

## Research Article

# Magnetic Properties of $\text{Co}_6\text{O}_n$ ( $n = 0-9, 12$ )

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We present quantum chemical investigations on magnetic properties of several  $\text{Co}_6\text{O}_n$  ( $n = 0-9, 12$ ) nanoparticles. The results of calculations show, that only  $\text{Co}_6$ , and  $\text{Co}_6\text{O}_8$  particles display paramagnetic properties while other nanoparticles investigated reveal diamagnetic ones. The reason of the derivative paramagnetizability is discussed here. Calculations reveal that the stability of these compounds increases with the increase of the number of O atoms. The limit when the future increase of oxygen atoms does not change binding energy per atoms remarkably is found. The reason why the O atoms could stabilize the Co nanoparticles and change magnetic properties of them is discussed.

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## 1. Introduction

Recently, nanoparticles and their magnetic properties are in the focus of many studies. It is established, that for magnetic nanoparticles the surface spins compete with the core spins resulting in unusual magnetic properties with a multiple assortment of technological applications such as biomedical and hard-drive densifying technologies. The size, shape, and composition of magnetic nanoparticles are very attractive as diagnostic tools for cancer tumors and a targeting treatment in HIV infection. In this content, the Co nanoparticles are studied very intensively. The application of these particles is ranging from ultrahigh density recording media to medicine and, in addition, they are traditional precursors of anode materials in Li-ion rechargeable batteries and an effective catalyst in the reduction of  $\text{SO}_2$  by Co and NO by methane [1]. The magnetic behavior of Co nanoparticles reveals how the magnetic metal nanoparticles can be used to enhance the signal from the imaging examinations of magnetic resonance [2].

Extensive studies on ferromagnetic bulk materials and thin films have highlighted the dependence of magnetic anisotropy energy on crystal symmetry and atomic

composition [3]. Even the structural parameters, such as the shape of the particles or the interatomic distances are affected by these processes. When assembling cobalt nanoparticles, containing up to 40 atoms, the magnetic anisotropy energy depends on single-atom coordination changes. These results confirm the theoretical predictions and are of fundamental value to understanding how magnetic anisotropy develops in finite-sized magnetic particles [4]. Besides this size effect, the nanoparticle behaviour is influenced by the proximity of neighbouring particles, that is, dipolar interparticle interactions lead to the appearance of collective behaviour [5]. On the other hand, the structure effects a high chemical stability of nanoparticles even if they are in contact with the ambient, in particular, with oxygen [6].

Pure CoO nanoparticles in the 4.5–18 nm range have been prepared by the decomposition of Co(II) cupferronate [7]. These particles exhibit a superparamagnetic behaviour at room temperature while a large orbital contribution to the magnetic moment at low temperatures has also been observed. The core-shell nanoparticles (Co–CoO) are examined and, it is established, that the magnetic properties of these particles depend strongly on the plane coverage. The reported results demonstrate the essential role played by

shells in stabilizing the magnetism of Co–CoO nanoparticles. Few reports on the preparation and properties of pure CoO in bulk are due to difficulties to obtain the materials in pure form by simple methods. The particles are often contaminated with  $\text{Co}_3\text{O}_4$  or Co metal. The greater stability of  $\text{Co}_3\text{O}_4$  than CoO is also defined. However, reports on other properties of  $\text{Co}_n\text{O}_m$  particles are not found. The trial investigations of  $\text{Co}_2\text{O}_m$  ( $m = 1-7$ ) exhibited, that the stability of these particles depends on oxidation state of Co atoms [8]. We obtained that the most stable nanoparticles are  $\text{Co}_2\text{O}_3$  and  $\text{Co}_2\text{O}_6$ , when Co oxidation states are +3 and +4, respectively. The investigation of magnetization indicates that a compound with high symmetry demonstrates paramagnetic features. The results of calculations show that only  $\text{Co}_2\text{O}_3$  and  $\text{Co}_2\text{O}_4$  display paramagnetic properties while other derivatives investigated ( $\text{Co}_2\text{O}$ ,  $\text{Co}_2\text{O}_2$ , and  $\text{Co}_2\text{O}_6$ ) reveal diamagnetic properties. The investigations of the most important orbitals and total electron density distribution show that the Co compound will be paramagnetic due to several reasons: (1) the unpaired electron location on the Co–Co bonds and (2) small total electron charge density between Co atoms which appears due to overlapping of p-orbitals of the oxygen atoms. Hence, the following questions arise:

- (1) Does the Co nanoparticle lose its magnetic properties because of dissipation of Co–Co bonds that possess antibonding character?
- (2) Is the magnetizability of Co nanoparticle dependent on the number of Co–Co bonds with antibonding character?
- (3) How do magnetic properties of these particles depend on their shape?

Hence, we try to answer the above questions.

Let us remember, that the stability of only  $\text{Co}_3\text{O}_4$  and CoO is reported. So, the investigation should additionally shed some light on the stability of the  $\text{Co}_n\text{O}_m$  particles.

## 2. Description of Method

The structural origin 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 nonlocal correlation provided by Lee, Yang, and Parr. The DFT method is commonly referred to as B3LYP [9]—a representative standard DFT method. The 6-31G basis set has been used as well [10]. The basis set has been chosen keeping in mind relatively minimal computational costs. The structures of the investigated nanoparticles have been optimized globally without any symmetry constraint and by starting from various initial geometry, constructed according to certain symmetry, in order to determine the lowest energy structures of each cluster.

Let us revise briefly the results that were obtained under investigation of  $\text{Co}_n$  particles [11]. These results indicate  $\text{Co}_6$  and  $\text{Co}_{12}$  as the most stable particles. Moreover, the structure of a  $\text{Co}_6$  particle occurred in all investigated derivatives, thus, this structure is called a key element of Co clusters.

In the case of this  $\text{Co}_6$  particle, we have three-dimensional structure with  $C_{2V}$  symmetry that was obtained after global optimization of the  $D_{4h}$  isomer of  $\text{Co}_6$ . To model  $\text{Co}_6\text{O}_n$  ( $n = 1-7$ ), we used the most stable geometrical structure of the  $\text{Co}_6$  particle (key element) as the starting point and examined almost all candidate configurations with different symmetry of cluster  $\text{Co}_6\text{O}_n$  ( $n = 0-9, 12$ ). The GAMESS and Gaussian program suites were used for all simulations [12, 13].

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 usage of this approach allows us to calculate accurate magnetizability even for quite large molecules at a moderate cost of computing time. In this case, the B3LYP method with Ahlrichs-pVDZ basis set was used [15]. Such a basis set was obtained by optimizing the exponents and contraction coefficients in the ground state ROHF calculations. It is showed, that the isotropic magnetizability and its anisotropy are remarkably constant with respect to the basis set and close to the experiment [16]. So, the obtained performances allow us to foresee how magnetic properties of particles depend on their structures.

## 3. Results

$\text{Co}_6\text{O}_n$  ( $n = 0-9$ ) derivatives were investigated to establish the number of O atoms that may be accepted by Co particles. On the other hand, the investigations allow us to foresee the condition of the breaking of metal Co–Co bond and shed some light on the magnetizability of  $\text{Co}_6\text{O}_n$ .

The stablest structures of the  $\text{Co}_6\text{O}_n$  derivatives are presented in Figure 1.

Firstly, it is necessary to mention that oxygen stabilizes the Co nanoparticle and the increasing number of oxygen atoms increases the binding energy per atom till  $n = 7$  (Figure 2). Furthermore, there is a reached limit when O atoms do not influence the stability of  $\text{Co}_6\text{O}_n$  particles. The binding energy per atom of  $\text{Co}_6\text{O}_{12}$  particles is equal to 3.26 eV which is similar to that of  $\text{Co}_6\text{O}_n$  ( $n = 7, 8, 9$ ). The difference of binding energy of the above particles is too small (0.2 eV or less) to make a conclusion of which of them is the stablest.

The difference of the binding energy per atom of  $\text{Co}_6$  and  $\text{Co}_6\text{O}$  is equal to 0.48 eV, while that between  $\text{Co}_6\text{O}_6$  and  $\text{Co}_6\text{O}_7$  is only 0.21 eV, that is, twice less. On the other hand, the changing of the number of oxygen atoms from 2 to 3 leads to the largest increase of binding energy per atom (0.72 eV), while the binding energy per atom increases only up to 0.13 eV when the oxygen atom number in a particle increases from 3 to 4. Thus, the results of our investigations allow us to foresee that starting with  $n = 6$  ( $n$  is the number of oxygen) with further increase of the number of oxygen atoms will not influence the stability of these particles very strongly and the main structure (the key element) is not considerably changed (Figure 2). The binding energy per atom of the  $\text{Co}_6\text{O}_6$ ,  $\text{Co}_6\text{O}_7$ ,  $\text{Co}_6\text{O}_8$ , and

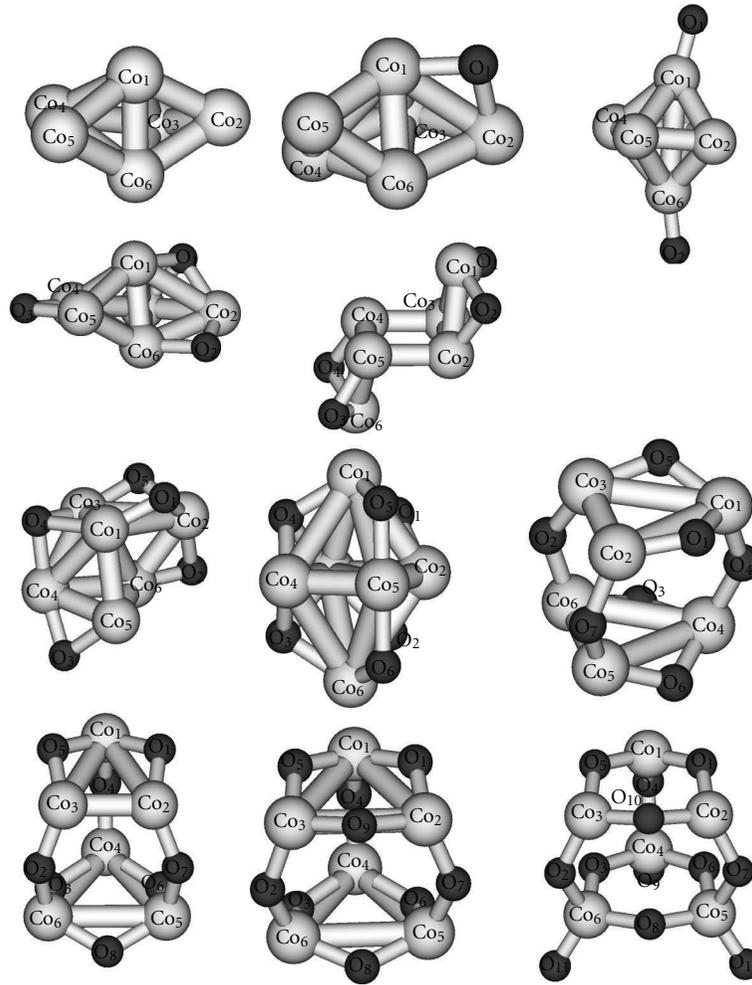


FIGURE 1: The views of  $\text{Co}_6\text{O}_n$  ( $n = 0-9, 12$ ).

$\text{Co}_6\text{O}_9$  is approximately equal and exhibits these particles as the stablest. These results coincide with experimental measurements that indicate the presence of  $\text{CoO}$  and  $\text{Co}_3\text{O}_4$ , but  $\text{CoO}_2$ ,  $\text{Co}_2\text{O}_3$ , and  $\text{Co}_6\text{O}_7$  particles should be found among them too [17].

Such changeability of binding energy per atom could be explained by changes in geometrical structure of Co particles. In the case when an additional oxygen atom does not significantly increase the binding energy per atom, the main part of this atom energy is used to deform the structure of the key element ( $\text{Co}_6$ ). Thus, the binding energies per atom of  $\text{Co}_6\text{O}_3$  and  $\text{Co}_6\text{O}_4$  or  $\text{Co}_6\text{O}_6$ , and  $\text{Co}_6\text{O}_7$  are approximately equal.

It is emphasized that the key element of the  $\text{Co}_6$  is present in the  $\text{Co}_6\text{O}_n$  ( $n = 0-9, 12$ ) derivatives. However, the key element is slightly deformed. The changeability of the initial form is oxygen-atom-depended. The largest deformation is obtained in  $\text{Co}_6\text{O}_7$  when the distance between the planes (formed by atoms 1, 2, 3 and of 4, 5, 6) is increased and one plane is rotated in respect of the other one by  $\pi/4$  angle. Actually, another structure of the  $\text{Co}_6\text{O}_7$  which looks like  $\text{Co}_6\text{O}_6$  was also obtained, but the energy of formation of

this particle is 1.23 eV higher than that of the particle the structure of which is described above.

In the  $\text{Co}_6\text{O}_4$  particle the key element ( $\text{Co}_6$ ) is deformed twice: (1) the distances between the atoms  $\text{Co}_2\text{--Co}_5$  decrease; (2)  $\text{Co}_1$  and  $\text{Co}_6$  position in respect of the plane that is formed by atoms 2, 3, 4, 5 is changed. It is emphasized, that the structure of this particle has been obtained after global geometry optimization, starting with several completely different initial geometries. Thus, the geometrical structure of the  $\text{Co}_6\text{O}_4$  particle is confirmed.

Hence, the largest particle  $\text{Co}_6$  deformations are obtained when the number of oxygen atoms is changed from 3 to 4 and from 6 to 7. In these cases the stabilization energy per atom is smaller than in other cases investigated. Thus, the main part of oxygen energy is used to deform the key structure of  $\text{Co}_6$ .

It is necessary to mention, that in the case of the number of oxygen atom 2 and 6, the structure of the  $\text{Co}_6\text{O}_m$  particle looks like the octahedron, while in the case of odd numbers of oxygen, the octahedron form is strongly deformed (except the results of  $\text{Co}_6\text{O}_4$ ). It is interesting, that the stablest structure of  $\text{Co}_6\text{O}_8$  (prototype of  $\text{Co}_3\text{O}_4$ ) has deformed the spinel structure [18]. Thus, it is not surprising, that

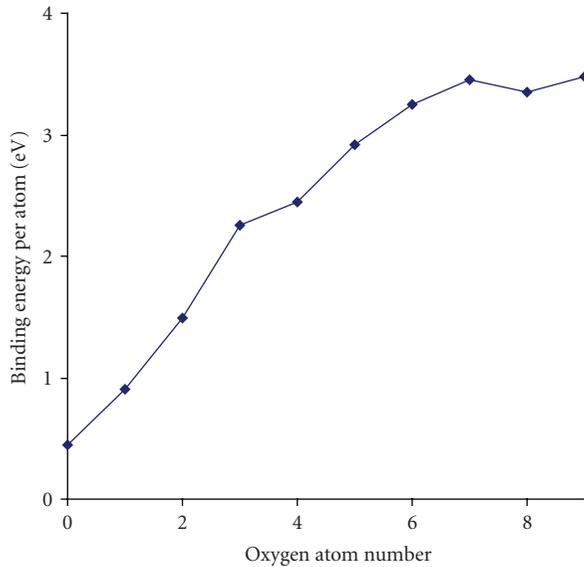


FIGURE 2: The binding energy dependence on oxygen atom number.

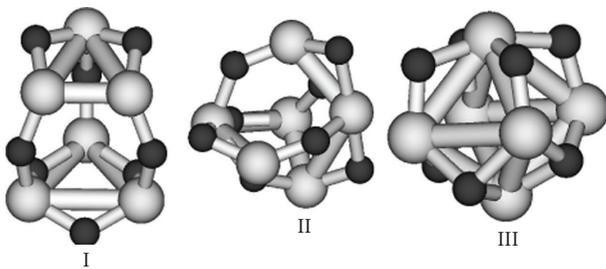


FIGURE 3: Several isomers of  $\text{Co}_6\text{O}_8$ .

a large effective magnetic moment, estimated from inverse susceptibility, has not been explained properly.

According to results obtained, the Co–Co bond length of the single bond in a  $\text{Co}_6$  particle is longer ( $2.2 \text{ \AA}$ ) than the bond length of a double bond ( $2.0 \text{ \AA}$ ) [11]. On the other hand, three bonds are obtained where the length is equal to  $2.3 \text{ \AA}$ . The bond order of the largest bond is twice smaller than that of a single bond. Here, the common observation is that the Co–Co bond lengths are marginally changed only between the atoms that are connected with O (Table 1) and, as a consequence, the bond enlargement leads to Co–Co bond dissolving.

As the example, the two, one, and zero Co–Co bonds are found, respectively, in the  $\text{Co}_6\text{O}_7$ ,  $\text{Co}_6\text{O}_8$ , and  $\text{Co}_6\text{O}_9$  nanoparticles.

The attention should be paid to the results of  $\text{Co}_6\text{O}_4$ . In this case, the bonds forming the Co atom connection with oxygen are shorter than those in  $\text{Co}_6$  particle, but the analysis of the bond order indicates that the above Co–Co bonds are weaker than those in the  $\text{Co}_6$  particle. As an example: in the  $\text{Co}_6$  particle the bond order between Co1–Co5 is equal to 1.018, while that in  $\text{Co}_6\text{O}_4$  is approximately twice smaller and equals to 0.55.

Roughly speaking, we may divide the described particles into the following groups:

- (1) The particles that possess shape of  $\text{Co}_6$ :  $\text{Co}_6$ ,  $\text{Co}_6\text{O}$ ,  $\text{Co}_6\text{O}_2$ ,  $\text{Co}_6\text{O}_3$ ,  $\text{Co}_6\text{O}_5$ ,  $\text{Co}_6\text{O}_6$  (A group),
- (2) the particles in which the distance between the planes (formed of atoms 1, 2, 3 and of 4, 5, 6) is increased and one plane is rotated in respect to the other one by  $\pi/4$  angle:  $\text{Co}_6\text{O}_7$ ,  $\text{Co}_6\text{O}_8$ ,  $\text{Co}_6\text{O}_9$  (B group),
- (3) the rest ( $\text{Co}_6\text{O}_4$ ).

It should be pointed out, that a lot of reports concluded that magnetic properties of the nanoparticles depend on their shape [18]. So, we may suspect that magnetizability of the particles belonging to the same group should be the same. However, the results of our investigations do not prove the above prediction (Table 2).

According to our investigations, a  $\text{Co}_6$  nanoparticle is a strong paramagnetic, while other particles, belonging to group A are diamagnetic. The same phenomenon is obtained in the case of group B. In this case,  $\text{Co}_6\text{O}_8$  particle is paramagnetic, while other particles are diamagnetic. Moreover, diamagnetic properties of the particles of the similar shape are quite the same only in the following cases:  $\text{Co}_6\text{O}_7$ ,  $\text{Co}_6\text{O}_{12}$  and  $\text{Co}_6\text{O}_9$ ,  $\text{Co}_6\text{O}_3$  and  $\text{Co}_6\text{O}_6$ ,  $\text{Co}_6\text{O}_2$  and  $\text{Co}_6\text{O}_5$ . It implies, that the shape of the particle has no influence on the magnetic properties of these nanoparticles. To confirm this conclusion, we have calculated magnetizability of several isomers of  $\text{Co}_6\text{O}_8$  particles (Figure 3). It is obvious, that the shapes of isomer II and III are similar, but the shape of isomer I is different. However, the magnetizability of isomer II and I with different shapes is approximately equal, while the magnetizability of isomer III is smaller than that of isomer II with the same shape (Table 3). Hence, the magnetic properties of these particles do not depend on their shape.

Let us remember, that nanoparticles, could be paramagnetic due to several reasons: (1) the unpaired electron location on the Co–Co bonds and (2) a small total electron charge density between Co atoms which appears due to overlapping of p-orbitals of oxygen atoms [8]. The second reason of the two mentioned above could not be realized in the case of  $\text{Co}_6\text{O}_n$  particles due to their relatively large size and small number of oxygen atoms. The first reason could also be realized, thus supporting the results that have been previously obtained. It is necessary to mention, that large spin uncompensation has also been observed for  $\text{CoO}/\text{SiO}_2$  multilayers [19].

Let us describe the particles of group B in detail. Firstly, it is necessary to mention that the particles of this group have different number of Co–Co bonds: 2, 3, and 0 in the  $\text{Co}_6\text{O}_7$ ,  $\text{Co}_6\text{O}_8$ , and  $\text{Co}_6\text{O}_9$ , respectively. Only the  $\text{Co}_6\text{O}_8$  particle exhibits paramagnetic properties.

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. This leads to the presence of electrons on the antibonding orbital and, as a consequence, to a weaker correlation of these electrons. The appearance of electrons on antibonding orbitals let us

TABLE 1: The distance between the Co atoms which are connected with the O atom.

Compounds	Co–Co bond length, Å								
	1-2	1-3	1-4	1-6	2-3	2-6	4-5	4-6	3-4
Co <sub>6</sub>	2.15	2.33	2.15	2.24	2.04	2.23	2.04	2.31	2.33
Co <sub>6</sub> O	2.54								
Co <sub>6</sub> O <sub>2</sub>				3.01					
Co <sub>6</sub> O <sub>3</sub>				2.18	2.37	2.33	2.14		
Co <sub>6</sub> O <sub>4</sub>	2.27	2.27	2.27	4.72				2.27	
Co <sub>6</sub> O <sub>5</sub>	2.25				2.61	2.25			2.39
Co <sub>6</sub> O <sub>6</sub>	2.83	2.67	2.89		2.32	2.87			2.44
Co <sub>6</sub> O <sub>7</sub>	2.93			3.11	2.93		2.93	2.93	
	1-2	1-3	1-4	2-3	2-5	3-6	4-5	4-6	5-6
Co <sub>6</sub> O <sub>7</sub>	2.92	2.93	3.21	2.21*	3.07	3.11	2.92	2.91	2.22*
Co <sub>6</sub> O <sub>8</sub>	2.88	2.90	3.21	2.24*	3.18	3.16	3.03	3.03	2.93
Co <sub>6</sub> O <sub>9</sub>	3.04	3.04	3.15	3.04	3.14	3.15	3.04	3.05	3.05

\* The Co–Co is present.

TABLE 2: Magnetizability and the number of Co–Co bonds. The number of Co–Co bonds is based on the investigation results of electron density. Only the bonds, where unpaired spin electrons could be present, are mentioned.

Compound	Magnetizability, a.u.	Number of Co–Co bonds
Co <sub>6</sub>	58.77	7
Co <sub>6</sub> O	-11.24	6
Co <sub>6</sub> O <sub>2</sub>	-15.47	6
Co <sub>6</sub> O <sub>3</sub>	-3.26	5
Co <sub>6</sub> O <sub>4</sub>	-9.62	4
Co <sub>6</sub> O <sub>5</sub>	-15.97	2
Co <sub>6</sub> O <sub>6</sub>	-2.11	1
Co <sub>6</sub> O <sub>7</sub>	-25.94	2
Co <sub>6</sub> O <sub>8</sub>	25.42	1
Co <sub>6</sub> O <sub>9</sub>	-24.28	0
Co <sub>6</sub> O <sub>12</sub>	-24.25	0

TABLE 3: Magnetizability of different isomers of Co<sub>6</sub>O<sub>8</sub> particle.

Isomers	I	II	III
Magnetizability, a.u.	25.42	24.76	14.24

assume a large orbital contribution to the magnetic moment of a small Co<sub>m</sub>O<sub>n</sub> particle [17] (Figure 4).

It implies, that noncompensate electron spin should be obtained. This situation is realized in the Co<sub>6</sub>O<sub>7</sub> and Co<sub>6</sub>O<sub>8</sub> particles. However, in the Co<sub>6</sub>O<sub>7</sub> particle two pairs of weakly correlated electrons are present which leads to disappearance of noncompensate spins. It is indicated by the isotropic  $g$ -tensor value which approximately equals to zero. However, in the case of Co<sub>6</sub>O<sub>8</sub> particle, only one Co–Co bond is present and only one pair of weakly correlated electrons could be found. This weak correlation indicates the nature of HOMO orbital, that consists of antibonding  $d_{z^2}$  type orbitals (Figure 4). Hence, a common spin of electrons is not compensated and, as a consequence, the particle exhibits

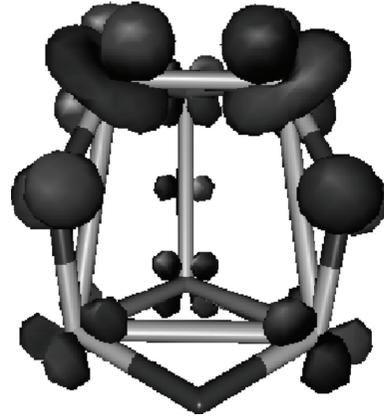


FIGURE 4: The HOMO orbital antibonding character of the Co<sub>6</sub>O<sub>8</sub> particle.

paramagnetic features. The presumption is confirmed by the isotropic  $g$ -tensor value of 0.18, that is, one of the largest between these particles. Additionally, we may assume, that Co<sub>6</sub>O<sub>n</sub> particles should be paramagnetic when the number of Co–Co bonds, on which the unpaired electrons are located, could be even (Table 2). Indeed, the investigated particles with the even number of Co–Co bonds have exhibited paramagnetic or weak diamagnetic properties. However, it is not absolutely clear why the magnetic properties are different, that is, some formally different features should be present.

To explain the above mentioned discrepancy, we investigated a dipole moment of particles. The dipole moment indicates electron concentration places in the particle. On the other hand, the components of these dipole moments allow us to foresee distribution of the above places. Both the concentration of electrons and their distribution helped us to find additional spins that appeared due to different oxidation state of the Co atoms (formally we call the above spin as an ion one). The components of the dipole moment of the particles that are paramagnetic or weak diamagnetic are shown in Table 4.

TABLE 4: Dipole moments and their components of the investigated particles that are either paramagnetic or weak diamagnetic.

Compounds	Dipole moment, a.u.	Dipole moment components, a.u.		
		$x$	$y$	$z$
Co <sub>6</sub>	0.096	-0.09	-0.01	-0.01
Co <sub>6</sub> O <sub>3</sub>	1.689	0.55	0.23	-1.58
Co <sub>6</sub> O <sub>6</sub>	1.639	-1.06	-1.16	0.44
Co <sub>6</sub> O <sub>8</sub> (I isomer)	2.652	2.60	0.45	0.23
Co <sub>6</sub> O <sub>8</sub> (II isomer)	2.059	-1.08	-0.01	-1.75
Co <sub>6</sub> O <sub>8</sub> (III isomer)	1.372	1.37	-0.06	-0.03

So, as it was mentioned, the two different types of magnetic interactions could be obtained in Co<sub>6</sub>O<sub>*m*</sub> nanoparticles: (1) an uncompensated spin of weakly interacting electrons on the antibonding orbital and (2) the presence of Co ions, that loose an odd number of electrons (Co<sup>+3</sup> and similar) leading to the emergence of an additional uncompensated spin.

The results obtained show that the magnetic properties of nanoparticles could depend on the above both interactions. For the former, the paramagnetic behaviour dominates when the uncompensated spin is present due to weak interacting electrons on the antibonding orbital and this spin is not quenched by the ion spins. Let us remember, that Co<sub>6</sub>O<sub>3</sub> and Co<sub>6</sub>O<sub>6</sub> particles are weak diamagnetics. In these particles the ion spin is also presented which indicates the high dipole moment. The number of the Co<sup>+3</sup> ions is 2 and 4, respectively, in the Co<sub>6</sub>O<sub>3</sub> and Co<sub>6</sub>O<sub>6</sub> particles. However, the components of the dipole moment indicate that the ion spins are delocalized. The interaction between these spins leads to the quench of an electron spin, that is, both spins (ion and an uncompensated spin of electrons located on the antibonding orbital of Co–Co bond) are oriented so that the total spin is equal to zero.

The opposite situation is obtained in the Co<sub>6</sub>O<sub>8</sub> particle: an ion spin is localized and one Co–Co bond is present. In this case, the spins are oriented so that they are relatively parallel to each other. This prediction is supported by additional investigations of the Co<sub>6</sub>O<sub>8</sub> particle isomers. It is necessary to mention, that one Co–Co bond is present in isomer II and a detailed investigation of the dipole moment indicates that it lies approximately in parallel to the Co–Co bond. Therefore, the unpaired spins of the different nature support each other. Thus, the magnetizability of isomers I and II of the Co<sub>6</sub>O<sub>8</sub> particle is the same. In the case of isomer III, all Co–Co bonds are dissolved, but an ion uncompensated spin is present. It implies that magnetic properties of the particle are determined by the localized ion spin only. Thus, the magnetizability of isomer III is lower than that of the other isomers investigated.

#### 4. Conclusion and Future Work

We have presented an extensive series of calculated stability and magnetizability of Co<sub>6</sub>O<sub>*n*</sub> ( $n = 0-9$ ) particles.

It is known, that organic coating on a particle prevents the surface oxidation, rendering it stable over a long period. Our results obtained confirm the above observation and allow one to foresee what could increase the stability of Co nanoparticle.

Firstly, our results indicate, that CoO<sub>2</sub>, Co<sub>2</sub>O<sub>3</sub>, and Co<sub>6</sub>O<sub>7</sub> particles should be found among very well-known CoO and Co<sub>3</sub>O<sub>4</sub> ones. The obtained results indicate that a stabilization effect is dependent on the number of the oxygen atoms till  $n = 7$  ( $n$  is the number of oxygen atoms). Further increasing of the number of atoms will not influence the stability of Co<sub>6</sub>O<sub>*n*</sub> particles strongly when the key structure (structure of Co<sub>6</sub> particle) is not dramatically changed.

The results of the present investigation exhibited that the magnetic properties of particles investigated do not depend on their shape.

Our results proved that magnetic properties of the Co nanoparticles are oxygen-atom-dependent.

The main reason of these phenomenon is the disappearance of Co–Co bonds where uncompensated spins are present. Particle magnetizability may be attributed to uncompensated spins and a large orbital contribution is confirmed. It is necessary to mention, that electron charge concentration and its distribution in the investigated particles are also important.

Hence, a paramagnetic behaviour dominates when the uncompensated spin is present due to weak interacting electrons on the antibonding orbital and this spin is not quenched by ion spins.

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#### References

- [1] D. A. Resnick, K. Gilmore, Y. U. Idzerda, et al., “Magnetic properties of Co<sub>3</sub>O<sub>4</sub> nanoparticles mineralized in *Listeria innocua* Dps,” *Journal of Applied Physics*, vol. 99, no. 3, pp. 08Q501.1–08Q501.3, 2006.
- [2] J. Neamtu, I. Jitaru, T. Malaeru, G. Georgescu, W. Kappel, and V.-V. Alecu, “Synthesis and properties of magnetic

- nanoparticles with potential applications in cancer diagnostic,” *Nanotechnology*, vol. 1, pp. 222–224, 2005.
- [3] M. Sakurai, K. Watanabe, K. Sumiyama, and K. Suzuki, “Magic numbers in Fe clusters produced by laser vaporization source,” *Journal of the Physical Society of Japan*, vol. 67, no. 8, p. 2571, 1998.
- [4] P. Gambardella, S. Rusponi, M. Veronese, et al., “Giant magnetic anisotropy of Co adatoms and nanoparticles on Pt(111),” *Science*, vol. 300, p. 1130, 2003.
- [5] J. Nogues, V. Skumryev, J. Sort, S. Stoyanov, and D. Givord, “Shell-driven magnetic stability in core-shell nanoparticles,” *Physical Review Letters*, vol. 97, no. 15, pp. 157–203, 2006.
- [6] Sh. Tsukamoto and N. Koguchi, “Magic numbers in Ga clusters on GaAs (0 0 1) surface,” *Journal of Crystal Growth*, vol. 209, no. 2-3, pp. 258–262, 2000.
- [7] M. Ghosh, E. V. Sampathkumaran, and C. N. R. Rao, “Synthesis and magnetic properties of CoO nanoparticles,” *Journal of Materials Chemistry*, vol. 17, no. 9, pp. 2348–2352, 2005.
- [8] J. Tamuliene, R. Vaisnoras, G. Badenes, and L. M. Balevicius, “Magnetic properties of  $\text{Co}_2\text{O}_n$  ( $n = 1-7$ ),” *Lithuanian Journal of Physics*, vol. 49, no. 2, pp. 137–143, 2009.
- [9] A. D. Becke, “Density-functional thermochemistry. iii. The role of exact exchange,” *The Journal of Chemical Physics*, vol. 98, no. 7, pp. 5648–5652, 1993.
- [10] M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, and W. J. Hehre, “Self-consistent molecular-orbital methods. 22. Small split-valence basis sets for second-row elements,” *Journal of the American Chemical Society*, vol. 104, no. 10, pp. 2797–2803, 1982.
- [11] J. Tamuliene, R. Vaisnoras, M.-L. Balevicius, and L. Rastiniene, “Geometrical structure of small Co nanoparticles,” in *Proceedings of the Advanced Optical Materials, Technologies, and Devices*, vol. 6596 of *Proceedings of SPIE*, p. 65961G, January 2007.
- [12] M. W. Schmidt, K. K. Baldrige, J. A. Boatz, et al., “General atomic and molecular electronic structure system,” *Journal Computational Chemistry*, vol. 14, p. 1347, 1993.
- [13] M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., *Gaussian 03, Revision C.02*, Gaussian, Wallingford, Oxfordshire, UK, 2004.
- [14] J. Dalton, “A molecular electronic structure program,” Release 2.0, 2005, <http://www.kjemi.uio.no/software/dalton/dalton.html>.
- [15] A. Schafer, H. Horn, and R. Ahlrichs, “Fully optimized contracted Gaussian basis sets for atoms Li to Kr,” *The Journal of Chemical Physics*, vol. 97, no. 44, pp. 2571–2577, 1992.
- [16] P.-O. Astrand, K. V. Mikkelsen, K. Ruud, and T. Helgaker, “Magnetizabilities and nuclear shielding constants of the fluoromethanes in the gas phase and solution,” *The Journal of Physical Chemistry*, vol. 100, pp. 19771–19782, 1996.
- [17] Y. Ichiyana and S. Yamada, “The size-dependent magnetic properties of  $\text{Co}_3\text{O}_4$  nanoparticles,” *Polyhedron*, vol. 24, pp. 2813–2816, 2005.
- [18] Ch. P. Graf, R. Birringer, and A. Michels, “Synthesis and magnetic properties of cobalt nanocubes,” *Physical Review B*, vol. 73, pp. 212–404, 2006.
- [19] M. Gruyters, “Spin-glass-like behaviour in CoO nanoparticles and the origin of exchange bias in layered CoO/ferromagnet structures,” *Physical Review Letters*, vol. 95, no. 7, Article ID 077204, 2005.



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