CrossMark

ORIGINAL RESEARCH

The electronic structure of nanoparticle: theoretical study of small Cobalt clusters (Co$_n$, n = 2–5) (part A)

A. H. Pakiari[1] · E. Dehghanpisheh[1]

Abstract Electronic and geometrical structures of small Cobalt cluster (Co$_n$, n = 2–5), which were used as building block in Cobalt cluster compounds, were fully investigated in this article. Since small Cobalt clusters as a nanoparticle have many applications in scientific works and technology, it is essential for understanding their relatively accurate *electronic* structure. The most stable symmetrically and electronically structure confirmed by frequency test for studied clusters is as follows: 5-et (quintet) Co$_2$ is of course linear, and its HOMOs described by degenerate d_{xy} orbitals in β-spin part located on both atoms; 8-et (octet) Co$_3$ is almost scalene triangle and its HOMO in s-orbital of α-spin part located on Co$_{(1)}$; 11-et Co$_4$ is rhombus, d_{xz} orbital of β-spin part located on Co$_{(2)}$ is its HOMO part. 12-et Co$_5$ is pyramidal with HOMO in p_x orbital located on Co$_{(5)}$ in β-spin part, which show very low (0.06) occupation number. This large depletion of electron in HOMO occupation of Co$_5$ explains high chemical reactivity of this species. Density functional theory, DFT, was used through software Gaussian 09. *Xc*-correlation functional was chosen among the many recommended *xc*-functionals for transition metal in the literature by calibration procedure in such a way that the results can match with experimental values. So suitable *xc*-functional B3P86 and *6-311++G** basis set were found. Natural bond orbital, NBO, has also been used for analysis.

Keywords Nanotransition metal Cobalt cluster · Calibration of DFT · NBO analysis · Electronic structures

Introduction

Metal cluster is the name of compounds having direct metal–metal bond. Our interest is electronic structure of transition metal cluster (*TM cluster*). F.A. Cotton was one of the first scientists who introduced the idea of "cluster chemistry" for transition metal in the early 1960s [1]. We can divide cluster types as "naked" clusters (without stabilizing ligands) and clusters with ligands. Since small TM clusters (with two, three, four and five atoms) have been used in this type of cluster chemistry compounds, we are interested in electronic structure of small TM cluster as building block of TM cluster compounds.

More than five decades have been passed: Many scientists have been attracted by TM clusters, in both theoretical and experimental approaches, especially the small ones [2–8]. It will be inexpensive and time saving to study small TM cluster theoretically to see the electronic properties, optical and magnetic behaviors of various structures in comparison with experimental values.

Each TM clusters shows different chemical properties, even though they are neighboring elements. Several industrial reactions make use of Cobalt (Co)-based catalysis. As an example, we can mention that Cobalt(III)-oxo cubane clusters act as catalysts for oxidation of organic substrate [9], and we can also find Cobalt clusters mixed by other atoms like selenide, as quantum dots [10]. Also in the world of nanoparticles and their applications [1], Cobalt

✉ A. H. Pakiari
  pakiariah@gmail.com

[1] Chemistry Department, College of Science, Shiraz University, Eram square, Eram street, 7146713565 Shiraz, Iran

clusters attract lots of attention. Some of the recent articles are as follows: nanocatalytic systems and high-density magnetic storage devices [11], silica coating of Cobalt nanoparticles increase their magnetic and chemical stability for biomedical applications [12], time-resolved observations of water oxidation intermediates on a Cobalt oxide nanoparticle catalyst [13], fabrication of silver-coated Cobalt ferrite nanocomposite and the study of its antibacterial activity [14], on some applications of nanoparticles synthesized in the gas phase by magnetron discharges [15], mass-filtered Cobalt clusters in contact with epitaxially ordered metal surfaces [16], magnetic nanoparticles: synthesis, stabilization, functionalization, characterization and applications [17], controllable growth of Cobalt oxide nanoparticles on reduced graphene oxide and its application for highly sensitive glucose sensor [18].

The main part of our studies focusses on natural bond orbital (NBO) analysis results which let us know the nature of each bonds, percentage of its hybridizations, occupancy and energy of each individual bonds. We also consider total Lewis and nonLewis parts of each α- and β-spin parts, types of radicals and their NBO shapes to predict the active sites where other molecules would attack to Cobalt clusters.

Computational method

In the present work, the quantum mechanical calculations have been done to investigate the electronic structures, types and nature of the bonds by utility of the density functional theory (DFT) part of the Gaussian 09 [19]. The calculations have been based on the gradient-corrected methods of the DFT [20] and the exchange–correlation functional B3P86. The B3P86 method is an example of a hybrid density functional, which explicitly includes exact HF exchange. This hybrid GGA functional contains Becke 3-parameter hybrid density functional with combined Perdew86 nonlocal correlation [21].We use $6\text{-}311{+}{+}G^*$ basis set.

Deep studies have been done by NBO. These analysis procedures convert molecular wave function into the terms which are common to the concept of chemist, as examples we can mention localized Lewis structures, charge, bond order, bond type, hybridization, resonance, etc. The essence of mathematical part of NBO came from LÖwdin's Natural orbitals that are eigen orbitals of the first-order reduced density operator [22–24]. Shull has proved that natural orbital can be a powerful tool for understanding the nature of chemical bonding in molecules [25, 26]. Localized Lewis-type NBO method is more valid than other pervious methods of localization. The history of localization is too long to explain and before NBO, it was not

possible to analyze the results according to the concept of chemistry. The NBOs are linear combinations of natural hybrid orbitals that are in turn obtained as linear combinations of natural atomic orbitals. In fact, NBO belongs to the natural localized, complete, orthonormal set of one electron functions, which can be used for expanding canonical delocalized molecular orbitals or forming matrix representation of one electron operators. The NBO program uses these natural localized sets to perform tasks connecting to localize analysis of wave-function properties, such as natural resonance theory (NRT) analysis.

Results and discussion

Applying DFT for the first-row transition metal complexes seems to be more reliable than the Hartree–Fock (HF) approach, because DFT considers more electron correlations than SCF. In the MP2 approach, a near-degeneracy problem affects the accuracy of the geometry optimization of the molecules, therefore, the perturbation series (MP2, MP3 and MP4) also fail to converge in some cases [27]. Although we know that logically, some post Hartree–Fock method calculations such as CCSD or CCSD(T) can be the better choice for our systems and results of the multi-configurational methods such as MCSCF and CASPT2 can be more reliable, we prefer DFT for our systems because of two reasons: first, its great balance between its computational costs and its accuracy. Second, for some problems, such as in the case of chromium clusters (dimer), MCSCF calculations could not reach to correct experimental bond length after tedious calculations [28].

It should be mentioned that the main results, tables and figures are presented in the manuscript, and more information, additional references and Cartesian coordinates of different Cobalt clusters will be offered in supplementary section.

Calibration of DFT for Cobalt cluster (Cobalt dimer, Co₂)

DFT procedure can be exact if exact exchange correlation functional (*xc*-functional) is known and appropriate basis set is selected. Since exact *xc*-functional has not been discovered yet [14], there are many suggested *xc*-functionals in the literature, and so, it can say that DFT is not a variational method. There are various articles in the literature as a benchmark test for some desired properties such as Holthausen and Truhlar calculations [29, 30].We should find the best *xc*-functional and appropriate basis set for our work which makes lower percentage of error with corresponding experimental values. This type of work for DFT method, which is finding a suitable *xc*-functional and

basis set of specific chemical species, is called *calibration* of DFT. So for calibration of DFT method in practical, first our geometry should be in a local minimum (with positive frequencies). The next step is to find experimental values for multiplicity (2S+1). Then check the best spin contaminations and its deviations (order of 10^{-2} is acceptable) among the other tested xc-functionals. And finally, we check the other experimental values which are available, i.e., bond length in this case.

Calibration for Cobalt clusters can be done for its dimer, Co_2, because of experimental bond length (1.95 Å) and multiplicity (2S+1 = quintet). Experimental bond length of Co_2 has been first reported by mass spectroscopy [31] to be 2.31 Å, then in 1993 by photo dissociation technique [32] found to be between 1.6 and 2.3 Å (average is 1.95 Å), and also in 1997 by spectroscopic tool shown to be 1.95 Å [33]. There are some recommended xc-functionals for first row of transition metals. These are BPW91, B3PW91, B3LYP, BLYP, B97-1, B97-2, M06, M06L, TPSS, BP86 and B3P86 [29, 34]. Results of relevant calculations for Co_2 are collected in Table 1, and the results of other works are tabulated in Table 1s in supplementary information (hereafter we mention table in supplementary information with its number and a lowercase s, example Table 1s). No imaginary frequencies have been detected. Quintet multiplicity had been found in all of the recommended xc-functionals. We obtained the correct quintet multiplicity with all tested functionals. The best spin contamination, with the acceptable deviation; see Table 1, about 0.0003, belongs to B3P86 xc-functional.

So our recommended xc-functional is B3P86 with the bond length of 1.925 Å, quintet multiplicity and fortuitously lowest energy among the other tested xc-functionals which has a close correspondence to experimental values.

Table 1 Considerations of the different results for Co_2

Method	Deviation of S^2 ($S^2 = 6$)[a]	Energy[b]	B.L.[c]
B97-1	0.0081	−2765.12	2.013
B3Pw91	0.0136	−2765.21	1.998
M06	0.0029	−2765.21	1.940
M06-L	0.0016	−2765.25	1.976
B3LYP	0.0029	−2765.41	1.941
TPSS	0.0006	−2765.48	1.972
BPW91	0.0054	−2765.58	2.049
BLYP	0.0033	−2765.58	1.998
BP86	0.0046	−2765.71	2.045
B97-2	0.0089	−2765.88	1.998
B3P86	0.0003	−2766.56	1.925

[a] $S^2 = S(S + 1)$

[b] Energy is in atomic units
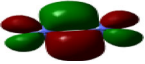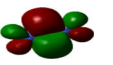
[c] B.L. = Bond length is in Angstrom
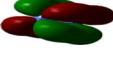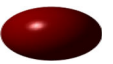
Its Mulliken analysis shows that each atom has two unpaired spins and quadruple moment is −30.49, −30.49, −21.43 (Debye-Ang) in XX, YY and ZZ directions, respectively.

NBO analysis of Co_2

Cobalt dimer contains 54 electrons, in which 36 electrons allocated for core parts and 18 electrons remain in valence parts. α-spin contribution at valence part is 11 electrons and seven electrons for β part. The total Lewis electron is 99.97 %, so it shows that all electrons can be localized. Due to multiplicity of 5-et, all orbitals in valence shell (whether bonding or nonbonding) are singly occupied and all are in the form of radical. Descriptions of these bonds are presented in Table 2. Natural bond orbital analysis (NBO) shows only one σ-bond orbital for α part. There are five electrons in bonding β part and all with occupation one: two σ-bonds, two degenerate π-bonds in different directions and one δ-bond. It is interesting that the first σ-bond in β-spin, with energy −206.28 kcal/mol, has the same energy of σ-bond in α-spin, with the same hybridization (both contain s–s orbitals), so it seems that they form closed shell electronic structures.

There are twelve electrons in nonbonding as radical, in which 10 electrons are α-spin and two electrons are β-spin. The nonbonding radicals and their types are illustrated in Table 3. All electrons in nonbonding have occupation almost one. Active space is β-spin part. Therefore, the d_{xy} degenerate orbitals on both atoms in β-spin (energy of each

Table 2 NBO descriptors of Co_2 cluster (for α- and β-spin parts), showing diatomic bonding orbital (σ, π, δ), hybridization and energy of each bond

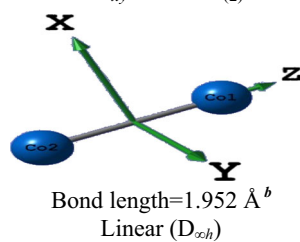| NBO bond	h_A–h_B %[a]	Occ	Energy[b]	NBO shape
β-spin				
1. $\sigma_{Co_{(1)}-Co_{(2)}}$	$s^{98.1}$–$s^{98.1}$	1	−206.28	
2. $\sigma_{Co_{(1)}-Co_{(2)}}$	$d_z^{299.5}$–$d_z^{299.5}$	1	−162.44	
3. $\pi_{Co_{(1)}-Co_{(2)}}$	$d_{xz}^{97.3}$–$d_{xz}^{97.3}$	1	−142.56	
4. $\pi_{Co_{(1)}-Co_{(2)}}$	$d_{yz}^{97.3}$–$d_{yz}^{97.3}$	1	−142.56	
5. $\delta_{Co_{(1)}-Co_{(2)}}$	d_{x-y}^{22100}–d_{x-y}^{22100}	1	−100.09	
α-Spin				
1. $\sigma_{Co_{(1)}-Co_{(2)}}$	$s^{99.1}$–$s^{99.1}$	1	−206.28	

occ Occupancy

[a] h_A–h_B% = type of maximum h_A–h_B%

[b] Energy is in kcal/mol

Table 3 Cobalt dimer cluster and all nonbonding radicals of both α- and β-spin parts, charge transfers, structure, symmetry and bond length

No	Orbital	Atom	Occ	Type	E[a]	Orbital	Atom	Occ	Type	E[a]	No
β-spin						α-spin					
1	d_{xy}	Co(1)	1	π	−137.3	d_z^2	Co(1)	1	σ	−205.3	1
2	d_{xy}	Co(2)	1	π	−137.3	d_z^2	Co(2)	1	σ	−205.3	2
						d_{xz}	Co(1)	1	π	−195.6	3
						d_{yz}	Co(1)	1	π	−195.6	4
						d_{xz}	Co(2)	1	π	−195.6	5
						d_{yz}	Co(2)	1	π	−195.6	6
						d_{x-y}^{22}	Co(1)	1	π	−180.9	7
						d_{x-y}^{22}	Co(2)	1	π	−180.9	8
						d_{xy}	Co(1)	1	π	−167.4	9
						d_{xy}	Co(2)	1	π	−167.4	10

Bond length = 1.952 Å[b]
Linear (D∞h)

occ Occupancy

[a] Energy is in kcal/mol

[b] Bond length is in angstrom

orbital is −137.3 kcal/mol.) are HOMOs. Except two electrons in α-spin, which are σ-radicals and are very stable, the rest of radicals are π-radicals and perpendicular to the plane of molecule. Therefore, the interactions will occur in the direction of π-radicals and almost with β-spin part.

Cobalt trimer cluster Co₃

The results of the literature search in the past for Co₃ by three different DFT (BLYP, PBE and PW91) have been summarized in Table 2s. In this table, three different symmetries have been reported; Fan et al. [35] and Pereiro et al. [36] found equilateral triangle (D_{3h}), Datta et al. [37] and Castro et al. [33] obtained isosceles triangle (C_{2v}), later in 2006 Ma et al. [4] and in 2008 Sebetci [34], calculated as a linear molecule ($D_{\infty h}$). The reported multiplicities are six or eight.

Two important points can be a good guide for selecting geometry and symmetry of polyatomic molecules: All Lewis structures for molecules with radical (lone pair) in valence shell obey Walsh rules and they must be bent (not linear). Geometries and structures with high symmetry such as D_{3h} cannot be real ground state, and they must be C_{2v} or C_s for triatomic molecules according to the Jahn–Teller effect. However, we have done calculations for Co₃ cluster with different mentioned symmetry and different multiplicities (4, 6, 8 and 10). Our obtained results show that the ground state with C_s symmetry and multiplicity of octet (8-et) calculated with B3P86 *xc*-functional is almost scalene triangle. Other symmetries and multiplicities show higher energy than C_s. The reasons for C_s symmetry are: 1) Cartesian coordinate (Table 7s) shows that molecule is positioned in xy-plane; x-coordinates of Co(1) and Co(2) are
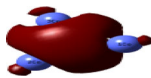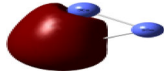
mirror image, toward z axis, (±1.286), but y-coordinates of these atoms are −0.627 and −0.622, respectively, and they are slightly different. 2) It has different components of dipole moment ($X = 0.41$, $Y = 0.26$, $Z = 0.0$ Debye). 3) Quadruple moment is: $XX = -45.82$, $YY = -37.69$, $ZZ = -44.95$ Debye-Ang, and it has one nonzero off-diagonal element in xy, which is $XY = -1.95$ Debye-Ang. 4) Mulliken spin densities of Co(1) and Co(2) are slightly different; 2.29 and 2.69, respectively (in the case of C_{2v}, they must be equal), for Co(3) is 2.01, which suggests to have quite different chemical properties.

NBO analysis for Co₃ Cluster

We have performed NBO calculations for Co₃. Cobalt trimer contains 81 electrons, in which 54 electrons allocated for core parts and 27 electrons remains in valence parts. Contributions of α-spins at valence part are 17 electrons, and 10 electrons belong to β valence part. Accuracy of total Lewis is 99 and 98.90 % for α-spin and β-spin part, respectively, so it can be said that all electrons are localized. NBO predicted only one σ-bond orbital with occupation number of 0.96 for α part and one three-center bond orbital with occupation number of 1.00 for β part. Results of NBO have been tabulated in Table 4.

We have 16 radicals for α-spins and 9 radicals for β-parts. Table 5 illustrates all nonbonding radicals of both α- and β-spin parts and charge transfers. Our active space is α-part. Interestingly, we notice that it is in contrast to Cobalt dimer. So in this cluster system, HOMO belongs to α-parts which is *s*-orbital concentrated on Co(1) (its energy is −115.9 kcal/mol), with 0.3 electron depletion. This attracted our attention immediately that causes electron charge transfers from *s*-orbital of Co(1) to p_x*Co(3) which are equal to 33.1 kcal/mol. We can
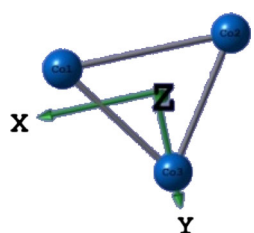
Table 4 NBO descriptors of Co$_3$ cluster (for α- and β-spin parts), showing bonding orbital, hybridization and energy of each bond

NBO bond	h_A–h_B%[a]	Occ	Energy[b]	NBO shape
β-spin				
$3C_{Co_{(1)}-Co_{(2)}-Co_{(3)}}$	$s^{85.8}$– $s^{84.0}$–$s^{86.6}$	1	−238.54	
α-Spin				
$\sigma_{Co_{(2)}-Co_{(3)}}$	s^{97}–s^{73}	0.96	−178.56	

occ Occupancy

[a] h_A–h_B% = Type of maximum h_A–h_B%

[b] Energy is in kcal/mol

Table 5 Cobalt trimer cluster, all nonbonding radicals of both α- and β-spin parts, charge transfers, symmetry and bond length

No	Orbital	Atom	Occ	Type	E[a]	Orbital	Atom	Occ	Type	E[a]	No
β-spin						*α-spin*					
1	d_z^2	Co$_{(3)}$	0.99	π	−144.6	d_{yz}	Co$_{(2)}$	0.99	π	−197.0	1
2	d_{yz}	Co$_{(3)}$	0.98	π	−142.9	d_{xz}	Co$_{(3)}$	0.99	π	−193.8	2
3	d_z^2	Co$_{(2)}$	0.99	π	−142.7	d_{xy}	Co$_{(3)}$	0.99	σ	−192.9	3
4	d_{xz}	Co$_{(2)}$	0.97	π	−140.8	d_{yz}	Co$_{(1)}$	0.99	π	−190.3	4
5	d_z^2	Co$_{(1)}$	0.99	π	−140.7	d_{xy}	Co$_{(2)}$	0.99	σ	−186.5	5
6	d_{xz}	Co$_{(1)}$	0.99	π	−140.5	d_z^2	Co$_{(2)}$	0.99	π	−185.9	6
7	d_{x-y}^{22}	Co$_{(3)}$	0.91	σ	−136.7	d_{x-y}^{22}	Co$_{(1)}$	0.99	σ	−183.9	7
8	d_{xy}	Co$_{(1)}$	0.88	σ	−130.8	d_{x-y}^{22}	Co$_{(2)}$	0.99	σ	−181.8	8
9	d_{x-y}^{22}	Co$_{(2)}$	0.88	σ	−128.5	d_z^2	Co$_{(1)}$	0.99	π	−180.5	9
Charge transfers					E$_{CT}$	d_z^2	Co$_{(3)}$	0.99	π	−180.5	10
d_{x-y}^{22}	Co$_{(2)}$	to	3C*		3.9	d_{x-y}^{22}	Co$_{(3)}$	0.99	σ	−177.8	11
d_{x-y}^{22}	Co$_{(2)}$	to	d_{xy}^*	Co$_{(3)}$	6.7	d_{xz}	Co$_{(2)}$	0.99	π	−175.7	12
d_{xy}	Co$_{(1)}$	to	d_{xy}^*	Co$_{(3)}$	6.7	d_{xy}	Co$_{(1)}$	0.99	σ	−175.4	13
d_{x-y}^{22}	Co$_{(3)}$	to	d_{xy}^*	Co$_{(2)}$	4.0	d_{yz}	Co$_{(3)}$	0.99	π	−173.9	14
d_{x-y}^{22}	Co$_{(3)}$	to	d_{x-y}^{22*}	Co$_{(1)}$	4.2	d_{xz}	Co$_{(1)}$	0.99	π	−173.5	15
d_{xz}	Co$_{(2)}$	to	d_{xz}^*	Co$_{(3)}$	4.2	s	Co$_{(1)}$	0.70	–	−115.9	16
						Charge transfers				E$_{CT}$	
						s	Co$_{(1)}$	to	p_x^*	Co$_{(3)}$	33.1
						s	Co$_{(1)}$	to	$\sigma_{Co_{(2)}-Co_{(3)}}^*$		6.4
						s	Co$_{(1)}$	to	p_y^*	Co$_{(3)}$	3.0
						$\sigma_{Co_{(2)}-Co_{(3)}}$		to	p_x^*	Co$_{(1)}$	10.8

$d_{Co_{(1)}Co_{(3)}}$ = 2.275 Å [b]
$d_{Co_{(2)}Co_{(3)}}$ = 2.276 Å, $d_{Co_{(1)}Co_{(2)}}$ = 2.573 Å
Almost scalene triangle (C_s)

occ Occupancy

[a] Energy is in kcal/mol

[b] Bond length is in angstrom

also notice that in β-part, there is reciprocity between three Cobalt atoms, that is, we have charge transfers from Co$_{(2)}$ to Co$_{(3)}$, from Co$_{(3)}$ to Co$_{(1)}$ and Co$_{(2)}$, and from Co$_{(1)}$ to Co$_{(3)}$ which are about 6.7 and 4 kcal/mol. These little charge transfers are due to 0.12 electron depletions in occupation numbers of Co$_{(1)}$ and Co$_{(2)}$.

Table 6 NBO descriptors of Co$_4$ (*THRESHOLD = 1.89*) cluster (for α- and β-spin parts), showing bonding orbital, hybridization, occupancy and energy of each bond

NBO bond	h_A–h_B%[a]	Occ	Energy[b]	NBO shape
β-spin				
1. $\sigma_{Co_{(1)}-Co_{(3)}}$	$d_{x-y}^{2258.5}-d_{x-y}^{2258.5}$	0.90	−183.16	
2. $\sigma_{Co_{(1)}-Co_{(2)}}$	$s^{36.9}, d_{x-y}^{2}{}^{234.4}-s^{49.4}, d_{xy}^{49.9}$	0.90	−167.69	
3. $\sigma_{Co_{(2)}-Co_{(3)}}$	$s^{49.4}, d_{xy}^{49.9}-s^{36.9}, d_{x-y}^{2234.4}$	0.90	−167.45	
4. $\sigma_{Co_{(1)}-Co_{(4)}}$	$d_{x-y}^{2255.6}-d_{xy}^{51.1}$	0.91	−163.85	
5. $\sigma_{Co_{(3)}-Co_{(4)}}$	$d_{x-y}^{2}{}^{255.7}- s^{48.4}, d_{xy}^{51.0}$	0.91	−163.58	
α-Spin				
1. $3C_{Co_{(1)}-Co_{(2)}-Co_{(3)}}$	$p_x^{67.1}- s^{98.3}-p_x^{67.0}$	0.90	−232.57	
2. $3C_{Co_{(1)}-Co_{(3)}-Co_{(4)}}$	$p_x^{68.4}-p_x^{68.5}-s^{98.7}$	0.90	−224.24	
3. $\sigma_{Co_{(1)}-Co_{(3)}}$	$p_y^{62.9}-p_y^{62.6}$	0.71	−79.63	

occ Occupancy

[a] h_A–h_B% = Type of maximum h_A–h_B%

[c] Energy is in kcal/mol

Cobalt tetramer cluster Co$_4$

Different initial geometries are reported in the literature for the Cobalt tetramer such as tetrahedron, square, rhombus, planar, Y-like and linear structures [34]. So we obliged to check all of them to find our ground state real symmetry. We also checked two different multiplicities of 9 and 11. Square geometry is against of Jahn–Teller effect (as explained in 3.2). The best structure is rhombus with multiplicity of 11-et. The results are close to some previous works. Calculations of Fan et al. [35], Ma et al. [4] and Sebetci [34] are coincident with our structure and multiplicity. Our results and previous works are summarized in Table 3s. The obtained symmetry of our structure is C_s.

The only dipole moment in X axis, equal to 0.15 Debye, and existence of nonzero off-diagonal quadrupole moment ($XY = -0.04$ Debye-Ang) fortify our obtained symmetry. In addition, we have gained quadrupole moment in directions of *XX*, *YY*, *ZZ* as follows −51.08, −60.75, −59.33 (Debye-Ang). Mulliken atomic spin densities of Co$_{(1)}$ and Co$_{(3)}$ are near to each other; 2.672 and 2.673, respectively, and the corresponding values for Co$_{(2)}$ and Co$_{(4)}$ are 2.265 and 2.388
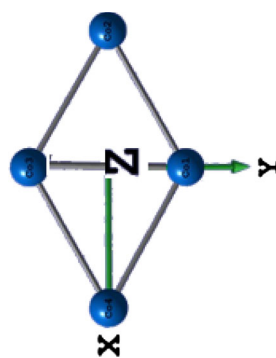
which are almost the same and different with previous pairs, and so to some extent, different chemical properties.

NBO analysis for Co$_4$ Cluster

We performed NBO to find out its bond types, percentage of orbital hybridization and the quality of localization procedure. Total electron for Cobalt tetramer is 108 which is divided into 72 core and 36 valence electrons. These 36 valence electrons fall into 23 valence electrons for α-spins and 13 valence electrons for β-spin parts. Table 4s reports the results of NBO bond types and energies. Although the bond length between Co$_{(2)}$–Co$_{(1)}$ and Co$_{(2)}$–Co$_{(3)}$ is somehow the same (about 2.430 Å) and also the bond length between Co$_{(4)}$–Co$_{(1)}$ and Co$_{(4)}$–Co$_{(3)}$ is near to each other (about 2.450 Å), NBO did not recognize any bond between Co$_{(2)}$–Co$_{(3)}$ and Co$_{(4)}$–Co$_{(1)}$. That is, similar inter-atomic bond distance shows two different descriptions. We also see some unusual charge transfers in this area. Table 5s listed these values. In order to reach reasonable structure, we change the threshold of orbital occupancy from 1.90 (its default) to

Table 7 Cobalt tetramer (*THRESHOLD = 1.89*) cluster, all nonbonding radicals of both α- and β-spin parts, charge transfers, symmetry and bond length

β-spin

No	Orbital	Atom	Occ	Type	E^a
1	d_{yz}	$Co_{(1)}$	0.99	π	−164.4
2	d_{z^2}	$Co_{(3)}$	0.99	π	−164.3
3	d_{z^2}	$Co_{(1)}$	0.99	π	−162.8
4	d_{yz}	$Co_{(3)}$	0.99	π	−162.7
5	d_{xz}	$Co_{(4)}$	0.99	π	−156.9
6	d_{z^2}	$Co_{(4)}$	0.99	π	−154.1
7	d_{z^2}	$Co_{(2)}$	0.99	π	−152.5
8	d_{xz}	$Co_{(2)}$	0.93	π	−147.7

Charge transfers

	Atom		Occ	Type	E_{CT}
$\sigma^*_{Co_{(1)}-Co_{(2)}}$	to	$\sigma^*_{Co_{(2)}-Co_{(3)}}$			10.74
$\sigma^*_{Co_{(1)}-Co_{(3)}}$	to	$d^{*}_{x^2-y^2}$	$Co_{(2)}$		7.32
$\sigma^*_{Co_{(1)}-Co_{(3)}}$	to	d_{x2-y2}^{*}	$Co_{(4)}$		7.73
$\sigma^*_{Co_{(1)}-Co_{(4)}}$	to	$\sigma^*_{Co_{(3)}-Co_{(4)}}$			7.19
$\sigma^*_{Co_{(2)}-Co_{(3)}}$	to	$\sigma^*_{Co_{(1)}-Co_{(2)}}$			10.79
$\sigma^*_{Co_{(3)}-Co_{(4)}}$	to	$\sigma^*_{Co_{(1)}-Co_{(4)}}$			7.22

α-spin

No	Orbital	Atom	Occ	Type	E^a
1	d_{xz}	$Co_{(1)}$	0.99	π	−215.3
2	d_{xz}	$Co_{(3)}$	0.99	π	−215.1
3	$d_{x^2-y^2}$	$Co_{(1)}$	0.99	σ	−212.5
4	$d_{x^2-y^2}$	$Co_{(3)}$	0.99	σ	−212.3
5	d_{z^2}	$Co_{(1)}$	0.99	π	−211.5
6	d_{z^2}	$Co_{(3)}$	0.99	π	−211.4
7	d_{xy}	$Co_{(1)}$	0.99	σ	−211.0
8	d_{xy}	$Co_{(3)}$	0.99	σ	−210.9
9	d_{yz}	$Co_{(4)}$	0.99	π	−208.8
10	d_{yz}	$Co_{(2)}$	0.99	π	−207.7
11	d_{yz}	$Co_{(1)}$	0.99	π	−201.7
12	d_{yz}	$Co_{(3)}$	0.99	π	−201.6
13	d_{z^2}	$Co_{(4)}$	0.99	π	−200.8
14	d_{z^2}	$Co_{(2)}$	0.99	π	−199.4
15	d_{xy}	$Co_{(4)}$	0.99	σ	−197.3
16	$d_{x^2-y^2}$	$Co_{(2)}$	0.99	σ	−197.1
17	$d_{x^2-y^2}$	$Co_{(4)}$	0.99	σ	−196.4
18	d_{xy}	$Co_{(2)}$	0.99	σ	−193.6
19	d_{xz}	$Co_{(2)}$	0.99	π	−188.7
20	d_{xz}	$Co_{(4)}$	0.99	π	−186.6

Charge transfers

	Atom		Occ	Type	E_{CT}
$3C_{Co_{(1)}-Co_{(2)}-Co_{(3)}}$	to	$\sigma^*_{Co_{(2)}-Co_{(3)}}$			9.88
$\sigma_{Co_{(1)}-Co_{(3)}}$	to	$3C_{Co_{(1)}-Co_{(2)}-Co_{(3)}}$			20.57
$\sigma_{Co_{(1)}-Co_{(3)}}$	to	$3C_{Co_{(1)}-Co_{(3)}-Co_{(4)}}$			20.47
$3C_{Co_{(1)}-Co_{(3)}-Co_{(4)}}$	to	$\sigma^*_{Co_{(1)}-Co_{(3)}}$			9.49

$d_{Co(1)Co(2)} = 2.428Å, d_{Co(2)Co(3)} = 2.430Å^b$
$d_{Co(3)Co(4)} = 2.449Å, d_{Co(4)Co(1)} = 2.447Å$
$d_{Co(1)Co(3)} = 2.392Å$
Rhombs (C_s)

occ Occupancy

[a] Energy is in kcal/mol

[b] Bond length is in angstrom

Table 8 NBO descriptors of Co_5 cluster (for α- and β-spin parts), showing bonding orbital, hybridization, occupancy and energy of each bond

NBO bond	h_A–h_B%[a]	Occ	Energy[b]	NBO shape
β-spin				
1. $3C_{Co_{(1)}-Co_{(4)}-Co_{(5)}}$	$d_{xy}^{50.5}-d_{xy}^{50.5}-d_{xy}^{56.8}$	0.94	−213.26	
2. $3C_{Co_{(3)}-Co_{(2)}-Co_{(5)}}$	$d_{xy}{}^{50.5}-d_{xy}^{50.5}-d_{xy}^{56.8}$	0.94	−213.26	
3. $3C_{Co_{(3)}-Co_{(4)}-Co_{(5)}}$	$s^{42.1}-s^{42.1}-d_{xy}^{56.7}$	0.94	−212.94	
4. $3C_{Co_{(1)}-Co_{(2)}-Co_{(5)}}$	$s^{42.1}-s^{42.1}-d_{xy}^{56.7}$	0.94	−212.94	
5. $\sigma_{Co_{(1)}-Co_{(4)}}$	$d_{yz}^{88.1}-d_{xz}^{88.1}$	0.96	−140.10	
6. $\sigma_{Co_{(2)}-Co_{(3)}}$	$d_{xz}^{88.1}-d_{yz}^{88.1}$	0.96	−140.10	
α-Spin				
1. $\sigma_{Co_{(2)}-Co_{(5)}}$	$s^{99.2}-p_x^{64.1}$	0.72	−176.49	
2. $\sigma_{Co_{(4)}-Co_{(5)}}$	$s^{99.2}-p_x^{64.1}$	0.72	−176.49	
3. $\sigma_{Co_{(1)}-Co_{(5)}}$	$s^{99.2}-p_y^{85.0}$	0.71	−162.53	

occ Occupancy

[a] h_A–h_B% = type of maximum h_A–h_B%

[b] Energy is in kcal/mol

1.89. With these new NBO results in Table 6, we found reasonable total Lewis, in both α-spin and β-spin parts, respectively, as 99.14 and 98.71 %, which means all orbitals are localized, and no significant charge transfers in comparison with its default threshold.

Now, our new NBO considers two 3C bond orbitals and one σ-bond for α-spin parts and five σ-bond orbitals for β-spin parts which seem to be acceptable. The results are shown in Table 6. Thereafter, we report our results in the base of this new NBO analysis. Multiplicity of 11-et is a
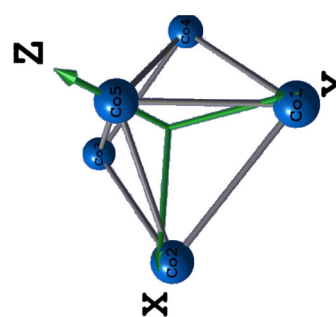
good hint that we have singly occupied orbitals in the valence shell which we can call them radicals. Table 7 shows all the radicals of α- and β-spins. NBO reported 20 and 8 radicals for α- and β-spin parts, respectively. The last radical of β-spin is d_{xz} orbital concentrated on $Co_{(2)}$ (with −147.7 kcal/mol energy) which is HOMO active space with 0.07 depletion of electrons.

All radicals in β-part are π-type. In α-spin parts, we see both σ and π-radicals. (Some charge transfers were reported in Table 7).

Table 9 Cobalt pentamer cluster, all nonbonding radicals of both α- and β-spin parts, charge transfers, symmetry and bond length

β-spin

No	Orbital	Atom	Occ	Type	E^a
1	d_z^2	Co$_{(5)}$	0.99	σ	−163.5
2	d_{yz}	Co$_{(2)}$	0.99	π	−145.5
3	d_{yz}	Co$_{(4)}$	0.99	π	−145.5
4	d_{xz}	Co$_{(1)}$	0.99	π	−145.4
5	d_{xz}	Co$_{(3)}$	0.99	π	−145.4
6	$d_{x^2-y}^2$	Co$_{(2)}$	0.98	σ	−141.3
7	$d_{x^2-y}^2$	Co$_{(4)}$	0.98	σ	−141.3
8	$d_{x^2-y}^2$	Co$_{(1)}$	0.98	σ	−141.3
9	$d_{x^2-y}^2$	Co$_{(3)}$	0.98	σ	−141.3
10	$d_{x^2-y}^2$	Co$_{(5)}$	0.50	π	−107.9
11	p_x	Co$_{(5)}$	0.06	π	−0.84

Charge transfers

Orbital	Atom	Occ	Type	E$_{CT}$
$d_{x^2-y}^2$	Co$_{(5)}$ to	$\sigma^*_{Co(1)-Co(4)}$		36.22
$d_{x^2-y}^2$	Co$_{(5)}$ to	$\sigma^*_{Co(2)-Co(3)}$		36.22
p_x	Co$_{(5)}$ to	$3C^*_{Co(1)-Co(2)-Co(5)}$		15.25
p_x	Co$_{(5)}$ to	$3C^*_{Co(3)-Co(4)-Co(5)}$		15.25

α-spin

Orbital	Atom	Occ	Type	E^a	No
d_{xz}	Co$_{(5)}$	0.99	π	−218.3	1
d_{yz}	Co$_{(5)}$	0.99	π	−218.3	2
$d_{x^2-y}^2$	Co$_{(5)}$	0.99	π	−211.2	3
d_z^2	Co$_{(2)}$	0.99	π	−197.6	4
d_z^2	Co$_{(4)}$	0.99	π	−197.6	5
d_z^2	Co$_{(1)}$	0.99	π	−197.6	6
d_z^2	Co$_{(3)}$	0.99	π	−197.6	7
d_{xy}	Co$_{(5)}$	0.99	σ	−196.8	8
d_z^2	Co$_{(5)}$	0.99	σ	−192.2	9
d_{xy}	Co$_{(2)}$	0.99	σ	−189.3	10
dx_z	Co$_{(4)}$	0.99	π	−189.3	11
d_{xy}	Co$_{(1)}$	0.99	σ	−189.2	12
d_{xy}	Co$_{(3)}$	0.99	σ	−189.2	13
d_{xz}	Co$_{(1)}$	0.99	π	−186.6	14
d_{xz}	Co$_{(2)}$	0.99	π	−186.6	15
d_{yz}	Co$_{(4)}$	0.99	π	−186.6	16
d_{yz}	Co$_{(4)}$	0.99	π	−186.6	17
d_{yz}	Co$_{(3)}$	0.99	π	−182.7	18
d_{xz}	Co$_{(2)}$	0.99	π	−182.5	19
d_{xz}	Co$_{(4)}$	0.99	π	−182.5	20
d_{yz}	Co$_{(1)}$	0.99	π	−182.5	21
$d_{x^2-y}^2$	Co$_{(3)}$	0.99	σ	−178.6	22
$d_{x^2-y}^2$	Co$_{(2)}$	0.99	σ	−178.6	23
$d_{x^2-y}^2$	Co$_{(4)}$	0.99	σ	−178.6	24
$d_{x^2-y}^2$	Co$_{(1)}$	0.99	σ	−178.6	25

Charge transfers

Orbital	Atom	Occ	Type	E$_{CR}$
$\sigma_{Co(2)-Co(5)}$	to	Co$_{(3)}$	s^*	51.10
$\sigma_{Co(2)-Co(5)}$	to	Co$_{(3)}$	p_y^*	10.08
$\sigma_{Co(4)-Co(5)}$	to	Co$_{(3)}$	s^*	51.10
$\sigma_{Co(4)-Co(5)}$	to	Co$_{(3)}$	p_x^*	10.08

$d_{Co(1)-Co(2)} = d_{Co(2)-Co(3)} = d_{Co(3)-Co(4)} = d_{Co(4)-Co(1)} = 2.625\,\text{Å}$

$d_{Co(1)-Co(5)} = d_{Co(4)-Co(5)} = d_{Co(3)-Co(5)} = d_{Co(2)-Co(5)} = 2.271\,\text{Å}$

Pyramidal (C_{2v})

occ Occupancy

[a] Energy is in kcal/mol

[b] Bond length is in angstrom

Cobalt pentamer cluster Co$_5$

Our preliminary examinations for Co$_5$ were five structures of trigonal bipyramidal, square pyramidal (pyramidal), W-like, capped tetrahedron and pentagon, with multiplicities of 12 and 14. Although our results coincident with both Fan et al. [35] and Ma et al. [4] in the aspect of structural geometry, our multiplicity differs from the former and in agreement with the latter. Castro et al. [33], Pereiro et al. [36] and Datta et al. [37] reported trigonal bipyramidal structure with multiplicity of 14-et. A. Sebetci [34] found W-like structure with multiplicity of 12-et. Table 6s summarizes these results for Co$_5$. So our structure is square pyramidal with multiplicity of 12-et and C_{2v} point group.

The bond length are as follows: $d_{Co(1)-Co(2)} = d_{Co(2)-Co(3)} = d_{Co(3)-Co(4)} = d_{Co(4)-Co(1)} = 2.625$ Å and $d_{Co(1)-Co(5)} = d_{Co(4)-Co(5)} = d_{Co(3)-Co(5)} = d_{Co(2)-Co(5)} = 2.271$ Å. Dipole moment is only in Z-direction equal to -0.71 (Debye), and quadrupole moments are equal to -70.44, -70.44, -68.20 (Debye-Ang) in XX, YY, ZZ, respectively, with no off-diagonal elements. Co$_{(1)}$, Co$_{(2)}$, Co$_{(3)}$ and Co$_{(4)}$ are positioned in xy-plane, and the coordinates of Co$_{(1)}$ and Co$_{(3)}$ in their y directions are mirror image of each other (with respect to z axis). This condition for coordinate of Co$_{(2)}$ and Co$_{(4)}$ occurred for their x directions (Table 7s). Mulliken atomic spin densities of Co$_{(1)}$ and Co$_{(3)}$ are exactly the same which equal to 2.268, and this amount for Co$_{(2)}$ and Co$_{(4)}$ is equal to 2.269 which is almost the same with Co$_{(1)}$ and Co$_{(3)}$. The different Mulliken atomic spin densities for Co$_{(5)}$ show the value of 1.925. All of these are evidence which fortify our obtained C_{2v} symmetry.

NBO analysis for Co$_5$ Cluster

According to the NBO analysis, we can find that total electron for Cobalt pentamer is 135 which is divided into 90 core and 45 valence electrons. Table 8 demonstrates our results for bonding orbitals. Forty-five valence electrons fall into 28 valence electrons for α-spins and 17 valence electrons for β-spin parts. The NBO of Co$_5$ can be classified as two degenerate σ-bond orbitals in addition to another σ-bond orbital for α-spins. In β-spin parts, we have four three-center bond orbitals (two by two degenerate) and two degenerate σ-bond orbitals.

Total Lewis in α-spin parts is 99.4 % and for β-spin parts is about 98 %. Deviations of total Lewis show that we have charge transfers which are shown with type of radicals, in Table 9. Orbitals of $dx^2 - y^2$ and p_x, both located on Co$_{(5)}$ in β-spin parts, have 0.5 and 0.94 depletion of electrons, respectively. These are caused to have expected charge transfers.

Further attention is demanded for p_x orbital centered on Co$_{(5)}$ in β-spin parts. Its low energy of stabilization (-0.84 kcal/mol) and very low occupancy (0.06) in contrast to others show that it is HOMO part in our active space. Deviation from Lewis type in β-spin parts is mainly due to characteristic of this orbital. Because of these depletion of electrons for Co$_{(5)}$, one can recognize that it has a specific characteristic which led to valuable site for reactions.

Notable charge transfers in β-spin parts which equal to 36.22 kcal/mol were reported as follows: from $dx^2 - y^2$ Co$_{(5)}$ to σ^*Co$_{(1)}$–Co$_{(4)}$ and also from this orbital to σ^*Co$_{(2)}$–Co$_{(3)}$ There are also 15.25 kcal/mol electron charge transfers from p_x Co$_{(5)}$ to 3C* Co$_{(1)}$–Co$_{(2)}$–Co$_{(5)}$ and to 3C*Co$_{(3)}$–Co$_{(4)}$–Co$_{(5)}$. We can also report notable charge transfers in α-spin parts, as tabulated in Table 9. These electron charge transfers can be justified as the sign of depletions of occupation in bonds and radicals.

Conclusions

Calculations for small Cobalt clusters (Co$_n$, $n = 2$–5) as nanoparticles have been done to find out their best geometrical and electronic structures. These nanoparticles act as building blocks of transition metal cluster compounds. NBO analysis was performed to describe electrons and the type of orbitals in valence shell, bonding and nonbonding of α- and β-spin parts. The results are as follows: Co$_2$ is linear ($D_{\infty h}$) with multiplicity of 5-et, and HOMO degenerate d_{xy} on both atoms in β-spin parts, with energy of -137.3 kcal/mol. It has also two σ-bonds, two degenerate π-bonds and one δ-bond in β-spin part and one σ-bond in α-spin part. Co$_3$ is almost scalene triangle (C_s) with multiplicity of 8-et and HOMO s-orbital on Co$_{(1)}$, chemically very active with 0.3 depletion in α-spin parts with energy of -115.9 kcal/mol. It has one three-center bond in β-spin part and one σ-bond in α-spin part: Co$_4$ rhombus (C_s) with multiplicity of 11-et, and HOMO of d_{xz} in π-type orbital on Co$_{(2)}$ atom in β-spin parts with electron depletion of 0.07 and energy of -147.7 kcal/mol. It has five σ-bonds in β-spin part and one σ-bond and two three-center bonds in α-spin part: Co$_5$ pyramidal (C_{2v}) with multiplicity of 12-et and HOMO of p_x in π-type orbital on Co$_{(5)}$, chemically highly active with depletion of 0.94 in β-spin parts and energy of -0.84 kcal/mol. It has four three-center bonds and two σ-bonds in β-spin part and three σ-bonds in α-spin part. Calculations have been performed by DFT procedure in Gaussian 09 software with calibrated B3P86 as xc-functional and $6\text{-}311++G^*$ as basis set. We reported all Cartesian coordinates of each atom, in each cluster, in Table 7s. So by aid of these calculations, we can determine and predict the active sites where other molecules would attack to Cobalt clusters. HOMOs, active bonds (which are known by depletion of electrons in

their occupancies), less Mulliken atomic spin densities, π- and δ-bonds (compare with σ-bonds) are the probable active choices.

References

1. Braunstein P, Oro LA, Raithby PR (1999) Metal clusters in chemistry. OWILEY-VCH Verlag GmbH, Weinheim, Federal Republic of Germany

2. Pereiro M, Mankovsky S, Baldomir D, Iglesias M, Mlynarski P, Valadares M, Suarez D, Castro M, Arias JE (2001) Model potential nonlocal density functional calculations of small Cobalt clusters, Co_n, $n \le 5$. Comput Mater Sci 22:118–122

3. Borisova SD, Eremeev SV, Rusina GG, Stepanyuk GVS, Bruno P, Chulkov E (2008) Vibrations of small Cobalt clusters on low-idex surfaces of copper: tight-binding simulations. J APS Phys Rev B 78:075428-1/075428-17

4. Ma QM, Liu Y, Xie Z, Wang J (2006) Ab initio study of geometries and magnetic properties of small Co clusters. J Phys Conf Ser 29:163–166

5. Nicolas G, Dorantes-Davila J, Pastor GM (2006) Calculation of orbital polarization effects in small Co clusters. Comput Mater Sci 35:292–296

6. Zhao HY, Wang J, Liu Y, Li YC (2009) The effects of nitrogen on the configurations and magnetic moments of small iron, cobalt and nickel clusters. Eur Phys J Appl Phys 48:30601/1–30601/8

7. Monroy CZ, Martinez- Magadan JZ, Ramos JE, Balderas RG (2009) A DFT study of the electronic structure of cobalt and nickel mono-sbstituted MoS_2 triangular nano-sized clusters. J Mol Catal A Chem 313:49–54

8. Borisova SD, Rusina GG, Eremeev SV, Chulkov EV (2009) Vibrational properties of small Cobalt clusters on the Cu(111) surface. Phys Solid State 51:1198–1206

9. Kumar Das B, Chakrabarty R (2011) Cobalt(III)-oxo cubane clusters as catalysts for oxidation of organic substrates. J Chem Sci 123:163–173

10. Roy X, Schenck CL, Ahn S, Lalancette RA, Venkataraman L, Nuckolls C, Steigerwald ML (2012) Quantum soldering of individual quantum dots. Angew Chem Int Ed 51:1–5

11. Aguilera-Granja F, Longo RC, Gallego LJ, Vega A (2010) Structural and magnetic properties of $X_{12}Y$ (X, Y = Fe, Co, Ni, Ru, Rh, Pd, and Pt) Nanoalloys. J Chem Phys 132:184507-1/184507-6

12. Connolly J, Pierre TGSt, Rutnakornpituk M, Riffle J.S (2002) Silica coating of cobalt nanoparticles increase their magnetic and chemical stability for biomedical applications. Eur Cell Mater 3:106–109

13. Zhang M, de Respinis M, Frei H (2014) Time-resolved observations of water oxidation intermediates on a cobalt oxide nanoparticle catalyst. Nat Chem. doi:10.1038/nchem.1874

14. Kooti M, Saiahi MS, Motamedi H (2013) Fabrication of silver-coated cobalt ferrite nano-composite and the study of its antibacterial activity. J Magn Magn Mater 333:138–143

15. Bouchat V, Moreau N, Colomer JF, Lucas S (2013) On some applications of nanoparticles synthesized in the gas phase by magnetron discharges. JSEMAT 3:184–189

16. Bansmann J, Getzlaff M, Kleibert A, Bulut F, Gebhardt RK, Meiwes-Broer KH (2006) Mass-filtered cobalt clusters in contact with epitaxially ordered metal surfaces. Appl Phys A 82:73–79

17. Faraji M, Yamini Y, Rezaee M (2010) Magnetic nanoparticles: synthesis, stabilization, functionalization, characterization, and applications. J Iran Chem Soc 7:1–37

18. Zheng Y, Li P, Li H, Chen S (2014) Controllable growth of cobalt oxide nanoparticles on reduced graphene oxide and its application for highly sensitive glucose sensor. Int J Electrochem Sci 9:7369–7381

19. Frisch MJ et al (2009) Gaussian 09 revision A.1. Gaussian Inc., Wallingford, CT

20. Parr RG (1995) Density functional theory of the electronic structure of molecules. Annu Rev Phys Chem 46:701–728

21. Liptak MD, Shields GC (2005) Comparison of density functional theory predictions of gas-phase de-protonation data. Int J Quantum Chem 105:580–587

22. Löwdin PO (1955) Quantum theory of many-particle systems. I. Physical interpretations by means of density matrices, natural spin-orbitals, and convergence problems in the method of configurational interaction. Phys Rev. doi:10.1103/PhysRev.97.1474

23. Shull H, Löwdin PO (1955) Natural spin orbitals for helium. J Chem Phys. doi:10.1063/1.1742383

24. Shull H, Löwdin PO (1959) Superposition of configurations and natural spin orbitals. Applications to the He problem. J Chem Phys. doi:10.1063/1.1730019

25. Shull H (1959) Natural spin orbital analysis of hydrogen molecule wave functions. Chem Phys. doi:10.1063/1.1730212

26. Hagstrom S, Shull H (1963) The nature of the two-electron chemical bond. III. Natural orbitals for H_2. Rev Mod Phys. doi:10.1103/RevModPhys.35.624

27. Niu S, Hall MB (1997) Comparison of hartree-fock, density functional, møller-plesset perturbation, coupled cluster, and configuration interaction methods for the migratory insertion of nitric oxide into a cobalt-carbon bond. J Phys Chem A 101:1360–1365

28. Dachsel H, Harrison RJ, Dixon DA (1999) Multi-reference configuration interaction calculations on Cr_2: passing the one billion limit in MRCI/MRACPF calculations. J Phys Chem A 103:152–155

29. Holthausen MC (2005) Benchmarking approximate density functional theory. I. s/d Excitation energies in $3d$ transition metal cations. J Comput Chem. doi:10.1002/jcc.20279

30. Schultz NE, Zhao Y, Truhlar DG (2008) Benchmarking approximate density functional theory for s/d excitation energies in 3d transition metal cations. J Comput Chem. doi:10.1002/jcc.20717

31. Kant A, Strauss B (1964) Dissociation energies of diatomic molecules of the transition elements. II. Titanium chromium, manganese, and cobalt. J Chem Phys 41:3806–3808

32. Russon LM, Heidecke SA, Birke MK, Conceicao J, Morse MD, Armentrout PB (1994) Photo-dissociation measurements of bond dissociation energies: Ti_2^+, V_2^+, Co_2^+ and Co_3^+. J Chem Phys 100:4747–4755

33. Castro M, Jamorski C, Salahub DR (1997) Structure, bonding, and magnetism of small Fe_n, Co_n, and Ni_n clusters, $n \le 5$. Chem Phys Lett 271:133–142

34. Sebetci A (2008) Cobalt clusters (Co_n, $n \le 6$) and their anions. Chem Phys 354:196–201

35. Fan HJ, Liu CW, Liao MS (1997) Geometry, electronic structure and magnetism of small Co_n ($n = 2$–8) clusters. Chem Phys Lett 273:353–359

36. Pereiro M, Baldomir D, Iglesias M, Rosales C, Castro M (2001) Model potential density functional study of small Cobalt clusters, Co_n, $n \le 3$. Int J Quantum Chem 81:422–430

37. Datta S, Kabir M, Ganguly S, Sanyal B, Saha-Dasgupta T, Mookerjee A (2007) Structure, bonding, and magnetism of Cobalt clusters from first-principles calculations. Phys Rev B. doi:10.1103/PhysRevB.76.014429