STABILITY AND MAGNETIC PROPERTIES OF Co_2O_m ($m = 1, \ldots, 7$) CLUSTERS

J. Tamulienė [a], R. Vaišnoras [b], G. Badenes [c], and L.M. Balevičius [d]

[a] *Vilnius University Institute of Theoretical Physics and Astronomy, A. Goštauto 12, LT-01108 Vilnius, Lithuania*
E-mail: gicevic@itpa.lt
[b] *Vilnius Pedagogical University, Studentų 39, LT-08016 Vilnius, Lithuania*
[c] *The Institute of Photonic Sciences, Av. del Canal Olímpic s/n, 08860 Castelldefels (Barcelona), Spain*
[d] *Faculty of Physics of Vilnius University, Saulėtekio 9, LT-10222 Vilnius, Lithuania*

In the present work theoretical investigations of Co_2O_m ($m = 1, \ldots, 7$) by applying density functional approach are performed. Calculations reveal that the stability of these compounds increases when the number of O atoms increases. The increase of the number of the oxygen atoms leads to the elongation of the Co–Co bond length. We obtain that the most stable nanoparticle (NP) is Co_2O_6. Investigation of magnetization indicates that the NP with high symmetry is demonstrating the paramagnetic features. Calculation results show that only Co_2O_3 and Co_2O_4 display paramagnetic properties while other investigated NPs (Co_2O, Co_2O_2, and Co_2O_6) exhibit diamagnetic properties.

Keywords: nanoparticles, magnetizability, stability

PACS: 31.15.Ar, 31.15.Ew, 33.15.-e

1. Introduction

Properties of nanoparticles (NPs) depend on their size. Magnetic cobalt NPs become very important for their applications in magnetic storage technology. The fast read-write processes in recording nanophotonic devices favour smaller size magnetic NPs, where reduction of magnetic coercivity is expected. However, the stability of NPs is an important factor. Usually a metallic NP easily oxidizes in air and cobalt NPs could loose their magnetic properties. At present NPs and their magnetic properties are the focus of many studies. It is established that for magnetic NPs the surface spins compete with the core spins, resulting in the unusual magnetic properties with a multiple assortment of technological applications which include the biomedical and hard-drive densifying technologies. In this content, the Co NPs are studied very intensively. The application of these particles is ranging from ultrahigh density recording media to medicine and, in addition, they are a traditional precursor of anode materials in Li-ion rechargeable batteries and an effective catalyst in the reduction of SO_2 by Co and NO by methane [1].

Extensive studies on ferromagnetic bulk materials and thin films have highlighted the magnetic anisotropy energy dependence on crystal symmetry and atomic composition [2]. Even the structural parameters such as the shape of the particles or the interatomic distances are affected by these processes. It has been found that the magnetic anisotropy energy is dependent on single-atom coordination changes. These results confirm the theoretical predictions and are of fundamental value in understanding how the magnetic anisotropy develops in finite-sized magnetic particles [3]. Besides this size effect, the NP behaviour is influenced by the proximity of neighbouring particles, i.e. dipolar interparticle interactions lead to the appearance of collective behaviour [4]. On the other hand, the structure effects a high chemical stability of NPs even if they are in contact with the ambient, in particular with oxygen.

Pure CoO NPs in the 4.5–18 nm range have been prepared by the decomposition of Co(II) cupferronate [5]. These particles exhibit a superparamagnetic behaviour at room temperature, and a large orbital contribution to the magnetic moment at low temperatures has been observed. The core-shell NPs (Co–CoO) are examined and it is established that the magnetic properties of these particles strongly depend on the plane coverage. The reported results demonstrate the essential role played by shells in stabilizing the magnetism of Co–CoO NPs. Some reports on the preparation and properties of pure

CoO in bulk describe the difficulties to obtain the materials in pure form by simple methods [6]. The particles are often being contaminated with Co_3O_4 or Co metal. The greater stability of Co_3O_4 than CoO is also established. However, the reports concerning the other Co_nO_m particle properties are not known and there is no clear indication on structure and stability of these Co NPs. Thus, the aim of our investigations is to shed some light on the stability and magnetic properties of the Co_nO_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 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 [7], – a representative standard DFT method. The 6-31G basis set has been used as well [8]. The basis set was chosen keeping in mind relatively minimum computational costs. The structures of the investigated NPs 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. We have examined almost all candidate configurations with different symmetry for cluster Co_2O_m ($m = 1, \ldots, 7$). The GAMESS and Gaussian program suites were used for all simulations here [9, 10].

Isotropic magnetizabilities of the most stable clusters were calculated by adopting the quantum mechanical response theory and London atomic orbital to ensure gauge-origin independent results and fast basis set convergence by using Dalton program [11]. The approach used allows us to calculate accurate magnetizabilities even for quite large molecules at a moderate cost of computer time. In this case the B3LYP method with Altrichs-pVDZ basis set was used [12]. This basis set has been obtained by optimizing the exponents and contraction coefficients in ground state Restricted Open Hartree–Fock (ROHF) calculations and there are in total 241 contracted functions. It is shown that the isotropic magnetizability and its anisotropy are remarkably constant with respect to the basis set and close to experiment, too [13]. So, the obtained performances allow us to foresee how magnetic properties of the particles depend on their structures.

3. Investigation results

Stability of small Co NPs is not very high [14]. On the basis of our previous investigation it is speculated that these NPs are non-rigid structures. It implies that the geometrical structure of these particles could change very quickly due to the tunnelling effect. Hence, we are trying to answer the question what and how can change the stability, structure, and, as a consequence, the properties of small Co NPs. So, Co_2O_m ($m = 1, \ldots, 6$) derivatives were investigated to find the most stable ones and to establish the number of O atoms that Co atoms may accept. On the other hand, the investigations allow us to foresee the condition for the breaking of metal Co–Co bond.

The most stable structures of the Co_2O_m derivatives are presented in Fig. 1.

Firstly, it is necessary to mention that two Co atoms could accept only six oxygen atoms. This structure is the most stable. The following increase of the oxygen number leads to O–O bond formation, i.e. new Co–O bonds are not created. Generally, the increase of the above number up to 6 leads to higher stability of the above derivatives (Fig. 2).

It is emphasized that a small binding energy decrease (the number of oxygen number is 4) is related with the Co atom oxidation state. In the compound Co_2O_m ($m = 1, 2, 3$), the oxidation state of Co is +3, while from $m = 4$ this state is +5. The appearance of O–O bonds lowers the stability of Co NPs.

The HOMO-LUMO gap investigations indicated that the stability increased with increasing the number of O when the Co oxidation state was 3 (Fig. 3). Alternatively, the HOMO–LUMO gap decreases with the growth of the O number in the case of Co^{+5} (when the number of O changes from 4 to 5 and from 6 to 7). The observations could be related with the Co–Co bond dissolving in the Co_2O_5 and Co_2O_6 compounds as well as with the O–O bond presence in the Co_2O_7 compound. In summary, the results of the investigation confirm that an O atom should stabilize Co NPs. However, our study indicates that Co_2O_3 is more stable than Co_2O_2 (or CoO) and Co_2O_6 (or CoO_3) should also be more stable than CoO derivatives.

The attention was paid to the magnetic properties of these derivatives. Magnetizability (commonly known as susceptibility) was investigated. Let us remember that the increase of the number of oxygen atoms in the compound and the changeability of the oxidation state lead to increase of the Co–Co bond length and weakening of Co–Co bonds that is important for the magnetic
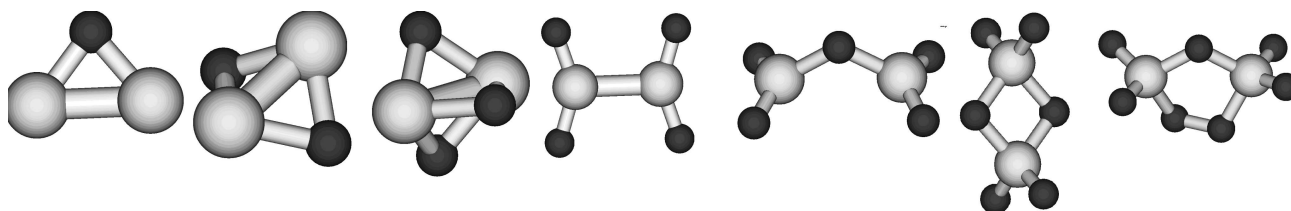
Fig. 1. Views of Co_2O_m ($m = 1, \ldots, 7$).

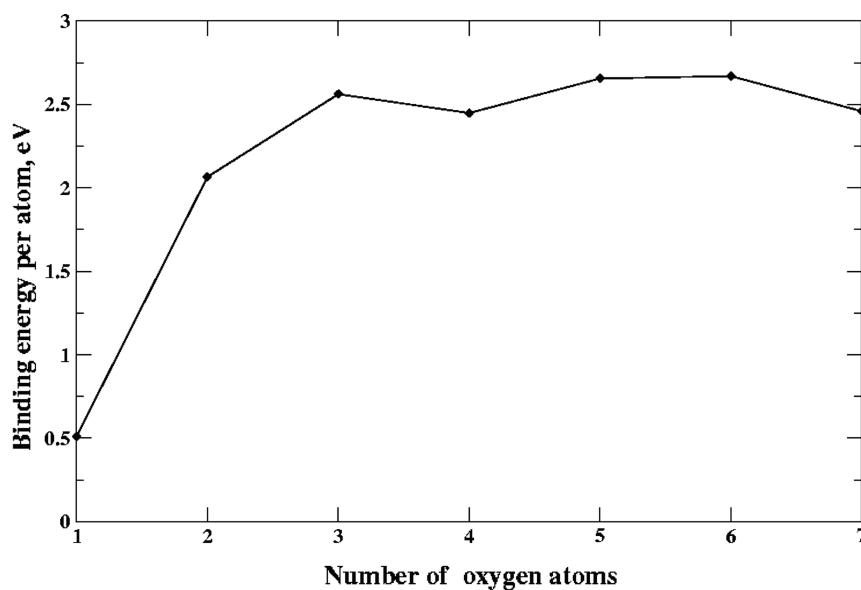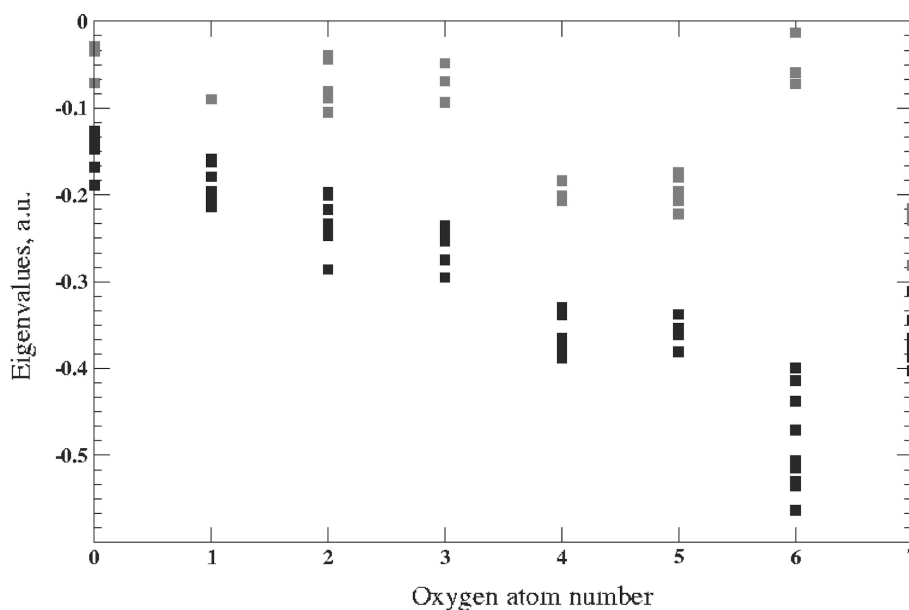Fig. 2. Dependence of binding energy per atom on the oxygen atom number.

Fig. 3. Schematic orbital diagrams for Co_2O_m ($m = 1, \ldots, 7$) compounds. Black colour represents occupied orbitals while virtual orbitals are marked in grey.

Table 1. Parameters of the Co_2O_m ($m = 1, \ldots, 7$) particles obtained by B3LYP/6-31G method.

Compound	Co–Co bond length, Å	Bond order	Symmetry	Magnetizability, a. u.	Isotropic g tensor, a. u.	Co oxidation state
Co_2O	2.11	1.53	C_{2v}	−3.26	−0.36	III
Co_2O_2	2.11	0.84	C_{1h}	−6.07	−0.24	III
Co_2O_3	2.24	0.24	D_{3h}	8.99	−0.58	III
Co_2O_4	2.29	0.68	D_{2h}	49.05	−1.17	V
Co_2O_5	2.99	0.06	C_{2v}	−1.82	−0.22	V
Co_2O_6	2.65	0.20	D_{2h}	−10.63	−0.16	V
Co_2O_7	3.00	0.20	C_1	−5.14	−0.18	V
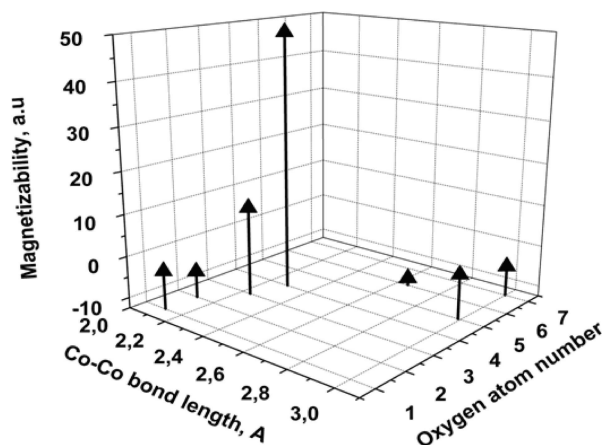
Fig. 4. Magnetizability dependence on Co–Co bond length and oxygen number.

Fig. 5. Total electron density of the Co_2O_m ($m = 1, \ldots, 7$) particle.

properties of these compounds, because magnetic properties depend on the bond length and nature (Table 1, Fig. 4). Thus, to explain the magnetic properties of the investigated molecules, attention should be paid to the Co–Co bond length, total electron density, and isotropic g tensor that represents the spin angular momentum.

It is possible to see that only Co_2O_3 and Co_2O_4 are paramagnetic while the other investigated derivatives (Co_2O, Co_2O_2, Co_2O_5, Co_2O_6, and Co_2O_7) possess diamagnetic properties. Moreover, the magnetizability of Co_2O_4 is higher than that of pure Co with magnetizability equal to 14.73 a. u. It is notable that the paramagnetic molecule symmetry is higher than in other investigated compounds, but there are not enough cases to make more general conclusions (Table 1).

Firstly, it is necessary to mention that the Co–Co bonds are absent in the Co_2O_5, Co_2O_3, and Co_2O_7 molecules, indicating that the distance between Co atoms is larger than single bond length, 2.46 Å [15, 16]. Views of the total electron density confirm the results (Fig. 5(a–g)). It is possible to see that in the case of paramagnetic Co_2O_4 the total electron density on Co–Co bond is smaller than that in the other investigated compound where the bond is present. We predict that in this case the unpaired electron density is present on

the Co–Co bond despite that the system posseses an even number of electrons, i. e. spins are not correlated (compensated), so the paramagnetic properties are observed. The value of the g tensor proves the prediction of unpaired electron spin presence. The absolute value of isotropic g tensor of Co_2O_4 is 1.17 – more than half of the free electron g value 2.00. Similar states are obtained in biradicals where the number of atomic orbitals

that may be occupied is larger than the number of electrons [17]. That leads to appearance of electrons on antibonding orbitals.

Let us remember that the increasing number of O atoms decreases the difference between the number of electrons and the number of atomic orbitals that they may occupy, so the uncorrelated spins disappear. In our investigated cases, the Co_2O_5 and Co_2O are worse diamagnetics than Co_2O_6 and Co_2O_2 respectively.

A most interesting situation arises in the case of Co_2O_7 and Co_2O_3 derivatives. The obtained properties do not correlate with general observations that the increasing number of oxygen atoms leads to uncorrelated spin disappearance and as a consequence the compounds become more diamagnetic. In the above case Co_2O_7 is a worse diamagnetic than Co_2O_6, while Co_2O_3 is paramagnetic. The assumption that in some cases the presence of O–O bond influenced the magnetic properties of Co_2O_3 was made. So far we confirm the assumption.

To shed some light on the obtained characteristics we intend to present here the most important orbitals of the paramagnetic compounds (Fig. 6). It is possible to see that adding an oxygen atom to Co_2O_3 compounds one makes the unoccupied orbitals the highest occupied molecular orbitals (HOMO-1) of Co_2O_4. Additionally, one bonding occupied orbital of Co_2O_3 is unoccupied in Co_2O_4. Moreover, the additional oxygen atom leads to the partial reversion to the Co_2O_3 orbitals, i. e. HOMO of Co_2O_4 again becomes LUMO (lowest unoccupied MO) of Co_2O_5 (Fig. 6). The energy of the unoccupied orbitals changes dramatically when the oxygen atom number increases from 3 to 4. Such change leads to the displacement of the two electrons on d_z^2 orbitals of Co atoms in the Co_2O_4 compound. The above electrons create Co–Co bonds. However, the energy of this orbital is similar to that of the other
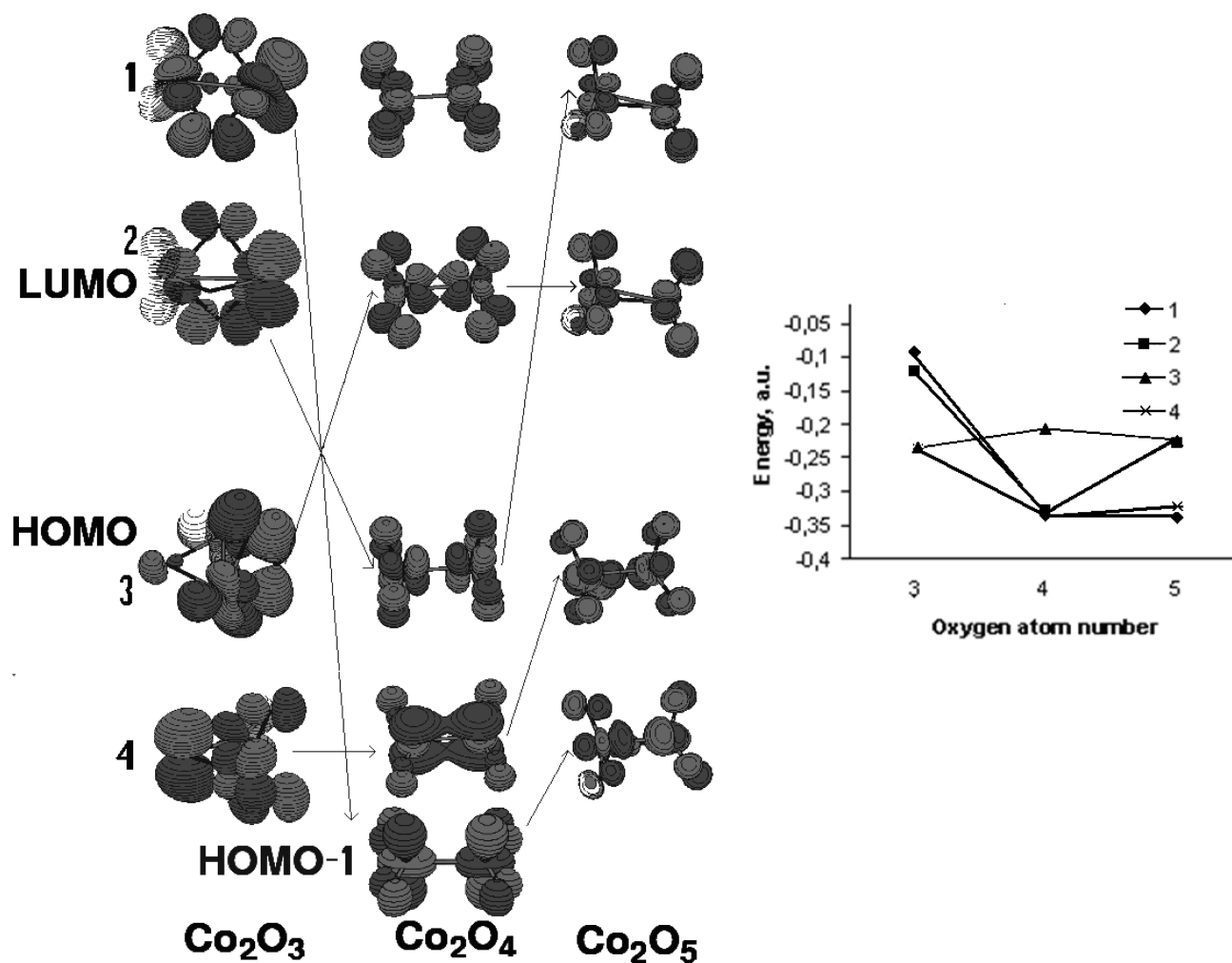

Fig. 6. Correlation diagram of molecular orbitals and their energy dependence on the oxygen atom number. Broad lines in picture represent the structure of the nanoparticles, narrow lines indicate changes of position of molecular function when O atom number is increasing. Darker structures represent positive parts of atomic functions while grey ones mark the negative parts.

high-lying antibonding occupied orbital, which are unoccupied in the Co_2O_3 compound. Thus, the repulsion between the electrons is larger than in the other investigated compound, therefore they tend to be as far as possible from each other and become non-strongly correlated. The phenomenon observed is the elongation of Co–Co bonds and, as a consequence, the unpaired spin presence. The additional oxygen atom presence leads to smaller electron repulsion and stronger electron correlation because one antibonding orbital becomes unoccupied and its energy decreases (Fig. 6).

Hence, one of the reasons why Co_2O_3 is paramagnetic is the lower electron density on the Co–Co bond than in Co_2O_4 (Fig. 5(d)). However, the presence of Co–Co bonds does not explain fully why the absolute values of isotropic g tensor of the above compound is equal to 0.58, being much more smaller than that of Co_2O_4 and slightly larger than that of the other investigated molecules (Table 1). In addition, it has been pointed out that an orbital shift is obtained when Co_2O_2 compound accepts an additional oxygen atom (that is the reason why the results are not presented). On the other hand, most probably the charge density between Co–Co bonds appears due to overlap of p orbital of oxygen atoms (Fig. 6). It implies that the paramagnetic properties of the Co_2O_3 are related with electrons occupying the p orbitals of different oxygen atoms. That leads to the formation of a biradical due to charge location on certain atoms and, as a consequence, to the appearance of repulsion electrons due to steric hindrance. Meanwhile, only Co_2O_7 derivative possesses O–O bonds and their diamagnetic properties are worse than those of Co_2O_7. Obviously, the prediction that the presence of O–O bond may decrease diamagnetic properties is confirmed.

In summary, it is possible to foresee that the Co compound will be paramagnetic due to several reasons: (i) the unpaired electron location on the Co–Co bonds, (ii) the small total electron charge density between Co atoms which appears due to overlap of p orbitals of the oxygen atoms.

4. Conclusion

In the effort to shed light on the stability and magnetic properties of the Co_2O_n derivatives the quantum mechanical investigations were performed. We obtained that the most stable NP is Co_2O_6, while only the stability of Co_3O_4 and CoO has been reported earlier. Investigation of magnetization indicates that the compound with high symmetry is demonstrating

paramagnetic features. Calculation results show that only Co_2O_3 and Co_2O_4 display paramagnetic properties while other investigated derivatives (Co_2O, Co_2O_2, and Co_2O_6) reveal diamagnetic properties. Investigation of the most important orbitals and total electron density distribution allows us to foresee that the Co compound will be paramagnetic.

References

[1] D.A. Resnick, K. Gilmore, Y.U. Idzerda, M.T. Klem, M. Allen, T.T. Douglas, E. Arenholz, and M. Young, Magnetic properties of Co_3O_4 nanoparticles mineralized in *Listeria innocua* Dps, J. Appl. Phys. **99**, 08Q501 (2006).

[2] M. Sakurai, K. Watanabe, K. Sumiyama, and K. Suzuki, Magic numbers in Fe clusters produced by laser vaporization source, J. Phys. Soc. Jpn. **67**, 2571 (1998).

[3] P. Gambardella, S. Rusponi, M. Veronese, S.S. Dhesi, C. Grazioli, A. Dallmeyer, I. Cabria, R. Zeller, P.H. Dederichs, K. Kern, C. Carbone, and H. Brune, Giant magnetic anisotropy of single cobalt atoms and nanoparticles, Science **300**, 1130 (2003).

[4] J. Nogués, V. Skumryev, J. Sort, S. Stoyanov, and D. Givord, Shell-driven magnetic stability in core-shell nanoparticles, Phys. Rev. Lett. **97**, 157203 (2006).

[5] Sh. Tsukamoto and N. Koguchi, Magic numbers in Ga clusters on GaAs (0 0 1) surface, J. Crystal Growth **209**, 258 (2000).

[6] M. Ghosh, E.V. Sampathkumaran, and C.N.R. Rao, Synthesis and magnetic properties of CoO nanoparticles, Chem. Mater. **17**, 2348 (2005).

[7] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. **98**, 5648 (1993).

[8] 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, J. Am. Chem. Soc. **104**, 2797 (1982).

[9] M.W. Schmidt, K.K. Baldrige, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, Shujun Su, T.L. Windus, M. Dupuis, and J.A. Montgomery Jr., General atomic and molecular electronic structure system, J. Comput. Chem. **14**, 1347 (1993).

[10] *Gaussian 03, Revision C.02*, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, and J.A. Pople, Gaussian, Inc., Wallingford CT (2004).

[11] *DALTON, a molecular electronic structure program, Release 2.0* (2005), see http://www.kjemi.uio.no/software/dalton/dalton.html .

[12] A. Schafer, H. Horn, and R. Ahlrichs, Fully optimized contracted Gaussian basis sets for atoms Li to Kr, J. Chem. Phys. **97**, 2571 (1992).

[13] P.-O. Åstrand, K.V. Mikkelsen, K. Ruud, and T. Helgaker, Magnetizabilities and nuclear shielding constants of the fluoromethanes in the gas phase and solution, J. Phys. Chem. **100**, 19771 (1996).

[14] J. Tamulienė, R. Vaišnoras, M.-L. Balevičius, and L. Rastinienė, Geometrical structure of small Co nanoparticles, in: *Advanced Optical Materials, Technologies, and Devices*, eds. S. Ašmontas and J. Gradauskas, Proc. SPIE **6596**, 65961G (2006).

[15] *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Supplement 1956–1959, ed. L.E. Sutton, Special publication No. 18 (Chemical Society, London, UK, 1965).

[16] L. Pauling, Evidence from bond lenghts and bond angles for enneacovalence of cobalt, rhodium, iridium, iron, ruthenium, and osmium in compounds with elements of medium electronegativity, Proc. Natl. Acad. Sci. USA **81**, 1918 (1984).

[17] A. Shimizu, M. Uruichi, K. Yakushi, M. Nakano, D. Shiomi, T. Kubo, T. Takui, Y. Morita, and K. Nakasuji, Singlet biradical character of phenalenyl-based Kekulé hydrocarbon with naphthoquinoid structure, Org. Lett. **9**, 81 (2007).

Co_2O_m (m = 1, ..., 7) KLASTERIŲ STABILUMAS IR MAGNETINĖS SAVYBĖS

J. Tamulienė [a], R. Vaišnoras [b], G. Badenes [c], L.M. Balevičius [d]

[a] *Vilniaus universiteto Teorinės fizikos ir astronomijos institutas, Vilnius, Lietuva*
[b] *Vilniaus pedagoginis universitetas, Vilnius, Lietuva*
[c] *Fotoninių mokslų institutas, Castelldefels, Ispanija*
[d] *Vilniaus universiteto Fizikos fakultetas, Vilnius, Lietuva*

Santrauka

Pateikti Co_2O_m (m = 1, ..., 7) dalelių kvantinės chemijos tyrimai atlikti tankio funkcionalo metodu (B3LYP) 6-31G bazės artinyje. Nustatyta, kad Co_2O_6 dalelės yra stabiliausios tarp visų tirtų darinių, todėl tikėtina, kad jos turi būti aptinkamos greta Co_3O_4 ir CoO dalelių, kurių savybės yra plačiai aprašytos. Įvertinus dalelių magnetinamumą ir izotropinio g tenzoriaus vertę nustatyta, kad tik Co_2O_3 ir Co_2O_4 yra paramagnetikai, o visos kitos tirtos dalelės – diamagnetikai. Pastebėta, kad paramagnetinių dalelių taškinių grupių simetrija yra aukštesnė nei diamagnetinių, tačiau šiuo metu turimų tyrimų rezultatų nepakanka, kad šis pastebėjimas būtų pateiktas kaip išvada. Remiantis rezultatais, kurie gauti išanalizavus paramagnetinių junginių aukščiausių užimtų (HOMO) ir žemiausių neužimtų (LUMO) orbitalių ir elektronų tankį, nustatyta, kad tirti dariniai gali būti paramagnetikai dėl kelių priežasčių: 1) dėl nesuporuotų sukinių elektronų išsidėstymo ant Co–Co jungties, 2) dėl nedidelio elektronų tankio tarp Co atomų, atsirandančio persiklojant deguonies atomų p orbitalėms.