

POINT OF VIEW ON MAGNETIC PROPERTIES OF Co_n ($n=6,8,10,12$) BASED ON QUANTUM CHEMISTRY INVESTIGATIONS

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Abstract. In this paper we present quantum chemical investigations on magnetic properties of several Co nanoparticles. Results of magnetizability, g-tensor, and the nature of bond and charge distribution in the particles are also presented. The results obtained allow us to propose reasons due to which magnetic properties of small particles are different and speculate what affected them.

1. Introduction

During the past decade cobalt nanoparticles have become very important for applications in magnetic storage technology due to their unique magnetic properties. The magnetic behavior of Co nanoparticles reveals how the magnetic metal nanoparticles can be used to enhance the signal due to magnetic resonance imaging [1].

It is known that magnetic properties of cobalt nanoparticles depend on their size. The coercivity of the particles at 10 K increases from 640 to 1250 Oe while the particle size increases from 1.8 to 4.4 nm. The saturation magnetization increases with decreasing particle size [2]. Extensive studies on ferromagnetic bulk materials and thin films have highlighted the magnetic anisotropy energy dependence on crystal symmetry and atomic composition [3]. Even the structural parameters such as the shape of particles or the interatomic distances in some cases are affected by these processes. While assembling cobalt nanoparticles containing up to 40 atoms, the magnetic anisotropy energy is dependent on single-atom coordination changes. These results confirm the theoretical predictions and are of fundamental value to understand how magnetic anisotropy develops in finite-sized magnetic particles [4]. Besides the size effect, the nanoparticle behavior is influenced by the proximity of neighboring particles, i.e. dipolar interactions between particles lead to the appearance of collective behavior [5]. On the other hand, the collective behavior due to dipolar interactions has been observed in the low susceptibility measurements corresponding to a highly ordered fine particles system [6]. It was found that when the density of particles per unit area was higher than a determined threshold, the two-dimensional self-assemblies behaved as a continuous ferromagnetic thin film [7].

Our results of Co_nO_m ($n=2, 6$ $m=1-12$) investigation exhibited that the magnetic properties of these particles did not depend on their shape but at the same time were oxygen number dependant. The main reason of this phenomenon is disappearance of Co-Co bonds where un-

compensated spins are present. Particle magnetizability was attributed to uncompensated spins and large orbital contribution was confirmed. It was obtained, that electron charge concentration and their distribution in the particle (i.e. particle dipole moment) are also important. Based on these results it was concluded that paramagnetic behavior dominates when the uncompensated spin is present due to a presence of a weakly interacting electrons on the antibonding orbital and this spin is not quenched by the ion spins [8].

In this paper the investigations of magnetic properties of Co_m ($m= 6, 8, 10, 12$) were performed to foresee that pure Co nanoparticles exhibit paramagnetic properties due to the presence of a weakly interacting electrons on the antibonding orbital and this spin is not quenched. Additionally, we tend to exhibit that the magnetizability of particles could be changed due to their interaction in the particle system.

2. Description of method

The structure of clusters has been studied by using the generalized gradient approximation for the exchange-correlation potential in the density functional theory (DFT) as it is described by Becke's three-parameter hybrid functional, using the non-local correlation provided by Lee, Yang, and Parr. The DFT method is commonly referred to as B3LYP [9] is a representative standard DFT method. The 6-31G basis set has been used [10]. The basis set was chosen keeping in mind relatively minimum computational costs. The structure of the investigated nanoparticles has been optimized globally without any symmetry constraint. It was obtained by starting with various initial geometry forms. In its turn, the form has been constructed according to certain symmetry in order to determine the lowest energy structure of each cluster.

Let us remind briefly the results that were obtained under investigation of Co_n particles [11]. These results indicate that Co_6 and Co_{12} are the most stable particles. To investigate the dipole particle interaction influencing the magnetic properties of these particles, the Co_6 and Co_6 , Co_6 and Co_{12} were created and investigated. Geometric and electronic structures of these compounds were obtained by using the above mentioned approach. The GAMESS and Gaussian program suites were used for all simulations [12, 13].

The isotropic magnetizability of the most stable clusters was calculated by adopting quantum mechanical response theory and London atomic orbital to ensure gauge-origin independent results and fast basis set convergence by using Dalton program [14]. The approach used allows us to calculate magnetizability accurately even for quite large molecules at a moderate cost of computer time. In this case the B3LYP method with Ahlrichs-pVDZ basis set was used [15]. These basis sets were obtained by optimizing the exponents and contraction coefficients in the ground state ROHF calculations. There are total 241 contracted functions in the basis mentioned. It is shown that the isotropic magnetizability and its anisotropy are remarkably constant with respect to the basis set and close to the experiment [16]. So, performances obtained allow us to foresee how magnetic properties of the particles depend on their structures.

3. Results of investigations

In our report the attention was paid to the magnetic properties of Co derivatives. Magnetizability (commonly known as susceptibility) was investigated as well. Let us remember that in the Co derivatives the number of bonding molecular orbitals that may be occupied is insufficient to locate all electrons of the system. As example, in Co_6 compounds all bonding orbitals are occupied and, as it has already been mentioned, some electrons are displaced on the antibonding orbitals, which energy is higher than that of the bonding orbitals. Hence the stability of the pure cobalt nanoparticle is low [17].

Let us mention that the increasing of the number of oxygen atom in the compound and the changeability of the oxidation state lead to the increasing of Co-Co length and weakening

of Co-Co bonds. This is important for the magnetic properties of these compounds because magnetic properties depend on the bonds' nature and the number of them as well as on the charge distribution [8]. Thus, aiming to explain the magnetic properties of the investigated particles, the attention is paid to the bonds' nature, dipole moment and its components as well as to the isotropic g -tensor which represents a spin angular moment.

In Table 1 the magnetizability, dipole moment, g -tensor and the number of bonds consisting of antibonding orbitals are presented. Here analysis of the most important orbitals (HOMO) of the described particles has been performed. It is possible to see that only Co_6 and Co_8 particles exhibit paramagnetic properties although the bonds that are consisted of antibonding character are present in all the particles investigated. In the mentioned particles, the different number of bonds that are formed from antibonding orbitals is present. The view of the location of the above bonds is presented in Figs. 1–2. The bond description by means of atomic orbitals on atoms is given in Table 2.

Table 1. Magnetic properties of cobalt compounds.

Compound	Magnetizability, a.u.	g -tensor	Dipole moment	Number of bonds having antibonding character
Co_6	58.77	-0.513	0.097	5
Co_8	25.79	-0.289	1.372	3
Co_{10}	-26.13	-0.071	0.084	5
Co_{12}	-35.11	-0.038	0.213	18

It should be emphasized that other atomic orbitals are not presented in Table 2 because of the value smallness, i.e. their numerical value is less than 0.07. However, atomic orbitals (they are not given in Table 1 because of their smallness) contribute the results very strongly. It indicates non-coincidence between the view of the atomic orbitals created on the full bond description and conclusion which follows from the results presented in Table 2. As example, the investigation of bond description by the most important atomic orbitals on atoms indicate, that the bond between atoms 2 and 6 of Co_6 particles possesses the bonding nature, however the contribution of other atomic orbitals shifts the orbital so that antibonding character occurs. The results indicate clearly the importance of a molecular orbital to magnetizability of Co nanoparticles (more details of this phenomenon will be given below). It implies that the conclusion on the character of bonds should be made based on the analysis of the most important atomic orbitals on atoms, bond lengths, bond order and views of the orbitals. All the above mentioned analysis was performed.

It can be seen that Co_{12} is diamagnetic because it has 18 symmetrically placed bonds with weakly interacting electrons that leads to the disappearance of noncompensated spins. The noncompensated spins quench each other. The isotropic g -tensor value equals to 0.038 and indicates the absence of free electrons or a non-compensate spin. This result coincides with the result obtained for Co_6O_7 particle [18]. In the case of Co_{12} , the oxidation state of Co atoms is even (Table 2). So, a non-compensate spin can not appear because some atoms loose the even number of electrons (below, it is shown that the oxidation state of atoms is also important for explaining Co particle magnetic properties). The magnetizability as well as g -tensor of the Co_6 particle is larger than that of Co_8 approximately twice. The above particles are paramagnetic, while Co_{10} , that possesses the odd number of antibonding character bonds like the particles mentioned, indicates diamagnetic properties.

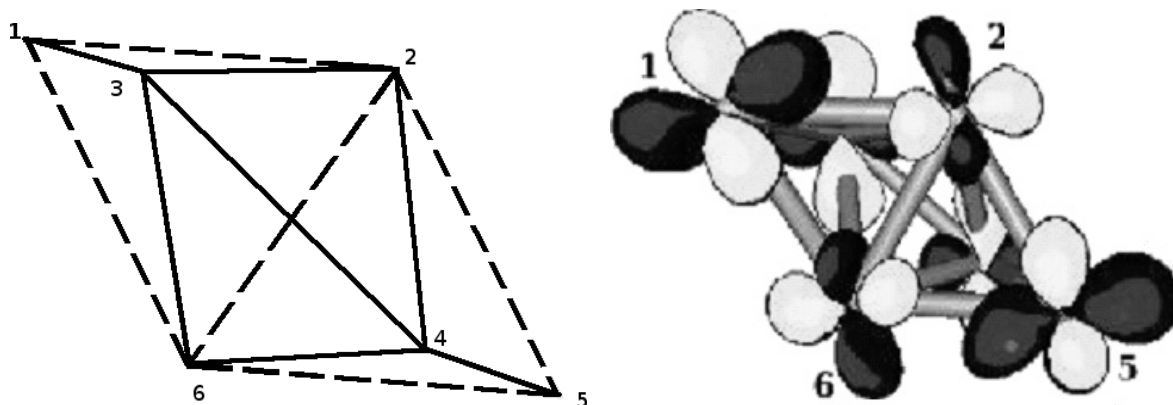


Fig. 1. View of Co_6 particle. The bonds consisting of antibonding orbitals are marked by dash lines on the left; the same view is given on the right when the most important orbitals (HOMO) are presented.

To explain the above mentioned noncoincidence, we investigated a dipole moment of these particles. The dipole moment indicates electron concentration places in a particle. On the other hand, the components of these dipole moments allow us to foresee the distribution of the above places. Both the concentration of electrons and their distribution helps us to find the appearance of the additional spins due to the different oxidation state of the Co atoms, i.e. if the even number of atoms loose the odd number of electrons and a particle possesses a dipole moment, we may suspect the localization of electrons and non-compensations of their spins.

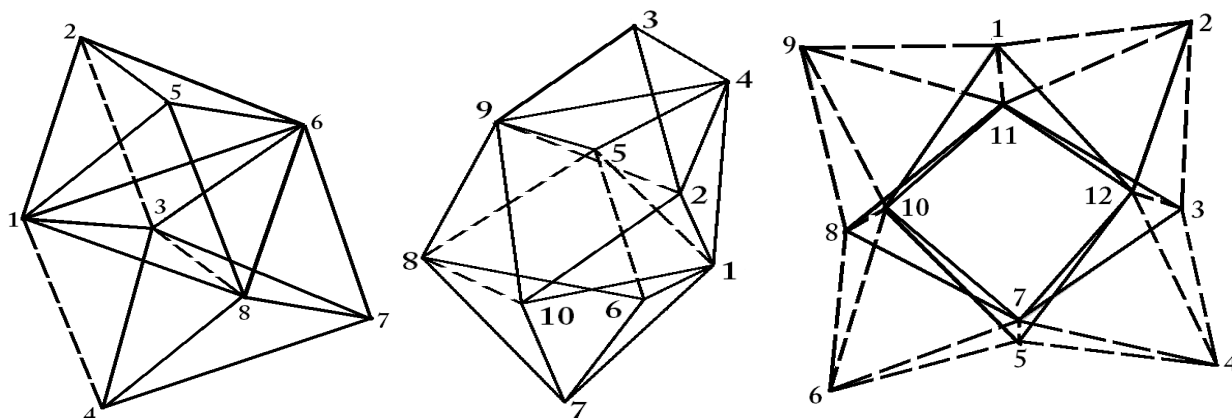


Fig. 2. View of Co_8 particle (on the left), Co_{10} particle (in the middle) and Co_{12} particle (on the right). The bonds consisting of antibonding orbitals are marked by dash lines.

The dipole moment components of the particles are presented in Table 3 and indicate electron charge delocalization in the Co_8 particle, while in case of the Co_{10} and Co_{12} particles, the charge localization occurred (see the component of dipole moment). It is necessary to add, that in the Co_8 and Co_{12} cases, the oxidation states of Co atoms are even. It allows us to predict that electron spins, appearing when the atoms loose electron, are compensated. An opposite situation occurs in case of Co_{10} particle where Co1 oxidation state is +5. Having in mind that the particle is diamagnetic despite the odd number of antibonding character bonds, it is possible to predict that in this case electron spins of the two types are compensated.

Therefore in case of Co_{10} particle, the four bonds with antibonding character are displaced like in case of Co_6 however one bond is in the same direction of the largest component of the dipole moment. Thus, it is possible to suspect, that in this case a weakly interacting electron spin is quenched by the ion spin. It may be concluded that paramagnetic behavior

dominates when the uncompensated spin is present due to the presence of a weakly interacting electron on the antibonding orbital and this spin is not quenched by the ion spins.

Table 2. The most important and largest atomic orbitals of atoms.

Particle	Atom No	dxx	dyy	dzz	dxy	dxz	dyz
Co ₆	1		-0.213	0.197			-0.088
	2		0.134	-0.176			0.076
	3		-0.139	0.195			-0.204
	4		-0.172	0.206			-0.204
	5		-0.218	0.197			
	6		0.110	-0.149			
Co ₈	1	-0.11	0.14				
	2	-0.105				0.10	0.24
	3	-0.08	0.10	-0.10			
	4			-0.054			
	5				-0.111	-0.082	-0.122
	6		-0.143	0.097			
	7				0.086		
	8					0.085	-0.128
Co ₁₀	1		0.070				0.157
	2					0.096	
	3			-0.087		0.080	-0.111
	4		-0.074	-0.111			
	5	0.081		-0.122			-0.086
	6	-0.076	0.077	0	-0.182	-0.111	
	7	-0.105		0.140			
	8	-0.090		0.101			-0.118
	9						-0.081
	10						0.074
Co ₁₂	1	0.161	-0.161				
	2	0.185	-0.213				0.074
	3	0.173	-0.173				
	4	0.213	-0.184				
	5	0.161	-0.161				
	6	0.184	-0.212				-0.075
	7	-0.119	0.119			0.085	0.085
	8	0.173	-0.173				
	9	0.213	-0.185			0.074	
	10	-0.104	0.104			-0.087	0.087
	11	-0.119	0.119			-0.085	-0.085
	12	-0.104	0.104			0.087	-0.087

Therefore in case of Co_{10} particle, the four bonds with antibonding character are displaced like in case of Co_6 however one bond is in the same direction of the largest component of the dipole moment. Thus, it is possible to suspect, that in this case a weakly interacting electron spin is quenched by the ion spin. It may be concluded that paramagnetic behavior dominates when the uncompensated spin is present due to the presence of a weakly interacting electron on the antibonding orbital and this spin is not quenched by the ion spins.

Table 3. Dipole moments and their components that are paramagnetic or weak diamagnetic.

Compound	Dipole moment, a.u.	Dipole moment components, a.u.		
		x	y	z
Co_6	0.096	-0.09	-0.01	-0.01
Co_8	0.468	0.147	0.298	0.329
Co_{10}	0.084	0.076	0.031	0.021
Co_{12}	0.213	0.198	-0.051	-0.061

One can see that the investigated systems are very flexible and it is possible to predict that any dipole interaction or Co particle agglomeration could change their magnetic properties. To confirm the prediction the magnetic properties of the Co_6 and Co_6 as well as Co_6 and Co_{12} derivatives was also investigated. The structure of Co_6 and Co_6 particles was found after global optimization. The results obtained indicate possible agglomeration of these particles, i.e. the Co_{12} particle should be formed. The magnetizability of this compound is -12.55 a.u. what indicates diamagnetic properties.

In the case of the Co_6 and Co_{12} compound, we do not perform any geometry optimization to avoid agglomeration of particles because change of geometrical structure lead to dramatic change of electronic structure and consequential change of magnetic properties. The investigated particles are placed randomly. Indeed, a compound consisting of Co_{12} and Co_6 particles is paramagnetic and its magnetizability is equal to 24.65 a.u. The results indicate clearly that dipole interaction and particle agglomeration change magnetic properties of Co nanoparticle.

4. Conclusions

We have presented an extensive calculation of magnetizability of Co_n ($n= 6, 8, 10, 12$) particles. Investigations of the most important orbitals, a dipole moment, and an oxidation state of the atoms in the particle exhibit the paramagnetic behavior domination when an uncompensated spin is present due to weakly interacting electrons on the antibonding orbital and this spin is not quenched by additional spins. The additional spins could occur because some atoms of a nanoparticle loose an odd number of electrons. Additionally, we may suspect that due to the particle dipole interaction their magnetic properties could be changed as well.

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