/DFT hybrid exchange functional (B3) [22]. The accuracy of the DFT results is found to be highly dependent on the functional employed [23–29], but even DFT in the local density approximations gives a quantitatively reasonable description of several ground state properties of these materials such as the ordered magnetic moment and the spin wave stiffness as calculated from the spin wave dispersion [24]. The lattice interatomic distances (2.4823, 2.5061 and 2.4916 Å for Fe, Co and Ni, respectively) are used in all calculations. It must be pointed out that we are not studying the diatomic molecules of these transition metals, in which optimised geometry calculations would be required.

Our model assumes that there are two spins in each atomic centre, i.e. the spin multiplicity of the M_2 cluster is $2S + 1 = 5$. Such assumption is in agreement with positron annihilation experiments [30], as well as localised spin statistical models [16,31,32], which indicate $S = 1$ for localised spins on Fe. According to Pauling [17], six of the eight external electrons of iron in the bulk are conduction electrons that occupy the d^3sp^2 hybrid orbitals and two are magnetic electrons. For Co, seven of the nine external electrons are conduction electrons that occupy d^3sp^3 hybrid orbitals and two are magnetic electrons. In the case of Ni, 8 of the 10 external electrons are conducting electrons and 2 are magnetic electrons.

3. Results and discussions

Isolated Fe, Co and Ni atoms have 8, 9 and 10 valence electrons, respectively, which are distributed in 3d and 4s sublevels. There should be thus six electrons with spin $\uparrow$, whereas one electron should be in the 4s orbital and five electrons in the 3d orbital. The other electrons should indicate spin $\downarrow$. Consequently, Fe, Co and Ni have non-zero spins. In individual atoms, the magnetic state is determined by Hund's rules, giving rise to large spin and orbital moments [33]. We know that the magnetic moment of a free electron is 1.73 μ_B and that the atoms of Fe, Co and Ni in the ground state have magnetic moments of 4.90, 3.87, and 2.83 μ_B, respectively. However, in the bulk, these metals have magnetic moments of 2.22, 1.72 and 0.60 μ_B, respectively. Isolated atoms of a metal have discrete energy levels and localised orbitals, but when these atoms are close to each other, the atomic orbitals become delocalised, whereas the discrete atomic levels disperse in energy. In the case of Fe, for instance, the electronic configurations found in the bulk could be $4s^1 3d^7$. Accordingly, our previous calculations [17] showed that in the $^5\Delta$ configuration, each atom collaborates with only one electron for the formation of the 4s band, different from the isolated atom that has two electrons in the 4s orbital. Table 1 shows the calculated electronic state, total energy and Fermi level of the triplet,

Table 1. Total energies and Fermi levels for the triplet, quintet and septet spin states.

Cluster	State	Total energy (a.u.)	Fermi level
Fe_2	$^3\Sigma_g$	−2527.011	π_u
	$^5\Delta_u$	−2527.038	σ_u
	$^7\Sigma_u$	−2527.120	π_u
Co_2	$^3\Pi_u$	−2765.242	σ_u
	$^5\Pi_u$	−2765.304	σ_u
	$^7\Pi_g$	−2765.276	π_u
Ni_2	$^3\Sigma_u^-$	−3016.357	δ_u
	$^5\Pi_g$	−3016.399	σ_u
	$^7\Delta_u$	−3016.053	σ_g

quintet and septuplet states of the Fe_2, Co_2 and Ni_2 clusters.

The Stoner theory [34], which has been widely used to rationalise the existence of ferromagnetism in transition metals, predicts that the Fermi level must be highly localised, which is in agreement with experimental observations. From the point of view of molecular orbital theory, this means that the Fermi level, identified as the highest occupied molecular orbital (HOMO), should correspond to the anti-bonding state. In molecular orbital theory, anti-bonding orbitals are strongly localised, whereas bonding orbitals are delocalised. Table 1 shows that only the quintet states of the Fe_2, Co_2 and Ni_2 clusters have σ_u anti-bonding states, in agreement with requirements of Stoner's theory. It is interesting to verify that the septet state of Fe_2 and the triplet of Ni_2, despite being more stable, do not comply with the criterion of Stoner. We note that the localised or delocalised character of the Fermi level is not a consequence of the assumed distances. According to Pauling [17], the stabilising energy of the metal can be taken as proportional to the number of resonant unsynchronised structures by atom. Thus, the quintet spin state for Fe_2 and Ni_2, although not the most stable, could in principle, be stabilised by unsynchronised resonances of covalent bonds.

One of the important factors for understanding the 3d transition metals is the nature of the electronic band, i.e. the structure of the energy bands and their widths arising from the electron–electron interactions. The s band, for example, is wider than the d band because their orbitals are not as concentrated around the atomic nuclei as the d-type orbitals. Figure 1 shows the energy diagram for Co_2,

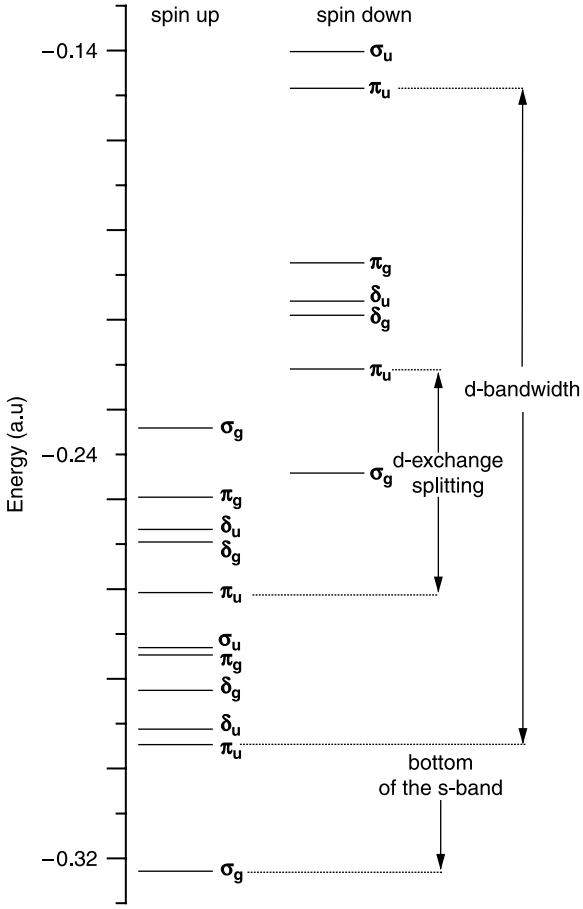

Figure 1. Energy diagram for the quintet spin state of Co_2.

illustrating definitions of d bandwidth, 3d exchange splitting and bottom of the s band.

Table 2 shows a comparison of the calculated and experimental widths of the occupied 3d bands, exchange splitting (d), as well as the bottom of the s band for the quintet state of the Fe_2, Co_2 and Ni_2 clusters.

The calculated d bandwidth and d exchange splitting are systematically higher than the experimental values determined via angle-resolved photoemission (ARP) with crystals of Fe(111), Co(0001) and Ni(111) [35]. A correct trend is found for the d exchange splitting, but for the d bandwidth, which is one of the most important properties of metals, the calculated trend is inverted.

Table 2. Calculated and experimental band properties (in eV).

	Fe		Co		Ni	
Property	Calc	Exp	Calc	Exp	Calc	Exp
d bandwidth	4.2	3.1[a]	4.0	3.8[a]	4.8	3.4[a], 4.3[b]
d exchange splitting	2.5	1.5[a], 1.7[c]	1.3	1,1[a]	0.8	0.3[a]
Bottom of s band (↑)	7.7	9.2[c]	8.8	–	8.2	–

[a] [35]. [b] [36]. [c] [37].

Table 3. Spin population for Fe_2, Co_2 and Ni_2 clusters.

Metal	d spin	s spin	μ_B exp.
Fe	2.664	−0.662	2.219
Co	2.461	−0.460	1.76
Ni	1.531	0.467	0.604

The discrepancies could possibly be attributed both to the B3LYP functional [38] and to the ARP measurements on superficial atomic layers, where a narrowing of the band occurs [35]. Comparison of ARP dispersion curves for several theoretical Ni bands widths showed that the individual d bands are theoretically about 1.4 times as wide as those found experimentally [39]. It has already been indicated that the B3LYP functional for atoms, molecules and solids can overestimate the exchange and correlation energies [22,40]. Table 2 also shows that the bottom of the s band tends to increase by increasing the atomic number. The present orbital population analysis of the quintet state of Fe_2, Co_2 and Ni_2 also confirms the importance of this state for the comprehension of the magnetic moment of these metals. According to Stearns [15], the d electrons gives the predominant contribution to ferromagnetism, whereas the contribution of the s electrons is small. Table 3 shows the B3LYP-calculated spin population for the Fe_2, Co_2 and Ni_2 clusters.

Analysis of the spin population given in Table 3 indicates that the contribution of the s orbital population is effectively small. For Fe and Co, the negative s component contributes to antiferromagnetism ordering, in agreement with Stearns [15]. Table 3 reproduces the expected reduction of magnetisation in the d band from Fe to Ni. Comparison with experiments shows that the present *ab initio* calculations describe magnetic moments of Fe and Co much better than Ni. Regarding Ni we note that due to the narrowing of the band on the surface, the calculated values for the spin d population could be larger than the experimental magnetic moment.

Since Fe, Co and Ni have relatively high spin, their magnetic behaviour shares a lot of similarities with the physics of small molecular magnets. Typical examples of high-spin small magnetic clusters (dimers, trimers, tetrahedral, etc.) have been successfully described by analytical expressions for the total magnetic moment and the static spin correlation functions of the classical Heisenberg model [41]. These systems, as well as the present dimer cluster model, provide a useful theoretical framework for calculating the magnetic properties of several recently synthesised molecular magnets.

4. Conclusions

Ab initio calculations on the quintet spin state of metal dimers describe well the magnetic properties of Fe, Co and Ni. It is found that all the calculated HOMO levels are anti-bonding states, in agreement with the Stoner theory regarding highly localised Fermi states. Our calculations yield suitable results for d bandwidth, exchange splitting, as well as the depth of the s band of these three metals. The orbital population analysis shows a reduction of the d band magnetisation in the Fe, Co and Ni series, in agreement with the experimental data. The proposed adjacent spin-pair model, taking advantage of a straightforward spin state definition and a high-level computational treatment, leads to results in agreement with experiments and Pauling's ideas regarding 3d magnetism. Particularly, this dimer model may also be a good theoretical framework for synthesised small molecular magnets and related devices.

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