CHAPTER 9

SMALL QUANTUM DOTS OF COBALT OXIDES:

ELECTRONIC, OPTICAL AND MAGNETIC

PROPERTIES, AND SPIN ALIGNMENT

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Running Title: QDs of Cobalt Oxides
SUMMARY

Electronic, optical and magnetic properties of small quantum dots (QDs) about 1.5 nm in linear dimensions and composed of Co and O atoms have been synthesized virtually (i.e., using first-principle theoretical and computational methods without any adjustable parameters) in “free space” and model quantum confinement. Some Co-O molecules appear to be “antiferromagnetic” singlets with their electron spins antiparallel, while the majority of the Co-O molecules are “ferromagnetic”, with their uncompensated electron spins parallel and localized in the vicinity of Co atoms. Notably, almost all of the virtually synthesized Co – O molecules are “non-stoichiometric”, and the octet rule does not hold for them. The Co – O and O – O bonds in such systems are stretchable and flexible enough to accommodate geometrical changes leading to lowering of the total energy of the systems through the spin re-alignment mechanism, in addition to minimization of Coulomb repulsion between electrons. With an increase in the size of a molecule, this mechanism is responsible for conversion of “antiferromagnetic” Co – O singlets to “ferromagnetic” spin multiplets. Such spin re-alignment may lead to Co/Co-O surface reconstruction in Co/Co-O nanosystems, and thus to the development or loss of exchange bias, and vice versa. Manipulations with the structure of the molecules synthesized in quantum confinement can be used to finely tune electronic, optical and magnetic properties of the investigated cobalt oxide nanosystems to match applications’ requirements.

Key words: nanostructures, quantum dots, exchange bias, magnetic properties, electronic properties, band gap
1. INTRODUCTION

Cobalt oxide nanoparticles have been used in a variety of chemical processing and materials synthesis industries. This includes heterogeneous catalysis (1–3), extraction of NO (4), hydrogenation (5), absorption of carbon monoxide, water and phosphate ions using porous and structured materials with embedded Co – O nanoparticles, and the development of Co – O nanoparticle-based sensor devices (6 – 10), such as solid-state and optical sensors (11,12). Co – O nanomaterials have been increasingly used in solar energy absorbers (13), electrochemical capacitors for high power devices (14 – 17) and as anode materials (18,19). Currently, several fields of nanoelectronics, and in particular oxide spintronics, stand to benefit from unique combination of electronic and magnetic properties of Co – O nanosystems. Large electron mobility, tunable unidirectional exchange anisotropy, enhanced coercivity, ferromagnetism, antiferromagnetism, semi-metallicity and semiconductivity offer numerous options for the development of novel nanoelectronic and magnetoelectronic devices (20-22). Exchange-biased core – shell Co – O quantum dots (QDs) are carriers of electrons whose spin states can be used as bits of quantum information for integrated information storage-processing and secure quantum communications (23-27).

Exchange bias is a unique phenomenon dependent of the size, surface structure and temperature of “magnetic” nanosystems, and thus can be used for manipulations with electron spin alignment at interfaces between such nanosystems and adjacent materials. Well-known experimental observations (28 – 30) established a critical size of about 6 nm for core-shell Co/Co – O nanoclusters associated with loss of exchange bias between ferromagnetic “core” (Co) and antiferromagnetic “shell” (Co-O). The origin of the development and loss of exchange bias in these and other nanosystems is not well understood, and can only be revealed by means of
fundamental quantum theoretical studies. Such studies are necessary to elucidate physical meaning of experimental correlations and other findings offered by existing semi-phenomenological approaches and models (31,32) that are currently used to explain exchange bias in larger systems. In this chapter the first-principle quantum many-body theoretical and computational methods of Chapters 1 and 2 are applied to characterization of the ground state structure, electronic, optical and magnetic properties of the smallest Co – O nanosystems. Among other findings, the obtained results reveal possible physical mechanisms responsible for the development and loss of exchange bias in these and similar nanosystems, and are in a good agreement with available data gathered by experimental and computational means (30,33,34).

2. ELECTRONIC, OPTICAL AND MAGNETIC PROPERTIES OF Co–O MOLECULES

2.1. Virtual synthesis procedure.

The electronic energy level structure (ELS), charge and spin density distributions (CDD and SDD, respectively), and the molecular electrostatic potential (MEP) of a range of Co – O atomic clusters have been investigated by means of the virtual synthesis methods (see Refs. 35 and 36, and Chapter 2 for detailed discussion) in the framework of the self-consistent field (SCF), restricted and restricted open shell Hartree-Fock approximations (RHF and ROHF, respectively). The majority of the virtually synthesized Co – O molecules has also been investigated at the level of configuration interaction (CI), complete active space (CAS) SCF and multi-configuration SCF (MCSCF) approximations. Notably, CAS in the considered cases are large, up to 16 electrons distributed over 10 orbits (16×10). GAMESS software package (37) with the SBKJC standard basis set (38) has been used to realize these calculations.
The goal of the virtual synthesis procedure has been to establish and characterize the structure and properties of an atomic cluster in its bounded states, such as the lowest total energy state, or in a state that realizes a local minimum of the total cluster energy. In chemical terms, any bounded state of a group of atoms is identified as an ion or a molecule, depending on whether the total charge carried by the group is non-zero or zero. Thus, the RHF or ROHF energy minimization procedure has been applied to pre-configured atomic clusters composed of Co and O atoms to determine the total energy, equilibrium geometry, ELS, molecular orbits (MOs), CDDs and SDDs of the emerging molecules in their ground and steady states. The virtual synthesis method (35,36,39) significantly improves the efficiency of the standard RHF/ROHF energy minimization procedure (37) in that that the initial configuration of atoms in a cluster to be optimized is chosen on the basis of symmetry considerations. Among other advantages, this feature permits to account for significant contributions due to quantum confinement effects [such as excluded volume effects and polarization of atomic orbit (AOs) of electrons due to confinement] in the case when a molecule is synthesized in confinement or on a surface, regardless of whether or not the confinement is reconstructed in detail at the atomistic level.

In the case of small Co – O clusters, the focus has been on identification of possible stable and equilibrium configurations of Co and O atoms. Covalent radii 1.25 Å and 0.66 Å of Co and O atoms, respectively, have been adopted from experiment and used to pre-design initial cluster structures. In such pre-designed structures, the centers of mass of the atoms have been fixed in their assigned positions, and the virtual synthesis routine is applied to minimize the total energy of the cluster when the cluster atoms cannot “move”. A configuration of atoms of the considered atomic cluster in a bounded state so obtained (if any) is called below a pre-designed molecule. The ground state energy of the pre-designed molecule in this case corresponds to a
local minimum of energy of the cluster, because motion of centers of mass of cluster’s atoms was spatially constrained to their fixed positions in the cluster. Pre-designed molecules model molecular synthesis in quantum confinement and/or on surfaces, where indeed, motion of clusters atoms is constrained to a small region in space by foreign atoms or electromagnetic fields framing the quantum confinement, or otherwise breaking spatial symmetry. The resulting structure and properties of pre-designed molecules reflect excluded volume effects of confinements and/or surfaces, and to a degree, polarization of AOs of their electrons. In addition to a possibility of modelling molecular synthesis in quantum confinement without detailed recovery of the entire environment at the atomic scale, intelligent design of initial configurations of atomic clusters before optimization permits to significantly decrease supercomputer time and memory involved in computations, thus overcoming severe hardware and software restrictions that at present reduce applications of the quantum many body theoretical methods to small systems of about 100 multi-electron atoms.

Once a pre-designed molecule is virtually synthesized and characterized, the spatial constraints applied to the centers of mass of its atoms are removed, and the virtual synthesis procedure (that is, the total energy minimization using RHF/ROHF/CI/CASSCF/MCSCF methods) is applied to the cluster again. In the absence of spatial constraints, the centers of mass of the atoms are moved somewhat from their positions in space, eventually easing the entire structure into the configuration that realizes the global minimum of the total energy of the cluster. Molecules so synthesized are called below unconstrained (or vacuum) molecules, because conditions of their synthesis mimic those in physical vacuum where no foreign atoms and electromagnetic fields are present. In many cases the unconstrained molecules have the structure very similar to that specific to the corresponding pre-designed molecules. This usually
signifies, that the total energy surface of the cluster is very flat near the global minimum of the total energy of the cluster, so that the structure of the pre-designed molecule has been very close to the unconstrained one. However, even very small displacements of about $10^{-2}$ Å of the atoms in unconstrained molecules from their former positions in the pre-designed molecules result in significant changes in the electronic, optical and magnetic properties of the vacuum molecules compared to those of their pre-designed parents. Depending of the synthesis conditions, the ROHF/CI/CASSCF/MCSCF direct optical transition energy (OTE) of the unconstrained Co – O molecules may increase by 1 eV and more comparatively to that of their pre-designed counterparts. This indicates that manipulations with synthesis conditions of Co – O molecules using model quantum confinements leads to changes in covalent radii of the atoms. Despite being very small, those changes have a significant impact on the structure of the pre-designed molecules leading to a dramatic change in their OTEs. The majority of the studied Co – O molecules possess ROHF/CI/CASSCF/MCSCF OTEs in the range from 2 eV to about 3 eV, in agreement with previous results (35,36,39,40) and other data discussed in this book and found elsewhere in literature. However, several small Co – O molecules have OTE significantly smaller than 1 eV.

2.2. Smaller Co – O molecules.

The ground state energies and OTEs of the studied molecules are collected in Table I. The smallest Co – O molecule synthesized in this work is the vacuum HF singlet Co$_2$O, a linear molecule with a deep ground state potential well of about -304 H. This molecule has two antiparallel electron spins each of which is localized near their respective Co atoms, and the electronic charge embracing the oxygen atom (Fig. 1a). The antiparallel electron spins manifest “antiferromagnetic” nature of this molecule, with its total magnetic moment equal to zero. RHF
OTE of this molecule is about 7.6 eV (Table I). The highest occupied molecular orbital (HOMO) of this molecule is highly hybridized. The major contributions to this HOMO come from $3d_{xy}$ and $3d_{xz}$ AOs of the Co atoms, and $2p_y$ and $2p_z$ orbits of the O atom (Fig. 1b).

TABLE I. The ground state of small Co-O molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>RHF/ROHF and MCSCF ground state energy, Hartree</th>
<th>RHF/ROHF and MCSCF direct optical transition energy, eV</th>
<th>Spin multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear Co$_2$O</td>
<td>-303.826382</td>
<td>7.6736</td>
<td>vacuum singlet</td>
</tr>
<tr>
<td>Linear Co$_2$O</td>
<td>-303.802796 (CAS 16×10)</td>
<td>1.5892 (CAS 16×10)</td>
<td>vacuum singlet</td>
</tr>
<tr>
<td>Linear Co$_2$O</td>
<td>-304.004531</td>
<td>0.3837</td>
<td>vacuum pentet</td>
</tr>
<tr>
<td>Linear Co$_2$O</td>
<td>-304.142254 (CAS 8×8)</td>
<td>0.4805 (CAS 8×8)</td>
<td>vacuum pentet</td>
</tr>
<tr>
<td>Triangle Co$_2$O</td>
<td>-303.713003</td>
<td>0.6558</td>
<td>vacuum triplet</td>
</tr>
<tr>
<td>Triangle Co$_2$O</td>
<td>-303.998615 (CAS 6×7)</td>
<td>1.3171 (CAS 6×7)</td>
<td>vacuum triplet</td>
</tr>
<tr>
<td>Square Co$_2$O$_2$</td>
<td>-319.581011</td>
<td>4.6096</td>
<td>vacuum triplet</td>
</tr>
<tr>
<td>Square Co$_2$O$_2$</td>
<td>-319.589368 (CAS 4×5)</td>
<td>7.4238 (CAS 4×5)</td>
<td>vacuum triplet</td>
</tr>
<tr>
<td>Modified Co$_2$O$_2$</td>
<td>-319.430628</td>
<td>0.0218</td>
<td>vacuum pentet</td>
</tr>
<tr>
<td>Modified Co$_2$O$_2$</td>
<td>-319.607564 (CAS 8×9)</td>
<td>0.9028 (CAS 8×9)</td>
<td>vacuum pentet</td>
</tr>
<tr>
<td>Pyramid Co$_4$O</td>
<td>-592.381710</td>
<td>0.5061</td>
<td>pre-designed nonet</td>
</tr>
<tr>
<td>Octahedral Co$_4$O$_2$</td>
<td>-607.924430</td>
<td>3.4341</td>
<td>vacuum pentet</td>
</tr>
<tr>
<td>Octahedral Co$_4$O$_2$</td>
<td>-607.638705</td>
<td>3.6599</td>
<td>vacuum singlet</td>
</tr>
<tr>
<td>Octahedral Co$_4$O$_2$</td>
<td>-607.676335 (CAS 4×4)</td>
<td>2.3257 (CAS 4×4)</td>
<td>vacuum singlet</td>
</tr>
<tr>
<td>Octahedral Co$_4$O$_2$</td>
<td>-607.715955</td>
<td>2.1170</td>
<td>pre-designed pentet</td>
</tr>
<tr>
<td>Octahedral Co$_4$O$_2$</td>
<td>-607.874473 (CAS 8×10)</td>
<td>0.0190 (CAS 8×10)</td>
<td>pre-designed pentet</td>
</tr>
</tbody>
</table>

CI/CASSCF/MCSCF calculations (see Chapter 2 for further description of these methods) for this molecule with a large CAS 16×10 produced much more reasonable value of its OTE (Table I). In the MCSCF approximation the ground state energy of this molecule is about
0.024 H larger than its RHF ground state energy, but its MCSCF OTE decreases dramatically to a very reasonable value of 1.5892 eV that correlates with experimental findings.

At the same time, there exists the “ferromagnetic” linear vacuum ROHF Co\textsubscript{2}O pentet, with its ground state energy lying within the calculation error brackets (of about 1 H) from that of the vacuum RHF Co\textsubscript{2}O singlet (Table I), its OTE about 20 times smaller than that of the singlet, and its uncompensated electron spins parallel. CI/CASSCF/MCSCF calculations with CAS (8×8) confirmed that the ground state energy of the pentet is slightly smaller than that of the singlet. However, its MCSCF OTE is about 3 times smaller than that of the singlet.

![Fig. 1. Linear vacuum RHF singlet Co\textsubscript{2}O. (a) Isosurface of the molecular electrostatic potential (MEP) corresponding to the fraction 0.01 of the maximum value (not shown) of the charge density distribution (CDD); MEP values vary from negative (red) to positive (deep blue). (b) Isosurface of the highest occupied molecular orbit (HOMO) corresponding to the fraction 0.01 of the maximum value; HOMO values vary from negative (magenta) to positive (light blue). Co and O atoms are represented by golden and red spheres, respectively. Electron charge is accumulated near the oxygen atom (reddish and yellow to green regions). In (a) all dimensions are to scale, in (b) atomic dimensions are reduced to show the HOMO structure.]

Given that energy surface of the C\textsubscript{2}O cluster is very flat, so the ground state energies of the vacuum Co\textsubscript{2}O singlet and Co\textsubscript{2}O pentet lie within the calculation error brackets from each other for both HF and CI/CASSCF/MCSCF calculations with large complete active spaces, it
cannot be deciphered at present, which of this molecules may be realized in nature. An important issue is that while the ground state energies of these molecules almost coincide, the molecules have very different spin alignments and OTEs that may have an impact on possible applications. Moreover, it’s very likely that depending on their environment (such as the presence of a specifically directed magnetic field), spins of the “ferromagnetic” linear Co\textsubscript{2}O pentet may realign to decrease the total energy of the molecule, so that the molecule may become the “antiferromagnetic” linear Co\textsubscript{2}O singlet. To ensure better understanding of the ground state of the linear Co\textsubscript{2}O molecules, more accurate calculations, such as MP2, are necessary.

![Fig. 2. Triangular vacuum ROHF triplet Co\textsubscript{2}O. (a) Isosurface of the molecular electrostatic potential (MEP) corresponding to the fraction 0.01 of the maximum value (not shown) of the charge density distribution (CDD); MEP values vary from negative (red) to positive (deep blue). (b) Isosurface of the highest occupied molecular orbit (HOMO) corresponding to the fraction 0.02 of the maximum value; HOMO values vary from negative (magenta) to positive (light blue). Co and O atoms are represented by golden and red spheres, respectively. Electron charge is accumulated near the oxygen atom (reddish and yellow to green regions). All dimensions are to scale.](image)

To add to complexity of the situation with the two linear vacuum Co\textsubscript{2}O molecules, there also exists the isosceles triangular Co\textsubscript{2}O molecule (Table I, Fig. 2a) with its ROHF/CI/CASSCF//MCSCF ground state energy values lying within the error brackets of calculations from the corresponding ROHF/CI/CASSCF/MCSCF ground state energy values of
the linear vacuum Co\textsubscript{2}O molecules discussed above. At the same time, ROHF/MCSCF OTE of this triangular molecule differ significantly from the corresponding OTEs of both linear vacuum Co\textsubscript{2}O molecules. In similarity with the case of the linear vacuum Co\textsubscript{2}O molecules, the initial configuration of the triangle molecule coincided with that delivered by unconstrained total energy minimization, so the geometry of the pre-designed molecule matched that of the vacuum one. [Other initial triangular arrangements of Co and O atoms may result in some other stable pre-designed molecules, but they were not discovered in this study.] The two electron spins of this molecule are localized in the vicinity of Co atoms, and the electron charge is accumulated in the vicinity of the oxygen atom, in similarity to those of the linear Co\textsubscript{2}O vacuum singlet. The spins of the triangular Co\textsubscript{2}O triplet are parallel to each other, resulting in “ferromagnetic” nature of this molecule. The HOMO of this molecule (Fig. 2b) is highly hybridized of 3\textit{d} AOs of Co atoms, and 2\textit{p}_z orbit of the O atom, but cobalt’s AOs participating in hybridization are 3\textit{d}s\textsubscript{2}, 3\textit{d}y\textsubscript{2} and 3\textit{d}z\textsubscript{2} orbits, rather than 3\textit{d}xy and 3\textit{d}xz AOs in the case of the linear Co\textsubscript{2}O molecules. Considering that the linear molecules can be derived as a limiting case of the triangular one, one may think that the triangular configuration should correspond to the “natural” Co\textsubscript{2}O molecule that is stable in “free space”. Indeed, MCSCF ground state energy of this triangular Co\textsubscript{2}O triplet is smaller than that of the linear Co\textsubscript{2}O singlet. However, it still is somewhat larger than both ROHF and MCSCF ground state energies of the linear Co\textsubscript{2}O pentet. At the same time, the linear pentet molecule is less stable geometrically, and can be easily converted to the triangular triplet. To ascertain whether the “ferromagnetic” triangular Co\textsubscript{2}O triplet, “ferromagnetic” linear Co\textsubscript{2}O pentet or “antiferromagnetic” linear Co\textsubscript{2}O singlet all survive in nature, more sophisticated MP2 and higher approximations should be used. Importantly, in the presence of polarizing potentials exerted by foreign atoms (lattice) or fields, there should exist other triangular Co\textsubscript{2}O molecules
both “ferromagnetic” and “antiferromagnetic” in nature, because such a change in geometry could accommodate polarization effects of the external potentials. An example of the three Co$_2$O molecules illustrates extreme importance of the use of very accurate, first-principle methods to obtain results of practical significance.

The existence of such “antiferromagnetic” linear Co$_2$O molecule whose ground state energy coincides (within the calculation error brackets) with those of the “ferromagnetic” linear and triangular Co$_2$O molecules points out toward a possible microscopic mechanism behind surface re-structuring and/or passivation that manifest themselves as some familiar phenomena on larger scale. In particular, re-structuring of an antiferromagnet-ferromagnet interface due to geometrical changes of the Co-O atomic clusters (for example, in the process of their growth, or due to temperature fluctuations), and the corresponding electron spin re-alignment, may result in the development or loss of exchange bias in small core-shell Co/CoO nanoclusters (28,29). When a cluster size becomes small enough for the “surface” energy to be comparable to that of the “volume” energy of the clusters, small changes in a Co-O-Co angle may provide for a change from “antiferromagnetic” to “ferromagnetic” electron spin alignment leading to a sufficient decrease of the surface energy of a cluster, and at the same time, to a loss of exchange bias at the interface. Such a spin re-alignment process is easily realizable due to flexibility and stretchability of the O-O bond in small Co-O molecules that is discovered in this study.

The initial structure of the “ferromagnetic” vacuum ROHF triplet Co$_2$O$_2$ depicted in Fig.3 has been derived from that of the triangular Co$_2$O cluster by addition of the second O atom in such a way that the centers of the atoms of the same species are located in the vertices at the ends of diagonals of a square with the side length equal to the sum of the covalent radii of Co and O atoms (below this molecule is called the square Co$_2$O$_2$ molecule). This cluster has been
optimized while the atomic centers’ of mass were fixed in their positions to derive the pre-designed molecule. The corresponding unconstrained molecule was obtained after lifting the spatial constraints applied to the atomic centers of the pre-designed molecule, so that the atoms could “move” to adopt equilibrium positions specific to the global minimum of the total energy of this Co$_2$O$_2$ cluster. Similar to the case of the linear and triangular Co$_2$O molecules, the structures of the pre-designed and vacuum Co$_2$O$_2$ molecules coincided, so that the initial configuration of the atoms corresponded to the global minimum of its total energy. An isosurface of the molecular electrostatic potential (MEP) of this molecule is depicted in Fig. 3a, and its ground state parameters are included in Table I.

![Fig. 3](image.png)

**Fig. 3.** Square vacuum ROHF triplet Co$_2$O$_2$. (a) Isosurface of the molecular electrostatic potential (MEP) corresponding to the fraction 0.01 of the maximum value (not shown) of the charge density distribution (CDD); MEP values vary from negative (red) to positive (deep blue). (b) Isosurface of the highest occupied molecular orbit (HOMO) corresponding to the fraction 0.005 of the maximum value; HOMO values vary from negative (magenta) to positive (light blue). Co and O atoms are represented by golden and red spheres, respectively. Electron charge is accumulated near the oxygen atoms (reddish and yellow to green regions). In (a) all dimensions are to scale, in (b) atomic dimensions reduced to show the HOMO structure.

In striking contrast to the rest of the molecules studied in this chapter, the vacuum square Co$_2$O$_2$ triplet has both its electron charge and the two uncompensated parallel electron spins accumulated in the vicinity of its oxygen atoms. The major contributions to the highly hybridized
HOMO (Fig. 3b) of this molecule are due to $3d_{xy}$ and $3d_{yz}$ orbits of the Co atoms, and $2p_z$ orbits of the O atoms. The ROHF OTE of this molecule is large (about 4.6 eV), and its MCSCF OTE even larger (about 7.4 eV), indicating that more accurate MP2 calculations are needed to ascertain the actual value of OTE of this molecule.

To demonstrate endless molecular design opportunities offered by the virtual synthesis methods, two neighboring O and Co atoms in the ROHF triplet Co$_2$O$_2$ were transposed, so that in the modified Co$_2$O$_2$ cluster the atoms of the same species become positioned side by side. This modified Co$_2$O$_2$ cluster was optimized while the centers of mass of the atoms were fixed in their positions, to obtain the pre-designed “ferromagnetic” Co$_2$O$_2$ pentet molecule (Fig. 4).

![Fig. 4. Modified pre-designed ROHF pentet Co$_2$O$_2$. (a) Isosurface of the molecular electrostatic potential (MEP) corresponding to the fraction 0.02 of the maximum value (not shown) of the charge density distribution (CDD); MEP values vary from negative (red) to positive (deep blue). (b) Isosurface of the highest occupied molecular orbit (HOMO) corresponding to the fraction 0.01 of the maximum value; HOMO values vary from negative (magenta) to positive (light blue). Co and O atoms are represented by golden and red spheres, respectively. Electron charge is accumulated near the oxygen atoms (reddish and yellow to green regions). All dimensions are to scale.](image)

This ROHF/MCSCF pentet (called the modified Co$_2$O$_2$ molecule in Table I) may be a spatial isomer of its parent ROHF/MCSCF triplet Co$_2$O$_2$. Indeed, the total ROHF and MCSCF ground state energies of the modified molecule differs from the corresponding ROHF/MCSCF
energies of its parent ROHF/MCSCF triplet within the error brackets of the ROHF/MCSCF calculations. At the same time, ROHF and MCSCF OTEs of these molecules differ almost by an order of magnitude (Table I), and the O-O bond length of 1.915 Å in this molecule is equal to that of the Co-Co bond, being much larger than other O-O bond lengths in Co – O molecules studied in this work. Moreover, the electron charge and 4 uncompensated electron spins in this molecule are accumulated in the vicinity of its Co atoms, in contrast to those of the square Co₂O₂ triplet. The extraordinary long O-O bond in the modified Co₂O₂ triplet is up to about 35% longer of its normal value, signifying that the O-O bond is significantly stretchable. This bond also is very flexible, as demonstrated by the mere existence of linear and triangular Co₂O molecules. Should appropriate external perturbations arise, such a stretchable and flexible O-O bond can support spin re-alignment in Co – O molecules from “antiferromagnetic” to “ferromagnetic” configurations, and vice versa. In its turn, such spin re-alignment may lead to re-construction of the antiferromagnet-ferromagnet Co/Co-O interface, and thus to the development or loss of exchange bias. Similar to the case of the square Co₂O₂ triplet, the pre-designed geometry of the modified Co₂O₂ molecule coincides with that of the unconstrained one. Considering that ROHF/MCSCF OTE of this molecule are extremely small, and the O-O bond length is extremely long, one cannot avoid a thought that the modified Co₂O₂ pentet should be unstable in “free space”, and thus the proper Co₂O₂ triplet is the one which is stable. More accurate calculations, at least at the MP2 level, are necessary to clarify this issue and ascertain the ground state energies and OTEs of both studied Co₂O₂ molecules.

Replacement of two oxygen atoms in the pre-designed square Co₂O₂ cluster of Fig. 3 with two cobalt atoms while keeping the interatomic distances fixed, and using this Co-defined square as a base of the pyramid with O atom on the top (the Co-O distance is 1.916 Å) produces
a Co₄O pyramidal cluster of Fig. 5. ROHF optimization of this cluster (with the initial positions of the centers of mass of its atoms fixed) results in the pre-designed, “ferromagnetic” pyramidal ROHF nonet Co₄O (Table 1). This molecule has a surprisingly deep ground state (its ground state energy is -592 H) and significant ROHF OTE of about 0.5 eV. Its electron charge and 8 uncompensated electron spins are accumulated near Co atoms, and the dipole moment is relatively small, 1.3058 D, due to high symmetry of the molecule. Notably, this molecule is obtained at the verge of applicability of the HF approximation. The existence of this molecule is entirely due to model quantum confinement that constrains atomic motion and enforces oxygen-mediated ligand bonding of 3d Co electrons. In other words, the molecule is stressed, with its Co-Co bond length of 2.500 Å being too small, and its only oxygen atom being relatively far and almost incapable to accept the large outer electron charge of the Co atoms. Once the spatial constraints applied to the cluster’s atoms are lifted, the unconstrained total energy minimization procedure results in ionization of the cluster, so the unconstrained Co₄O molecule does not exist.

Fig. 5. Pyramidal pre-designed ROHF nonet Co₄O. (a) Isosurface of the molecular electrostatic potential (MEP) corresponding to the fraction 0.02 of the maximum value (not shown) of the charge density distribution (CDD); MEP values vary from negative (red) to positive (deep blue). (b) Isosurface of the highest occupied molecular orbit (HOMO) corresponding to the fraction 0.003 of the maximum value; HOMO values vary from negative (magenta) to positive (light blue). Co and O atoms are represented by golden and red spheres, respectively. Electron charge is accumulated near the oxygen atom (reddish and yellow to green regions). In (a) all dimensions are to scale, in (b) atomic dimensions reduced to show the HOMO structure.
Thus, it comes somewhat unexpectedly that an addition of only one oxygen atom to the Co₄O pre-designed pyramid in such a way that the resulting structure is a proper octahedral cluster Co₄O₂, with O atoms on the tops of both pyramids, leads to stabilization of this atomic configuration. The pre-designed octahedral molecule Co₄O₂ is a “ferromagnetic” ROHF/MCSCF pentet, with a deep potential well of its ground state (Fig. 6). Its 4 uncompensated electron spins are in the vicinity of their respective 4 Co atoms, and some of the electron charge is accumulated near both oxygen atoms. ROHF OTE of this molecule is about 2 eV (Table I), and its dipole moment exceeds 3 Debye. The value of MCSCF ground state energy of this molecule calculated using a rather large CAS 8×10 lies within the calculation error brackets from its ROHF value, but MCSCF OTE is diminishingly small, indicating that at MCSCF level of approximation this molecule may be unstable.

**Fig. 6.** Octahedral pre-designed MCSCF pentet Co₄O₂. (a) Isosurface of the molecular electrostatic potential (MEP) corresponding to the fraction 0.01 of the maximum value (not shown) of the charge density distribution (CDD); MEP values vary from negative (red) to positive (deep blue). (b) Isosurface of the highest occupied molecular orbit (HOMO) corresponding to the fraction 0.005 of the maximum value; HOMO values vary from negative (magenta) to positive (light blue). Co and O atoms are represented by golden and red spheres, respectively. Electron charge is accumulated near the oxygen atoms (reddish and yellow to green regions). In (a) all dimensions are to scale, in (b) atomic dimensions reduced to show the HOMO structure.
At the HF level of approximation there exist two unconstrained octahedral-like molecules (Table I) corresponding to the pre-designed octahedral Co₄O₂ pentet. Both vacuum Co₄O₂ molecules are obtained by lifting the spatial constraints applied to the centers of mass of atoms in the pre-designed octahedron, and then minimizing the total energy of the structure again. Visually, these molecules are indistinguishable from their octahedral pre-designed counterpart, as their oxygen atoms moved only slightly from their former positions on the tops of the octahedral pyramids toward the Co-defined base. However, both unconstrained molecules have more evenly spread CDDs, so that less of electron charge is accumulated near the oxygen atoms.

![Fig. 7. Octahedral vacuum MCSCF singlet Co₄O₂. (a) Isosurface of the molecular electrostatic potential (MEP) corresponding to the fraction 0.01 of the maximum value (not shown) of the charge density distribution (CDD); MEP values vary from negative (red) to positive (deep blue). (b) Isosurface of the highest occupied molecular orbit (HOMO) corresponding to the fraction 0.01 of the maximum value; HOMO values vary from negative (magenta) to positive (light blue). Co and O atoms are represented by golden and red spheres, respectively. Electron charge is evenly spread near the oxygen atoms (reddish and yellow to green regions). In (a) all dimensions are to scale, in (b) atomic dimensions reduced to show the HOMO structure.](image)

One of these is a ROHF pentet, and another RHF/MCSCF singlet (Fig. 7). While the vacuum octahedral-like ROHF Co₄O₂ pentet has a slightly deeper ground state minimum than that of the singlet, both values fall within the calculation error brackets from each other, and
OTEs values of both molecules are very similar. However, at the MCSCF level of approximation with CAS 4×4 the octahedral-like pentet shown all signs of instability (the energy minimization procedure diverged), while the octahedral-like MCSCF Co₄O₂ singlet was stabilized and demonstrated large OTE. Electron charge of this “antiferromagnetic” molecule is evenly spread near the oxygen atoms (Fig. 7a), its bonding 2p-3d HOMO has almost perfect donut-like shape (Fig. 7b), and its dipole moment is zero. Similar to HOMOs of all other Co – O molecules of this study, HOMOs of the vacuum octahedral-like Co₄O₂ molecules are hybridized with the major contributions coming from 3d AOs of cobalt and 2p AOs of oxygen.

2.3. Larger Co – O molecules.

It appears that building Co – O nanowires by addition of Co and O atoms to the square Co₂O₂ configuration in the plane defined by the centers of atoms of this flat cluster does not result in clusters that cannot develop bonded states. Similarly, adding pairs of Co and O atoms to the octahedron Co₄O₂, so that Co atoms were arranged in a flat sheet and O atoms in two quasi-linear wires on each side of the sheet, is next to impossible, as such thin nanowires cannot be stabilized. Thus, molecules composed of Co and O atoms and larger than Co₂O₂ are essentially three-dimensional. This is strikingly different from the case of Ni – O molecules (see Chapter 7 for details), where flat molecules and very thin nanowires containing up to 28 Ni and 26 O atoms have been easily stabilized. Large nuclear spins and uneven number of electrons in 3d shells of Co atoms makes it difficult to realize stable larger Co – O molecules in a fashion similar to that of larger Ni – O molecules.

There are three larger Co – O molecules synthesized virtually in this study. They are three-dimensional “ferromagnetic” structures with all uncompensated electron spins parallel and
localized in the vicinity of Co atoms, and their HOMOs built primarily of 3d AOs of Co and 2p AOs of O atoms.

TABLE II. The ground state of larger Co-O molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>RHF/ROHF and MCSCF ground state energy, Hartree</th>
<th>RHF/ROHF and MCSCF direct optical transition energy, eV</th>
<th>Spin multiplicity</th>
</tr>
</thead>
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<tr>
<td>Prismatic Co₆O₆</td>
<td>-959.563038</td>
<td>2.2014</td>
<td>vacuum septet</td>
</tr>
<tr>
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<td>6.0365 (CAS 10×11)</td>
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<td>0.6231</td>
<td>pre-designed pentet</td>
</tr>
<tr>
<td>Ball-like Co₈O₇</td>
<td>-1262.451471 (CI)</td>
<td>2.2033 (CI)</td>
<td>pre-designed pentet</td>
</tr>
<tr>
<td>Ball-like Co₈O₇</td>
<td>-1262.750263 (CAS 8×8)</td>
<td>0.0258 (CAS 8×8)</td>
<td>pre-designed pentet</td>
</tr>
</tbody>
</table>

**Fig. 8.** Hexagonal prism of vacuum MCSCF septet Co₆O₆. (a) Isosurface of the molecular electrostatic potential (MEP) corresponding to the fraction 0.01 of the maximum value (not shown) of the charge density distribution (CDD); MEP values vary from negative (red) to positive (deep blue). (b) Isosurface of the highest occupied molecular orbit (HOMO) corresponding to the fraction 0.001 of the maximum value; HOMO values vary from negative (magenta) to positive (light blue). Co and O atoms are represented by golden and red spheres, respectively. CDD is almost evenly spread over the molecule, with some accumulation near the oxygen atoms (reddish and yellow to green regions). In (a) all dimensions are to scale, in (b) atomic dimensions reduced to show the HOMO structure.

The structure of the pre-designed hexagonal prismatic ROHF/MCSCF septet Co₆O₆ (Fig. 8) coincides with that of the corresponding unconstrained one. The molecule is built of two co-
axial ideal hexagons with alternating Co and O atoms in the verges of each hexagon. The side length and the distance between the hexagons are equal to the sum of the covalent radii of Co and O atoms. One of the hexagons is turned by the angle $\pi/6$ around the joint rotation axis with regard to another. If other pre-designed isomers of the unconstrained prismatic $\text{Co}_6\text{O}_6$ molecule exist, they cannot be discovered by incremental changes in positions of atoms in the unconstrained molecule. A rather large OTE of about 2 eV of this molecule (Table II) indicates that the molecule may be stable, despite being ROHF septet. This conclusion is further confirmed by “semiconductor” properties of the ROHF septet $\text{Co}_6\text{O}_6$. Thus, CDD of this molecule is almost evenly spread over the entire “surface” of the molecule reaching beyond the space occupied by its atoms. Such CDD is similar in nature to those of small semiconductor compound molecules studied previously (35, 36, 38-40). Among small Co – O molecules of this work, the hexagonal prismatic ROHF septet $\text{Co}_6\text{O}_6$ seems to be the smallest Co-O structure showing such CDD properties. MCSCF studies with large CAS 10×11 produced even larger MCSCF OTE value of this “ferromagnetic” molecule, with its 6 uncompensated electron spins parallel and localized near their respective Co atoms. In contrast to the majority of molecules studied here, there is only small electron charge accumulation near oxygen atoms in the unconstrained prismatic MCSCF septet $\text{Co}_6\text{O}_6$.

The largest Co – O structure considered here is the ball-like $\text{Co}_8\text{O}_7$ cluster. It is built of three co-axial polygons: two pre-designed perfect Co – O squares of Fig. 3, and a perfect Co – O hexagon with a Co atom in its center, with the hexagon placed in the middle between the squares (Fig. 9). All three polygons have the centers of Co and O atoms placed in polygons’ vertices in an alternating manner. The Co – O squares are stacked over each other and turned with regard to each other by the angle $45^\circ$ around the vertical axes running through their centers of rotation, and
have the same side length equal to the sum of the Co and O covalent radii. The hexagon is positioned in the middle between the squares in such a way so that each of its Co atoms form two triangles with two Co-O pairs of atoms each of which belongs to their respective square. The center of the hexagon with a Co atom in it coincides with the center of the entire structure.

**Fig. 9.** Ball-like pre-designed MCSCF pentet Co₈O₇. (a) Isosurface of the molecular electrostatic potential (MEP) corresponding to the fraction 0.005 of the maximum value (not shown) of the charge density distribution (CDD); MEP values vary from negative (red) to positive (deep blue). (b) Isosurface of the highest occupied molecular orbit (HOMO) corresponding to the fraction 0.0005 of the maximum value; HOMO values vary from negative (magenta) to positive (light blue). Co and O atoms are represented by golden and red spheres, respectively. CDD is almost evenly spread over the molecule, with some small accumulation near the oxygen atoms (reddish and yellow to green regions). In (a) all dimensions are to scale, in (b) atomic dimensions reduced to show the HOMO structure.

Minimization of the total energy of this cluster, while the centers of mass of its atoms were kept in fixed position in space, resulted in the pre-designed, ball-like ROHF/MCSCF pentet molecule Co₈O₇ (Fig. 9). Notably, the ROHF and CI values of the ground state energy of this molecule coincide to the third digit after the dot (Table II), and only MCSCF calculations with CAS 8×8 bring about a decrease in its value by merely 0.3 H. At the same time, the corresponding OTE values differ by at least an order of magnitude, with ROHF OTE being about
0.6 eV, CI OTE about 2.2 eV, and MCSCF OTE very small, 0.0258 eV. The 4 uncompensated spins of this “ferromagnetic” molecule are localized near their respective Co atoms, and the charge is spread over the “surface” of this molecule reaching beyond the space occupied by its atoms. Thus, in similarity to the Co₆O₆ molecule, the pre-designed ball-like pentet Co₆O₇ possesses semiconductor-like CDD, yet it has conductor-like, negligibly small MCSCF OTE. In depth MP2 studies are necessary to ascertain the OTE value of this molecule and to reveal the true nature of its electronic structure and properties.

3. CONCLUSIONS

The majority of small and larger Co – O molecules synthesized virtually in this study are “ferromagnetic” spin multiplets with uncompensated spins parallel and localized near Co atoms, and surprisingly deep potential wells of their ground states. HF/CI/CASSCF/MCSCF OTE values of these molecules are strongly dependent of the structure of the molecules.

Two HF/CI/CASSCF/MCSCF singlets have also been synthesized. Both of the “antiferromagnetic” singlets, linear vacuum Co₂O and octahedral-like vacuum Co₄O₂, have all their electron spins antiparallel and compensated. Incremental geometrical changes in such “antiferromagnetic” singlets may be caused by interaction with the environment, including acquisition of additional Co and/or O atoms by the clusters, thus leading to a change in their electron spin alignment similar to those demonstrated in the case of spin multiplets Co₂O and octahedral-like vacuum Co₄O₂. In small Co-O molecules such transitions are either favorable or neutral energetically, and also accommodated for by the stretchable and flexible O – O and Co – O bonds. Moreover, enlargement of such molecules is also energetically advantageous, because and addition of a Co atom to a cluster brings the ground state energy value down by about 144 H, while addition of an O atom by about 16 H. [This observation holds for all molecules of this
study. Notably, in the studied cases of “non-stoichiometric” Co – O molecules ligand Co bonding plays a leading role in re-distribution of electron charge and spin among Co atoms themselves, thus providing for molecular stability. Similar to the majority of nanosystem cases, in the case of small Co – O molecules the nature of such oxygen-mediated strong ligand bonding is not described by the octet rule.

The above observations correlate perfectly with experimental evidence, including the facts that Co clusters are easily oxidized. While in the process of oxidation a small Co (core) – Co-O (shell) cluster forms and reaches some critical size, electron spin re-alignment (that is one of the major driving forces of the process) may lead to a Co/Co-O interface re-construction, facilitating a decrease in the “interface” energy of the system. Depending on the electron spin re-alignment results, this process may manifest itself at a larger scale as a loss of exchange bias. Further CI, CASSCF, MCSCF and MP-2–based synthesis of larger pre-designed and unconstrained Co – O molecules is necessary to characterize and describe in detail the spin re-alignment process and its effects.

The results of virtual synthesis of Co – O molecules of about 1.5 nm in linear dimensions obtained in this study are in excellent agreement with available experimental (20,29,33,41) and theoretical (34,42) data for comparable small Co-O molecules. Notably, with an increase in the size of molecules, their OTEs decrease toward 2 eV to 3.5 eV values, in agreement with experimental observations specific to somewhat larger Co – O nanoparticles. Also, the obtained results agree well with DFT-based PBE0 studies of bonding in bulk Co – O (43). At the same time, the ground state energy minima of Co₄O₂ and Co₆O₆ molecules synthesized virtually in this work are over an order of magnitude deeper than overly shallow ground state of about -47 H obtained in DFT studies of a Co₄O₄ cluster using VASP software (34).
ACKNOWLEDGEMENTS

This work was supported by NSF grants DMR #0340613 and DMR #0647356.

REFERENCES


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