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Principles determining the activity of magnetic oxides for electron transfer reactions

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ABSTRACT

Electrons in covalent oxides are fermions interacting through overlapping atomic orbitals, and quantum exchange interactions incorporate influential spin-dependent potentials in their electrocatalytic properties. The Goodenough-Kanamori rules explain the magnetic coupling between metals connected via ligands, known as super- (or double-) exchange interactions, which regulate their charge transport properties. To describe the electrocatalytic activity of magnetic metal oxides, we must extend their spin-dependent mechanisms of electron tunnelling to catalytic interfaces, because the exchange coupling between orbitals, in the catalysts and with the chemisorbed reactants, influences the kinetics of electron transfer reactions. The principles for developing magnetic coupling rules in electrocatalysis must guarantee spin passages, which are optimum for intrinsically degenerate configurations of the frontier orbitals oriented in the direction of the bonds at both sides of the Fermi level. A continuous energy landscape between the reactants and the catalyst minimizes the overpotentials during coherent redox electron tunnelling. Consequently, in this paper we derive the guidelines of the ferromagnetic (FM) exchange interactions, an extension of the Goodenough-Kanamori rules, to electrocatalytic interfaces, which anticipates minimum Gibbs energy of activation. We focus on the electronic coordinates, targeting reaction conditions where the electrons are the main energy carriers to trigger the steps; nonetheless they are interrelated with the atomic movements. We will use the oxygen evolution and reduction reactions as examples where quantum exchange interactions, a landmark of solid-state magnetism, and the chemistry of the triplet state O_2 molecule, are crucial for optimum kinetics.

One sentence summary: Delocalizing spin potentials facilitate the coherent propagation of electrons at covalent magnetic interfaces; this is a physical principle that links ferromagnetic exchange interactions, antibonding orbitals and optimum viable electrocatalysis: *spintro-catalysis*.

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1. Introduction

Some of the most important catalytic reactions for civilisation centre around steps that involve the triplet state O_2 molecule. The best catalysts for the oxygen evolution and oxygen reduction reactions (OER and ORR, respectively), essential for energy technologies, are magnetic mixed oxides (MMOs), the properties of which can only be understood with the consideration of internuclear spin dependent interactions related with electronic mobility [1–5]. Similarly, mixed-valence magnetic complexes are commonly found catalysts in nature for optimum electron-transfer steps; for instance, the oxygen evolution complex during photosynthesis [6], and biological N_2 fixation via molybdenum-iron complexes in proteins, are associated with spin-coupled metals [7–9].

When two antiparallel electrons pile up into the energy levels of Pauli metals, like $LaNiO_3$ or RuO_2, the wavefunction is symmetric in space ($\psi_{Fermi.level}^{sym.space}$) and optimizes the classical Coulomb potentials. On the other hand, in MMOs, exchange interactions and strong spin-orbit (s.-o.) coupling for the heavier transition-metals determine the state of the valence and conduction bands [10,11]. Non-magnetic metals maximise the electronic density in between nuclei, charge mobility being due to the overlap of unfilled neighbouring orbitals. $LaNiO_3$ and RuO_2 are excellent charge conductors and good oxygen electro-catalysts [12–16] while ultimately spin-polarized FM oxides without a band gap and with abundant holes

$(h_\downarrow^+)$ at the Fermi level, like the extensive $A_{1-X}A'_XCo_{1-Y}Fe_YO_{3-\delta}$ perovskite families [17–19] and $Ni_WCo_XFe_YO(OH)_Z$ oxyhydroxides [20], are more active for OER. Equally, FM-metals with conduction bands richer in electrons $(e_\uparrow^-)$ than $h_\downarrow^+$ give better rates for ORR [2,21–24]; or even high current efficiency for N_2 reduction, like $Sm_{1-X}A'_XFe_{1-Y}B'_YO_{3-\delta}$ oxides [25,26].

The Pauli exclusion principle leads to an effective coupling between the intrinsic angular momentum of the electrons and the orbital ordering in MMOs, known as quantum exchange energy. The coherent relocation of a fermion from one orbital to the neighbour is only possible if there is not already an electron of the same spin occupying that orbital. Fast ballistic wave-like propagation occurs in a coherent process, referred to as tunnelling, where electrons move from one site to another maintaining a definite phase relationship [27]. On the contrary, hopping is incoherent, a thermally activated process in which an electron moves from one site to another but loses information about its phase. In MMOs, the spin-correlation, exchange or spin-orbit interactions, created on an atom to its neighbours serves to mediate the charge transfer, revealing a more conductive behaviour for dominant FM orderings; whereas materials with intra-plane and inter-plane antiferromagnetic (AFM) coupling require higher thermal activation [28]. Stable AFM insulators, at working conditions, are poor oxygen electrocatalysts; however, activity increases above conventional metallic oxides with increasing FM conductivity [5]. The Goodenough-Kanamori rules explain the dominant magnetic ordering observed in MMOs, see Fig. 1, based on the orbital physics applied to electron transfer between metal atoms carrying a net spin and mediated by shared ions [29–31]. Because $e_\uparrow^-$ transfer in MMOs occurs through a magnetic junction, a review and extension of the FM spin exchange rules in catalysis is pertinent.

In spin-polarized metals with preferential FM interactions, the orbitals of the valence electrons at the active sites are antisymmetric in space $\left(\psi_{Fermi.level}^{anti.space}\right)$, while the spin function is symmetric. As Fig. 1 shows, the spin density of the ferrimagnetic $CaCu_3Fe_4O_{12-\delta}$ (Fe $3d\text{-}e_g^{1.25}$) ground state (G.S) occupies more of the interstitial spaces in between bonds than the AFM type-G $LaCu_3Fe_4O_{12}$ G.S. (Fe $3d\text{-}e_g^2$). The delocalized π-character via orthogonal orbitals at the oxygen atoms in FM orderings contrasts with the localized σ-character of AFM bonds. In this example, archetypal of excellent OER activity but bad for ORR [32], between half-filled $3d\text{-}t_{2g}^3e_g^2$ and hole-rich $3d\text{-}t_{2g}^3e_g^{1.25}$ bands, the sign of the exchange potentials and the free energy of the charge carriers ($e_\uparrow^-$ & $h_\downarrow^+$) fully determines their catalytic differences: no spin-gap n-type excellent OER catalyst versus an insulator with poor activity at ambient conditions [5]. $La_{1-X}Sr_XMnO_{3\pm\delta}$ p-type conductors, associated with FM $e_\uparrow^-$-rich $3d\text{-}t_{2g}^3e_g^{0.75}$ bands, serve as the inverse examples with good ORR activity but poor performance for OER [14]. An overall positive value of the exchange energy between the electrons in the valence and conduction band, in the Heisenberg model $\Delta_{magnetic}^{\Psi_{T.S.}^{\pm}} = J_{exc.} \cdot (\widehat{s_{Cat.}} \cdot \widehat{s_{e^-}}) > 0$, indicates that FM interactions reduce the classical electronic repulsions ($C_{e^-\text{-}e^-}$) at the expense of the Coulomb attractions ($C_{n^+\text{-}e^-}$) [2]. The less influential the localizing Coulomb interactions are, the more facile the tunnelling of the electrons is.

Founded on previous principles, we extend the rules of quantum FM exchange interactions to catalytic interfaces, where they will serve as guidelines to realise the best compositions for spin-dependent electron transfer reactions. The term "*spin*-electronics" refers to the study of the role played by the spin of the electrons in solid state physics, which specifically exploit spin properties instead of or in addition to charge degrees of freedom. Then, in

an analogous terminology, we differentiate with the term "*spintro*-catalysis", where mainly FM exchange interactions, in $\psi_{Fermi.level}^{anti.space}$, set the optimum thermodynamic conditions for spin-assisted electron transfer.

Double-exchange guidelines in *spintro*-catalysis, see Fig. 2[1]:

Rule 1) The spin angular momentum is conserved during an electron transfer in the catalyst and with the reactants.

Description. Overall the electronic transport at a catalytic interface depends on the transition probability, $k_{ST}^\pm \cdot e^{\Delta S_{T.S.}^{e^-/h+}/k_B}$, associated to the wavefunctions between the reactants and the active sites in the conduction band of the catalyst, Eq. (1), and between atoms in the conduction and valence band, Eq. (2):

$$k_{ST.reac.\rightarrow cond.}^\pm \cdot e^{\Delta S_{T.S.read.\rightarrow cond.}^{e^-/h+}/k_B} \propto \left| \left\langle \Phi_{cat.cond.}^{space} | \Phi_{reac.}^{space} \right\rangle \cdot \left\langle \chi_{cat.cond.}^{spin} | \chi_{reac.}^{spin} \right\rangle \right|^2, \tag{1}$$

$$k_{ST.val.\rightarrow cond.}^\pm \cdot e^{\Delta S_{val.\rightarrow cond.}^{e^-/h+}/k_B} \propto \left| \left\langle \Phi_{cat.cond.}^{space} | \Phi_{cat.val.}^{space} \right\rangle \cdot \left\langle \chi_{cat.cond.}^{spin} | \chi_{cat.val.}^{spin} \right\rangle \right|^2. \tag{2}$$

Within these equations, Φ and χ represents the spatial and spin parts of the wavefunction, respectively. Subindices *reac.*, *cat.cond.* and *cat.val* refer to the reactants and the catalyst conduction and valence bands, respectively. The spin integrals are zero when there is a change in the angular momentum of electrons, that is, $\left\langle \chi_{cat.cond.}^{spin} | \chi_{reac.}^{spin} \right\rangle$ and $\left\langle \chi_{cat.cond.}^{spin} | \chi_{cat.val.}^{spin} \right\rangle = 0$. Spin tunnelling decays exponentially with potential barriers [33], and via statistical mechanics we can express the oxidation rate ($e_\uparrow^-$ from the reactants) or reduction step ($h_\uparrow^+$ from the reactants) as $K(T)_{STST}^\pm = k_{ST}^\pm \cdot e^{\Delta S_{T.S.}^{e^-/h+}/k_B} \cdot e^{-\Delta H_{T.S.}^{e^-/h+}/k_BT}$. The total electronic energy of activation for half-reaction is $\Delta H_{T.S.}^{e^-/h+} = \Delta H_{T.S.reac.\rightarrow cond.}^{e^-/h+} + \Delta H_{val.\rightarrow cond.}^{e^-/h+}$. In this analysis we are responding from theoretical and physical meaningful principles to the dependence of electrocatalysis on the conductivity [34]; the band gap, $\Delta H_{val.\rightarrow cond.}^{e^-/h+} \geq 0$ was similarly included in the outstanding work of Gerischer [35]. Electrocatalysis is still catalysis and the factor $\Delta H_{T.S.reac.\rightarrow cond.}^{e^-/h+}$ represents the activation energies on the catalysts, initiated via the charge transfer.

Accompanying rule 1, the Pauli exclusion principle restricts the transfer of an electron from one orbital to its neighbour if there is already an electron of the same spin occupying that orbital. For instance, during the reduction or evolution of the triplet state oxygen molecule in FM manganites, the tunnelling electrons are antiparallel to the half-filled O_2 π^* orbitals [3,36], see Fig. 3. With this approach we demonstrate the need for consideration of reaction mechanisms including the adsorption of triplet state O_2 on to the active metals .

Rule 2) The ***intra*-atomic** and the ***inter*-atomic** exchange interaction in the covalent **-B-O-B-O-** framework are ferromagnetic in oxides with minimum $\Delta G_{T.S.}^{e^-/h+}$.

Description. The orbitals of FM conductors create an intrinsically degenerate spin-polarized metallic state that optimizes the wavefunction based on the reduction of the electron-electron repulsions, $\psi_{Fermi.level}^{anti.space}$. Magnetic oxides with intermediate valence states can have resonating orbital configurations and $\Delta H_{val.\rightarrow cond.}^{e^-/h+} = 0$, as in conventional metals. This guarantees that the transfer rate of spin-oriented electrons between the conduction band in the bulk and the surface states is fast, represented on the right side of Fig. 2, and the charge transport between the