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Chemical activity of materials based-on Earth-abundant magnetic model / band theory electronic analysis in heterogenous catalysis like the d-band centre in compositions with open-shell configurations, electronic and magnetic transitions in metal oxides established the foundations of the theoretical understanding of the catalyst and the intermediates. Separately, Goodenough has achieve high rates of oxygen evolution due to mild bonding between towards the ligands (O) overlap with the lobes of the reactants activity of perovskite oxides in terms of molecular orbital theory towards the ligands (O) overlap with the lobes of the reactants. Water oxidation enables conversion of electricity into storable hydrogen, needed for clean energy and a sustainable economy. In water electrolysis, the oxygen evolution reaction (OER) is the rate limiting step of the overall process. Therefore much attention has devoted to understand the rationale behind triplet state O₂ evolution in order to develop active, stable and abundant catalysts that accelerate it². In 1980 Matsumoto and co-workers examined the OER activity of the LaₓSrFe₁₋ₓO₃₋δ (0 ≤ X ≤ 1 and 0 ≤ y ≤ 1) family of perovskites in alkaline solution; even though the group could not synthesise the (Co⁵⁺)SrCoO₃₋δ composition, they predicted that it will show the lower overpotentials. The LaₓSrFe₁₋ₓO₃₋δ structure was obtained by Matsumoto as an excellent and stable electrocatalyst for OER; similar compositions and oxidation states typically lead to good catalysts³,⁴,⁵. In the smaller LaₓSrCoO₃₋δ group, SrCoO₃₋δ shows the optimum OER kinetic and is, in fact, one of the best catalysts⁶,⁷.

In 1984 Bockris and Otagawa described the electrocatalytic activity of perovskite oxides in terms of molecular orbital theory; they show that the antibonding (AB) 3d-metal orbitals directed towards the ligands (O) overlap with the lobes of the reactants forming AB a*-type orbitals, e₂g-2p shells in octahedral coordination. The authors explained that the catalysts having occupied e₂g-2p levels achieve high rates of oxygen evolution due to mild bonding between the catalyst and the intermediates. Separately, Goodenough has established the foundations of the theoretical understanding of the electronic and magnetic transitions in metal oxides⁸,⁹,¹⁰. These works have been key to derive the significant influence of quantum spin exchange interactions (QSEI) in the orbital chemistry of magnetic catalysts, also known as spintro-catalysis¹¹. Due to the impact of QSEI in compositions with open-shell configurations,¹² conventional electronic analysis in heterogenous catalysis like the d-band centre model / band theory¹³ is insufficient to describe the highly-correlated electrons; and then lead to rough approximations for the catalytic activity of materials based-on Earth-abundant magnetic elements. As in spintronics, the spins of many electrons can act together, affect the magnetic and electronic properties of a material, and influence significantly its catalytic behaviour.

QSEI reduce the electronic repulsions and are key for charge mobility in magnetic systems¹². A ferromagnetic (FM) conduction band indicates that the physics of the itinerant electrons is significantly influenced by Fermi holes, a fundamental requirement for optimal electrocatalysts based on 3d-metals¹³,¹⁴. By looking carefully, we can see examples where magnetic structures associate overall with active heterogeneous catalysis. FM oxides show better activity than Pt in the oxidation of nitrous oxide (NO has doublet ground state)¹⁵,¹⁶, FM nitrides improve ammonia synthesis¹⁷, or Co doping in MoS₂ induces FM¹⁸ and enhances the activity in various reactions. In addition of particular interest for electrocatalysis, inter-atomic FM orderings leads to favourable spin-charge transport, avoiding antiferromagnetic (AFM) electronic localization.¹² Fully AFM insulators like LaCrO₃ or LaFeO₃ are poor oxygen catalysts¹⁹,²⁰. Spin selection in polarized density of states facilitates the oxidation/reduction of triplet state O₂-²¹,²². Nature has evolved excellent magnetic catalysts from abundant 3d-metals, e.g. during photosynthesis²³, via engineering QSEI.

In a broad context, the rationalisation of the orbital physics in magnetic structures is important in theoretical heterogeneous catalysis, because it will allow to study activities across the whole periodic table based on the interplay between chemical composition, and electronic configuration. Successful catalytic design based on orbital occupation²⁴,²⁵ may proceed from the rigorous analysis of the quantum chemistry²⁶. In the LaₓSrCoO₃₋δ family two ends for the OER activity can be defined: LaCoO₃ as the less active and SrCoO₃₋δ as the most efficient. The orbital physics behind the intrinsic activity of SrCoO₃₋δ is unknown, as well as the effect of the iron ions in compositions like LaₓSrFe₁₋ₓCo₂₋ₓO₃₋δ. Also, the specific orbital configuration of LaCoO₃ at room temperature is controversial, because three spin states representing the 3d-2p AB-orbitals in octahedral coordination, t₂g⁵eₘ (low-spin, LS), t₂g⁵eₘ⁺ (high spin, HS) and t₆g⁵eₗ (intermediate spin, IS), are accessible for the Co⁺-O bonds. LaCoO₃ presents the following, not fully understood, electronic transitions as a function of temperature²⁶,²⁷:

- 0 K < T < 35 K: bulk cobalt cations are preferentially in the Low-Spin (LS) t₆g⁵eₘ⁰ diamagnetic state.
- 35 K < T < 110 K: cobalt cations coexist in intermediate-spin (IS) t₆g⁵eₘ⁺ and high-spin (HS) t₆g⁵eₗ configurations with a ratio of LS(HS + IS) = 0.5.
110 K < T < 350 K: a mixture of approximately 50% LS and 50% HS cobalt cations forms a semi-conductive paramagnetic (PM) phase.

350 K < T < 650 K: the semi-conductive phase coexists with a metallic phase, possibly due to the presence of IS cations. An insulator-to-metal transition occurs near 450 K.

The phases of LaCoO$_3$ accommodate diverse Jahn-Teller (JT) distortions as the XRD patterns indicate$^{28,29}$. Below 90 K (Tab. 1) the experimental Co-O distances are similar, 1.918-1.934 Å, and shorter than those at higher temperatures$^{30}$. Different electronic configurations coexist in cobalt-based oxides; the present manuscript explains via DFT(GGA+U) calculations the electronic structure behind the poor or good OER activity in the oxides; the present manuscript explains via DFT(GGA+U) calculations the electronic structure behind the poor or good OER activity in the oxides.

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Results and discussion

In our calculations, the LaCoO$_3$ ground-state has all the Co$^{3+}$ cations in LS configuration. The $t_{2g}^{1}g_{e}^{0}$ structure presents no JT distortion and the predicted Co-O distance is about 1.893 Å. The density of states (DOS), Fig. 1a, shows that LS LaCoO$_3$ is an insulator with a band gap of about 0.5 eV. The second most stable phase is the $\frac{3}{4}$ LS + $\frac{1}{4}$ HS configuration, Fig. 1b; the interatomic exchange interactions are favourably ferromagnetic, because the $e_{g}$ band is overall more empty than occupied.$^{9}$

![Figure 1: Top: density of states (DOS) versus energy in eV. Bottom: Spin density for the configurations a) LS, b) FM $\frac{3}{4}$ LS + $\frac{1}{4}$ IS and c) FM $\frac{3}{4}$ LS + $\frac{1}{4}$ HS. The spin density is shown in yellow and the Fermi level is 0 eV.](image)

<table>
<thead>
<tr>
<th>State</th>
<th>Co-O (Å)</th>
<th>ΔE</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIA</td>
<td>1.893</td>
<td>1.893 │ 0</td>
</tr>
<tr>
<td>FM $\frac{1}{4}$ LS</td>
<td>1.870</td>
<td>1.870 │ 12</td>
</tr>
<tr>
<td>FM $\frac{3}{4}$ LS</td>
<td>1.908</td>
<td>1.944 │ 1.945</td>
</tr>
<tr>
<td>FM $\frac{3}{4}$ IS</td>
<td>1.894</td>
<td>1.894 │ 41</td>
</tr>
<tr>
<td>FM $\frac{1}{4}$ IS</td>
<td>1.886</td>
<td>1.886 │ 0.910</td>
</tr>
<tr>
<td>AFM $\frac{1}{4}$ LS</td>
<td>1.871</td>
<td>1.883 │ 1.883</td>
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<tr>
<td>AFM $\frac{3}{4}$ HS</td>
<td>1.944</td>
<td>1.964 │ 1.970</td>
</tr>
<tr>
<td>FM $\frac{3}{4}$ IS</td>
<td>1.893</td>
<td>1.893 │ 57</td>
</tr>
<tr>
<td>FM $\frac{3}{4}$ HS</td>
<td>1.905</td>
<td>1.905 │ 1.907</td>
</tr>
<tr>
<td>FM $\frac{1}{4}$ HS</td>
<td>1.895</td>
<td>1.954 │ 1.955</td>
</tr>
</tbody>
</table>

Theoretical methods

We have performed periodic Density Functional Theory (DFT) calculations using VASP (Vienna Ab-initio Simulation Package), a program that combines ab-initio energy calculations with plane-wave basis sets$^{30-33}$. The electron-ion interactions for the atoms are described by the projector augmented wave method developed by Blöchl$^{34,35}$. The exchange-correlation energy has been calculated within the generalized gradient approximation$^{36,37}$. The electron-ion interactions for the atoms are described by the projector augmented wave method developed by Blöchl. The exchange-correlation energy has been calculated within the generalized gradient approximation using the Perdew-Burke-Ernzerhof functional revised for solids$^{38}$. We used a cut-off energy of 400 eV for the expansion of the wave function into plane waves. The Monkhorst-Pack scheme has been chosen for the integration in the reciprocal space$^{39}$. We have used the so-called DFT+U approach for the corrections accounting for the strong correlation among the electrons at the Co and Fe atoms.$^{38}$ The Hubbard +U correction is desirable in 3d-metals to consider explicitly non-local interactions between localized electrons$^{39}$. The value of U is a constant, thus, in order to get accurate results, a structure-dependent parametrization of U is necessary$^{40}$. An initial calibration of GGA +U method was performed in order to match the electronic configurations of the LaCoO$_3$ and SrCoO$_{6.5}$ catalysts. The lattice parameters for monoclinic I2/a LaCoO$_3$ were optimized using a single unit cell, 4 La, 4 Co and 12 oxygen atoms, versus U. Optimizations indicate that for U 2.0 - 2.5 the Hubbard correction is suitable to both experimental Jahn-Teller distortions$^{29,41}$ (see Table 1) and expected relative stability of competing electronic configurations$^{21}$. The reciprocal space has been sampled with a (7x7x5) k-point grid for the ground-state optimized lattice parameters (experimental within brackets): a = 5.309 Å (5.367), b = 5.417 Å (5.433), c = 7.719 Å (7.637), $\beta$ = 90.8º (91.0). The SrCoO$_{6.5}$ (001) slab model has lattice parameters of a = 5.333 Å, b = 5.333 Å and c = 30.0 Å and about 15 Å vacuum gap. The reciprocal space has been sampled with a (5x5x1) k-point grid. The climbing-image nudged elastic band (cNEB) method is used to determine minimum-energy paths, via 5 iterations and 50 % HS cobalt cations forms a semi-conductive paramagnetic (PM) phase.

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The FM ½ LS + ½ HS ordering is slightly more stable than the AFM configuration, and above 120 K entropy disorders the spins. These structures accessible at 300 K present cooperative Jahn-Teller type distortions with ~5% of maximum deviation between the average experimental distances and the calculated ones. Both LS and HS Co$^{3+}$ atoms show localization of spin density within the 3d-metal and 2p-oxygen orbitals. This suggests the presence of a mixed valence occupations and enhanced 3d-2p hybridization with the increment of on-site magnetism. Overall, the electrocatalytic activity of LaCoO$_3$ observed at room temperature is at least initially restricted by the limited charge conductivity.

SrCoO$_3$ is a FM conductor ($T_C$ = 305 K) with a total magnetization of ~2.5μ$_B$ per octahedral shell$^{34}$ and a percentage of oxygen vacancies typical of Co$^{4+}$ oxides$^{6}$. Calculations on the SrCoO$_2$ and SrCoO$_2.75$ stoichiometries result in FM metallic ground states with a total spin of ~2.5μ$_B$ within Co-O bonds, in perfect agreement with experimental data. Fig. 3 shows the conduction band constituted by the frontier t$_{2g}$-2p and e$_g$-2p orbitals, for the majority and minority of spin. The on-site QSEI in the open-shells are crucial to investigate the correct electron paring and the partial population of the AB-orbitals.

The participation of the SrCoO$_3$-δ family is a FM conductor (T$_C$ = 305 K) with a total magnetization of ~2.5μ$_B$ per octahedral shell$^{34}$ and a percentage of oxygen vacancies typical of Co$^{4+}$ oxides$^{6}$. Calculations on the SrCoO$_2$ and SrCoO$_2.75$ stoichiometries result in FM metallic ground states with a total spin of ~2.5μ$_B$ within Co-O bonds, in perfect agreement with experimental data. Fig. 3 shows the conduction band constituted by the frontier $t_{2g}$-2p and $e_g$-2p orbitals, for the majority and minority of spin. The on-site QSEI in the open-shells are crucial to investigate the correct electron paring and the partial population of the AB-orbitals.

alternate orientation pattern in the adjacent orthogonal atomic 3d-orbitals reduces the electronic repulsion without JT elongations and instead with some short Co-O bonds of 1.83 Å. A hypothetical AFM configuration, about 0.8 eV higher in energy from the FM configuration, recovers the JT distortions, with an elongation of some Co-O bonds to about 1.93 Å.

The admirable agreement between the GGA+U calculations and the experimental structural, electronic and magnetic properties for the two oxidation extremes, LaCoO$_3$ and SrCoO$_3$, indicates a high degree of confidence in the comparison with the following stoichiometries: La$_{0.75}$Sr$_{0.25}$CoO$_3$, La$_{0.5}$Sr$_{0.5}$CoO$_3$, La$_{0.25}$Sr$_{0.75}$CoO$_{3.5}$ and La$_{0.25}$Sr$_{0.75}$Co$_{0.75}$Fe$_{0.25}$O$_{3.5}$.

All the compositions in the La$_{3-δ}$Sr$_{2+δ}$CoO$_3$ family are extended FM gapless conductors apart from LaCoO$_{3.5}$ p-type semi-conductor. In their ground-states, the AB-eigenvectors show a concomitant increment of the 3d-2p hybridization with the magnetization, which is maximum in SrCoO$_3$ (Fig. 3 and 4). The participation of the 2p-orbitals of the ligands in the AB-shell at the conduction band increases with the number of Fermi holes. The relative number of $t_{2g}$-2p electrons with minority spin decreases with the increasing oxidation states, and the magnetic density in the Co-O bonds growths, favoured by the QSEI.

Fig. 4 shows the trend of the accumulated FM spin-moment in Co-O bonds (in the ground state) versus the experimental relative intrinsic OER activity$^{31}$; we could have also used only the spin-density on the oxygen atoms ($\mu_{O}^FM$). The electronic structure of La$_{0.25}$Sr$_{0.75}$Co$_{0.75}$Fe$_{0.25}$O$_{3.5}$ shows that this material possesses the same overall average magnetization as SrCoO$_{3.5}$. The presence of Fe ions increases the magnetism due to their own $t_{2g}$-$e_g$ shells, while the spin-polarization overall decreases on the Co-O AB-orbitals. Overall La$_{0.25}$Sr$_{0.75}$Co$_{0.75}$Fe$_{0.25}$O$_{3.5}$ has less FM ligand holes, this explains that iron atoms serve to increase the stability of the Co$^{4+}$ oxides, but not the intrinsic OER activity. The trend shown in Fig. 4 is mathematically expressed by Eq. 1, that is derived from Eq. 3 by assuming that $\Delta H_{act_{cat1}}^{(0)cat_{1}} \approx \Delta H_{act_{cat2}}^{(0)cat_{2}}$. For the La$_{3-δ}$Sr$_{2+δ}$CoO$_3$ family, $\Delta_{QSE}^{OER}$ gives almost a quantitative prediction of the relative OER activity. The composition with the highest OER activity has a maximum $\mu_{cat}^FM$ value.

![Figure 2](image2.png)

**Figure 2.** *(Top)*: density of states (DOS) versus energy in eV. *(Bottom)*: spin density for the Co$^{3+}$ atoms in the two ½ LS + ½ HS accessible configurations of LaCoO$_3$ at 110 K < T < 350 K. *(a)* FM ½ LS + ½ HS, *(b)* AFM ½ LS + ½ HS. Different colours for the spin density on the cobalt atoms indicate a relative change in the orientation of the spins.

![Figure 3](image3.png)

**Figure 3.** Frontier orbitals in the ground state of SrCoO$_3$: *(a)* $t_{2g}$-2p (yellow), *(b)* $e_g$-2p (blue) and *(c)* density of states, DOS.

![Figure 4](image4.png)

**Figure 4.** Experimental and predicted, obtained using Eq. 1, relative OER intrinsic activity for the La$_{3-δ}$Sr$_{2+δ}$CoO$_3$ family with respect to LaCoO$_3$ in alkaline media. It indicates that increasing FM in the G.S. seems inherent to the OER activity in cobalt-based oxides.
serve to compare the relative intrinsic OER activity of different structures and 3d-metals by using $\mu_\text{cat}^{\text{FM}}$.

Eq. 1) $K_{\text{Relative OER}} = e^{\Delta H_{\text{OER}}^{\text{QSEI}}/\kappa}$

The enthalpy of any chemical event mainly depends upon three kinds of energy terms, Eq. 2. In magnetic catalysts, the additional non-classical QSEI$_\text{open shells}$, $\Delta\text{Exc}_{e^{-}}^{\text{QSEI.open shells}} \ll \Delta\text{H}_{\text{OER}}^{\text{QSEI}} - \mu_\text{cat}$, are part of the stabilizing potentials, and relatively as higher is their value smaller are the Coulomb terms.\textsuperscript{[14]}

Eq. 2) $\Delta H_{\text{cat}}^{\text{event}} = \Delta H_{\text{kinetic}}^{\text{event}} + \Delta H_{\text{rep}}^{\text{event}} + \Delta H_{\text{cat}}^{\text{event}} - \Delta H_{\text{cat}}^{\text{classical}} + \Delta\text{Exc}_{e^{-}}^{\text{QSEI.open shells}} + \Delta\text{Exc}_{e^{-}}^{\text{QSEI.open shells}}$

Cooperative QSEI$_\text{open shells}$ are indispensable to understand magnetic catalysts, since spin-potentials are responsible of the electronic conductivity and important in the orbital interactions, but how much? Limiting our study to the formation triplet $O_2$, Fig. 5 shows the thermodynamic steps of two possible mechanisms over a SrCoO$_{3-\delta}$ (001) surface for oxygen evolution. We compare between hypothetical close-shell (non-spin-polarized) calculations (Fig. 5 top) and the open-shell spin-polarized mechanisms (Fig. 5 bottom). QSEI reduce the energy of open-shells by a contribution of around $\pm$0.5 eV; this is not a trivial value. The kinetic is also significantly improved in the spin-polarized calculations, the activation barriers and the adsorption energies decrease considerably between 15% and 35% in comparison with the fictious close-shell system. The initial surface formation of an O-O bond has an activation energy of $\sim$0.56 eV, while the same step requires $\sim$0.73 eV in the non-spin-polarized calculations. Fig. 5 is in agreement with the specialized GGA+U literature\textsuperscript{[46]}. Moreover, calculations reveal structural discrepancies between close-shell and open shells calculations, for instance M-O bond distances vary by $\sim$0.1 Å.

We considered two possible pathways for O-O coupling (centre-to-left and centre-to-right): calculations of a classical surface mechanism go from the centre to the right; and a sub-surface pathway is from the centre to the left. The surface mechanism is more favourable mainly due to the restricted mobility of sub-surface O-O$^*$ units. Our observations are in line with the work of Mefford and co-workers: the group noticed the presence of bulk oxygen mobility in OER on SrCoO$_{3-\delta}$ catalysts.\textsuperscript{[5]} It is also consistent with the role of lattice oxygen in the computational work of Yoo and co-workers: the group noticed the presence of bulk oxygen mobility in OER on SrCoO$_{3-\delta}$ catalysts\textsuperscript{[47]}. The peculiar property of the highly oxidised mixed-valence SrCoO$_{3-\delta}$ composition is the ability to insert nucleophilic lattice oxygen towards the formation of O$_2$; which after desorption, leaves concomitant oxygen vacancies. These mobile vacancies can be rapidly occupied by oxygen atoms through the diffusion of bulk atoms and by gas phase intermediates, alike. This phenomenon creates a high turnover in the numbers of the active centres at the surface\textsuperscript{[48]}. Then excellent OER activities seem associated with an overall Mars-van Krevelen type mechanism that is characteristic of total oxidations\textsuperscript{[48,49]}. We already knew that coupled mixed-valence spin acceptors (or donors), showing preferential FM interactions in the partially occupied $AB\ v_{2p}$ orbitals, are good conductors and excellent oxygen spintron-catalysts.\textsuperscript{[52]}. Furthermore, prototypical oxides for OER are those structures with metals in a high oxidation state, and then sufficiently electronegative. Eq. 3 correlates the overall activation energy of FM catalysts with the specific influence of QSEI$_\text{open shells}$, added via a Heisenberg type exchange term\textsuperscript{[14,22]}.
Materials and Methods

Physical Chemistry Chemical Physics

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Notes and references


