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Quantum catalysts

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There is a non-local energy wave reality that rules our local observable experiences, which is non-observable directly using quantum mechanics based on continuous functions in space-time. Thus, wavefunctions start the transition from a classical deterministic realm to a probabilistic and discrete one. The principles of quantum mechanics fundamentally diverge from classical intuitions; thus, quantum materials have emerged as materials that cannot be described in terms of semiclassical particles and low-level approximations of quantum mechanics. Quantum materials have unique properties including non-weak (strong) electronic correlations and some type of electronic orders, such as superconducting and spin–orbital (magnetic) orders, and multiple coexisting interdependent phases, which are associated with new perceptions such as superposition and entanglement. Examples of quantum materials include superconductors, topological materials, Moiré superlattices, quantum dots and magnetically ordered materials. Many (solid) catalysts show distinctive quantum behaviours, which are frequently associated with open-shell orbital configurations. Thus, this perspective aims to show that the literature is already full of quantum catalysts, and it is necessary to distinguish them and adapt/improve their theoretical models for better understanding. Part of this work is focused on clarifying the complex language of many-body quantum physics, isolating the approximations that are not fundamentally complete, and connecting the non-classical interactions with more familiar concepts in chemistry. This approach is also valuable for the physics community, since it gives a more chemical view to the properties of quantum materials, with its adapted terminology. In this case, we aim to go beyond mathematics to try to explain the possible meaning and plausible real interpretation of quantum correlations. Only the understanding of true quantum potentials and their interplay within the transition state theory would enable a complete conceptual description of the most relevant electronic interactions in catalysis. Consequently, there is almost no new science in this article; it is mainly a collection of examples of quantum catalysts and the origin of the successful theoretical models that predicted the results. Finally, a perspective on the status of this emerging field is presented, emphasizing the imminent significant role of quantum correlations. Currently, the advanced incorporation of the fundamental principles of orbital physics in solid-state quantum catalysts is leading the technological transition towards a greener and more sustainable economy. Quantum correlations unify catalysis and embrace advanced physics, because the rivalry between quantum interactions is likewise the reference electronic background that explains the properties of quantum materials.

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Broader context

Quantum potentials are present in any composition, but the properties of some structures are distinctive because significant non-classical quantum correlations arise, quantum catalysts, which are frequently associated with open-shell orbital configurations. Consequently, it is necessary to discuss quantum correlated catalysts (QCCs) and try to explain/incorporate concepts such as quantum-entanglement and -superposition, in relation with the meaning and symmetry of wavefunctions and their energetic influences in the transition state theory, the understanding of which is one of the most profound challenges in catalysis.

1. Introduction

Quantum materials are compositions which exhibit properties that cannot be explained by classical interactions and mostly involve non-weak quantum electronic correlations. According to the previous definition, many catalysts are quantum phases, Fig. 1. This perspective is about interpreting the physical reality, and although there is no hypothesis in this case, most citations are experimental examples of quantum correlated catalysts (QCCs), where authors have identified/observed influential non-classical interactions. Theoretically, we attribute the

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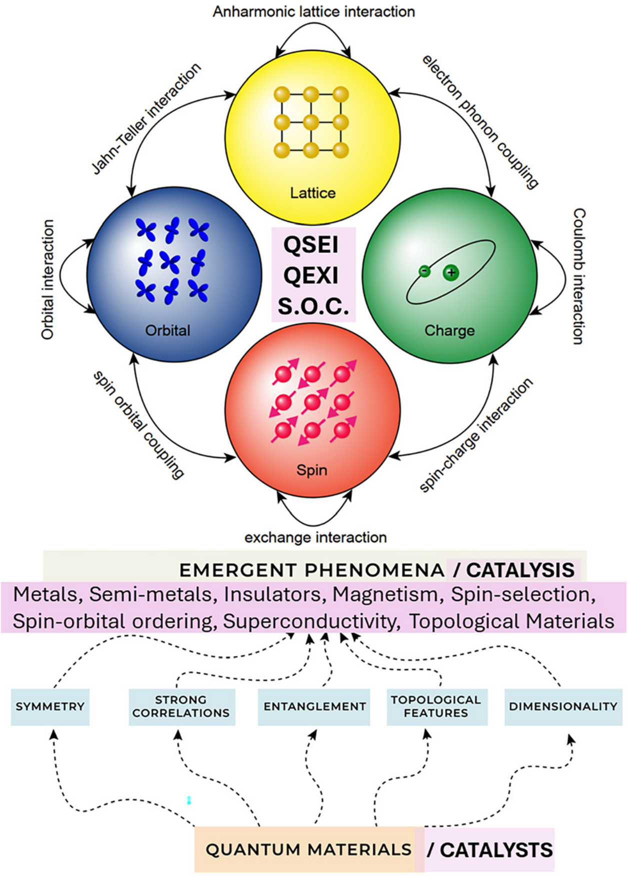


Fig. 1 Quantum materials show subtle quantum effects in controlling the macroscopic behaviour of materials, which also provide them with unique functionalities in catalysis. Adapted from **https://www.jncasr.ac.in/faculty/abhishekkumar/research-area/ultrafast-physics-emerging-quantum-materials**; accessed 18/05/2025.

orbital physics from the wavefunction approach to many-body physics. The only hypothetical parts are the interpretation of the most counterintuitive phenomena such as entanglement, superposition, nonlocality, and the possibility of non-imaginary wavefunctions. Actually, several competing and intervened quantum potentials are involved in catalysis, the relevance of depends on composition, oxidation state, and structure;[1,2] thus, they must be recognized individually to advance and provide a complete independent evaluation in the future. Specifically, to highlight the quantum origin and spin dependence, we clarify the "exchange interaction" commonly referred to in orbital physics as quantum spin exchange interaction (QSEI). This also helps to distinguish this interaction from the double-"exchange" or super-"exchange" mechanism or ion-"exchange" in chemistry. QSEI is part of the non-classical quantum electronic correlations; accordingly, we use the term quantum excitation interactions (QEXI) to refer to the more undefined term "correlation energy". In chemistry, QEXI gives a clearer definition for its multiconfigurational physical meaning. QSEI and QEXI are both different parts of the quantum correlation interactions between electrons, and thus we should distinguish them properly. The corrections to electronic repulsions from QSEI (or "spin exchange" if preferred) due to the quantum entanglement between electrons with the same spin or from QEXI (or "correlation energy" if you prefer) due to the quantum superposition of configurations is essential in any case. Not all quantum materials are/have strongly correlated systems/electrons, but they all have non-weakly correlated/electrons, *e.g.* ferromagnets are at the border of the class of strongly correlated materials, but they are not inside.[3] Thus if we want to use a general term that covers all the electronic interactions in quantum catalysts, a good way is the complementary name (non-weakly) quantum correlated compositions (QCC), which obviously includes strongly correlated. QCC frequently arise from open-shell (OS) orbital configurations with unpaired electrons, and although in the literature not all magnetic materials are strongly correlated materials, they are all QCC and frequently QCC-OS. There is no clear borderline, for instance, graphene is not typically classified as a strongly correlated material, but under certain conditions, it can exhibit strong electronic correlations. Thus, overall, non-classical graphene-derived catalysts appear as QCC-OS.[4–7] We try to maintain a clear nomenclature, as close as possible to the literature, but that covers all the chemistry richness in catalysis including open-shell structures, spin–orbital orderings, and spin–orbital couplings. Researchers familiar with many-body physics should expect different adapted terminologies, but complementary explanations. Actually, the peculiar improved activity of many catalysts is due to their stronger non-classical quantum interactions, which are more relevant than in the classical weakly correlated materials; thus, we must understand their additional quantum behaviours. This long introduction will now continue with references to the many quantum catalyst examples where, in most cases, the authors identified the non-classical catalytic enhancement. Regarding the details about the numerical method-data-results, we refer to the citations; our aim here is to provide the simplest figures, the overall view/link that unifies all the examples, and outline the most challenging plausible viewpoints.

The same electronic interactions, including non-classical quantum potentials, that determine surface chemistry, condensed-matter physics, enzymatic reactions, electron transfer, and homogenous-, electro- and photo-catalysis are valid for solid (heterogeneous) catalysts, together with the same physical principles as in quantum biology.[8] The conceptual basis is common, independently of the composition, size and conditions; thus, to have this unified fundamental view in catalysis, we must fully incorporate quantum chemistry and avoid incomplete approximations. Chiefly, the activity of catalysts can only be fully understood by the individual and direct analysis of their true quantum potentials.[1,2] Specifically, we cannot have a general conceptual basis in catalysis from approximations that try to describe all real electrons as non-interacting particles in an effective potential or local non-wavefunction mean field approximation, or with incomplete approximations only valid for certain transition metals.

The wavefunction is the heart of quantum mechanics, connecting abstract mathematics to measurable physical phenomena; and Schrödinger famously described quantum entanglement as the essential feature of quantum mechanics.[9] Many catalysts are effectively quantum materials, and we need to achieve a complete perspective from appropriate wavefunctions. Nonetheless, it is still true that although we understand a lot about the mathematical behaviour of a wavefunction, its precise meaning remains an open question. Is the wavefunction a real physical entity, or is it just a tool for predicting outcomes? According to some, it represents an objective reality; others argue it is simply a way to encode our knowledge or information about a quantum system. We will explain how the construction of a wavefunction is related with quantum superposition and entanglement, and how all these interactions represent a tangible energetic reality that influences catalysis. We attempt to give a real interpretation to these still enigmatic interactions. The community must also distinguish appropriate numerical methods and acknowledge more clearly their limitations, such as local density functional theory approximations (DFT-A), which are only valid in certain cases.

Quantum electronic correlations refer to the non-classical interactions between electrons, which influence their energy states. Spin exchange interactions (QSEI) are the most relevant part of the electronic quantum correlations. Before 2016, QSEI were specifically not part of most reports on the design/analysis of solid catalysts; at that time, "standard simplifications" treated all structures as if they were weakly correlated closed shell (WCCS) metals (which we will define later). Part of the unacceptable errors for quantum catalysts of low level computational and theoretical approaches, for false metals, can be inferred from the outstanding descriptions by Zunger,[10] Fig. 3. The higher level to cover all possible cases to tackle the huge need for revision in sold catalysis is to relate these sources with the fundamental origin in the QSEI (magnetic order), QEXI and spin–orbit coupling (S.O.C.). In a historical context, the 13th European Congress on Catalysis (EuropaCat) was held on August 2017 in Florence, where I was the only speaker talking about the spin potentials in solid catalysts, specifically, spin selection through ferromagnetic bonds in oxygen electrocatalysis,[11–13] and the contribution of the position of the conduction band to overpotentials,[14] as shown in Fig. 7. Later, in EuropaCat 2023 in Prague, about half of the catalysts in the presentations/posters had open-shell orbital configurations mainly due to the presence of V, Cr, Mn, Fe, Co, Ni, Cu and Ru in different oxidation states stabilised by QSEI; nevertheless, there were only two talks directly addressing the spin potentials in solid catalysts. This field was/is used to simpler views and additional non-general simplifications, models of non-correlated electrons, parametrizations and linearizations. However, in reality, a complete theoretical description must be based on the direct recognition of the differentiating role of quantum correlations, *i.e.*, quantum materials/catalysts with their unique properties. Prior to 2016, the number of papers focusing on spin-enhanced solid catalysts were only a few (nearly unknown) dozens. As far as we could find, the early works were reported by Buchachenko,[15,16] a few computational indications,[17–19] specially by M. Escaño,[18–25] and some concepts by Minaev can be extended to heterogeneous catalysis.[26–29] Of course, they include the works by Naaman using chiral-induced spin selectivity (CISS),[30,31] and some other examples.[32,33] These early observations on the spin effects in heterogeneous catalysis were still unclear, disconnected, and did not have a consistent and complete theoretical base. Perusing the literature in solid catalysis, most of the community thought that if any type of spin-potential had an effect, it would be weak and irrelevant in practical observations or to describe solid catalysts; most likely, considering the usually weak direct spin–spin or hyperfine interactions. There were also no experimental works observing that spin–orbital orderings, intra- and inter-atomic QSEI are key for the activity of solid catalysts. In mid-2015, when we started putting the pieces together, no one seemed to expect that in 2025 the number of publications on spin catalysis would reach thousands and on some of the most important reactions. What has changed since then? More complete quantum chemistry explanations, ranging from kinetics to thermodynamics, have inspired theoretical predictions that are now proven in numerous successful experiments. We must recognize that the majority of catalysts are spin polarized with open-shells, and then non-classical quantum correlations,[1,2] mainly intra- and inter-atomic QSEI coupled with quantum excitation interactions (QEXI) are particular key factors in their activity and stability. The activity enhancements from quantum correlations can sometimes be improved, ordered, and even induced by an external magnetic field[34,35] or CISS effect. Spin-dependent potentials are not only relevant but sometimes the essential part in the catalytic activity and stability, *e.g.*,[34,36–41] and thus it is not news that many catalysts are quantum materials.

Considering that this perspective targets the catalysis community in general, our efforts should explain the meaning of the quantum concepts and refine and sometimes adapt the language in physics. It would have been a mistake to just refer to the physics literature because it is not directly related to catalysis and some concepts still need clarification. Non-classical quantum interactions are counterintuitive, *e.g.* in a possible Feynman space-time representation, QSEI implies the nonlocal teleportation or space-time entanglement of the energy of electrons with the same spin between orbitals; and QXEI implies the energetic superposition of all possible electronic configurations. Interpretations help to understand the stabilizing QSEI and QEXI as a reduction of the Coulomb repulsions.[2] It is indeed odd in catalysis to observe that a reduction in temperature results in an increase in activity, which is small, in this case about 5–6%, but noticeable for the triplet-state oxygen evolution reaction (OER) in the paramagnetic to ferromagnetic transition with a decrease in temperature, as shown in Fig. 4.[39] In contrast to the transition-state theory (T.S.T.), experimental evidence proved the reduction in activation energies caused by an increase in the extended inter-atomic QSEI and QXEI, as shown in Fig. 2.[42] In the literature, huge variations in activity can be observed, increasing from few % to several times, as shown in Fig. 9 for OER or in ferromagnetic ordered PtFe-alloys for ORR.[43] Alternatively, on antiferromagnetic (AFM) insulators, where the electron-spins are trapped, decreasing the electrocatalytic activity, which is typical of AFM type-G orderings,[13,42] then thermal-stimulated spin disordering accelerates water electrolysis.[44,45] The massive success of this modern evolution of theoretical solid catalysis is the understanding of previous advanced experiments.[1,2] Quantum correlations are stabilising non-classical potentials, which also

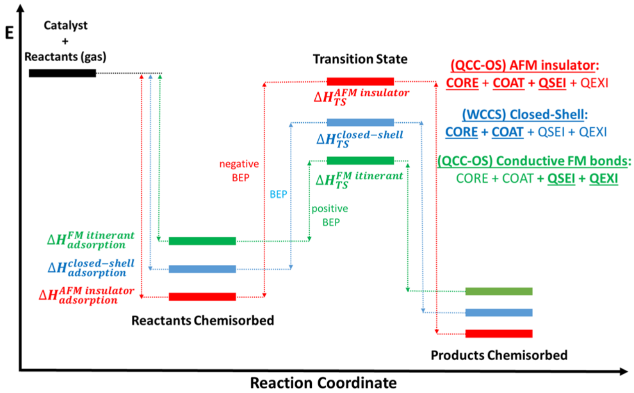
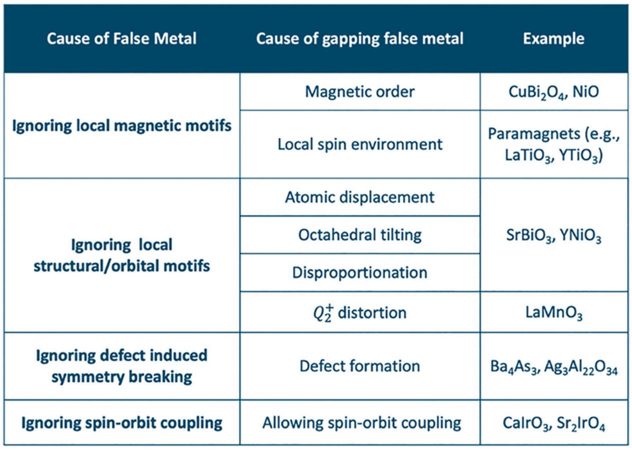


Fig. 2 In relation to the Bell–Evans–Polanyi (BEP) principle, the relative energy position of the transition states ($\Delta H^{\mathrm{T.S.}}$) *versus* the reaction enthalpy (ΔH^{step}) in QCC-OS is different from WCCS.[1] Typically, QCC-OS with conductive FM bonds optimize inter-atomic (non-local) QSEI and QEXI in quantum catalysts, showing positive BEP deviations. Although the opposite typically occurs, the worst catalytic activity is observed for the most insulating AFM phases (AFMI), specifically type-G, unless the surface of the topological material is conductive.



Cause of False Metal	Cause of gapping false metal	Example
Ignoring local magnetic motifs	Magnetic order	$CuBi_2O_4$, NiO
	Local spin environment	Paramagnets (e.g., $LaTiO_3$, $YTiO_3$)
Ignoring local structural/orbital motifs	Atomic displacement	$SrBiO_3$, $YNiO_3$
	Octahedral tilting	
	Disproportionation	
	Q_2^+ distortion	$LaMnO_3$
Ignoring defect induced symmetry breaking	Defect formation	Ba_4As_3, $Ag_3Al_{22}O_{34}$
Ignoring spin-orbit coupling	Allowing spin-orbit coupling	$CaIrO_3$, Sr_2IrO_4

Fig. 3 False metals and set of symmetry-breaking energy lowering mechanisms resulting in band gap opening with illustrative examples.[10] Copyright © 2021, the American Chemical Society, reproduced with permission from the reference.

reduce the relevance of the classical potentials and promote the reorganization of the electronic structure of catalysts, affecting their thermodynamics and kinetics.[1,2,14] Quantum correlations can lead to the significant reordering of the electronic structure, and these interactions extend beyond simple mean-field approximations, affecting the distribution of electronic states and their energy levels. These effects are particularly relevant in all non-weakly quantum correlated compositions (QCC), playing a dominant role in shaping the properties of materials. In addition, the increase in the activity and stability of intended open-shell catalysts with several magnetic domains in the presence of additional macroscopic magnetization from an external magnetic field (EMF)[34,36,38,46] is sometimes beyond our initial expectation.

There are many types of catalysts with magnetic ground states, as shown in Fig. 5; however, thus far, mostly ordered ferromagnetic spin conducting surfaces show enhanced catalytic performances. The different spin–orbital orderings, which are studied by doping quantum materials/catalysts, as shown in Fig. 6, alter the conduction properties (bulk and surface), as shown in phase diagrams.[47,48] The initial connection with electrocatalysis is shown in Fig. 7 *via* spin-transport from enhanced inter-atomic QSEI in quantum-correlated catalysts/compositions (QCC). Fortunately, the literature is now full of discussions about competing double-exchange and super-exchange interactions, as shown in Fig. 7, or the spin in catalysis, but still sometimes does not properly identify the interactions that cause them. Our advice is always if a work states that the spin is relevant in catalysis, look to see if the origin of the quantum mechanics is explained. Accordingly, articles on spin/magnetic-dependent catalysis with compositions with open-shell orbital configurations that do not explain intra- and inter-atomic QSEI are indubitably incomplete.

The role of the other main electronic correlations, quantum excitations interactions (QEXI)†, is more subtle; however, they are presented to settle the position of the conduction band[2,42] and the potential energy.[1] Over these years, or course, we did not discover QSEI (spin exchange) and QEXI (post Hartree–Fock correlation), the two main electronic correlation energies; spin exchange and post Hartree–Fock correlation are discussed in quantum chemistry books.[52] However, we did interpret them as space-time energy scattering events,[53] which involve spin- and space-time entanglement and superposition of different configurations. We were also not the first ones with the idea that spin plays a role in catalysis, where Minaev was already was working on this in 1995;[27,28] nonetheless, it remained unclear and mainly described as spin–flip through spin–orbital couplings, ideas extended by Buchachenko.[15,16] We clarified and generalized spin-selection[11–13] to prevent spin-forbidden steps, showing that the most relevant interactions are intra- and inter-atomic QSEI,[2] which lead to cooperative magnetic phenomena, spin–orbital orderings (Fig. 5–7). Collective inter-atomic QSEI are also related to Kondo spin-screening or the super- and double-exchange mechanisms of Goodenough.[54–56] The overall meaningful role of quantum correlations in catalysis, kinetics and thermodynamics, chemisorption and activation barriers (overpotentials) became clear by 2021,[2,11–14,34,38,42,57–66] and shown to be valid for any composition. Furthermore, to begin a general discussion about quantum catalysts, eqn (1) and Fig. 19 provide a consistent comprehensive quantification, explaining how the quantum potentials influence each other, *e.g.* describing the works of Goodenough in oxygen electrocatalysis,[67–71] to include any non-weakly quantum correlated material.[72,73] Many quantum catalysts have been reported to date; thus, complete direct and advanced quantum theoretical unification in catalysis are needed to guide future computational studies and explain the now

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† QEXI in orbital physics literature are simply called "correlation energy", but this historical definition is not optimum, given that QSEI, "exchange interactions", are also part of the non-classical correlation energy of electrons. QEXI give more chemical meaning given that they are directly related to several accessible electronic configurations, only comprehensible with more complete wavefunction approximations.

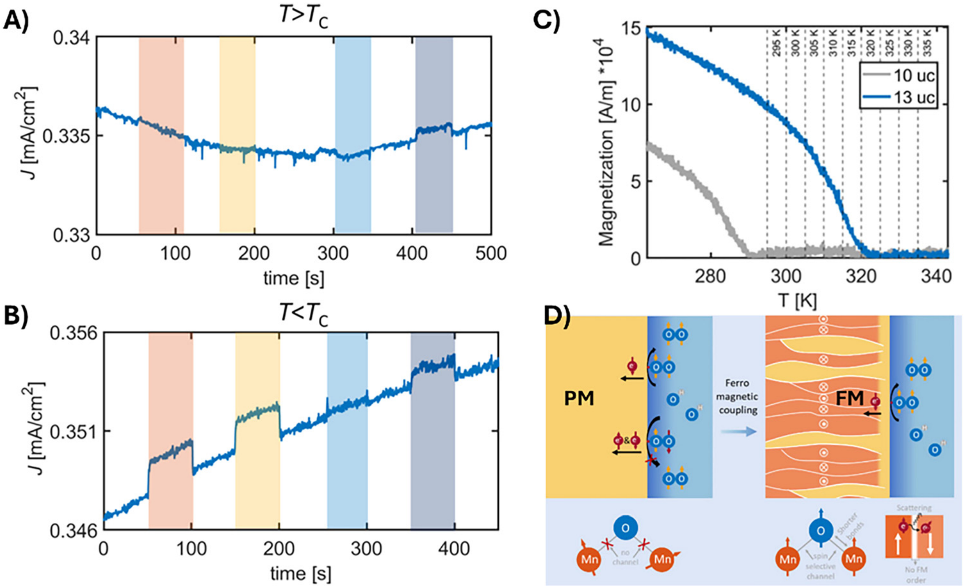

Fig. 4 Chronoamperometry measurement at a potential of 1.69 V *vs.* RHE for a 13 unit cell (uc) thick $La_{0.67}Sr_{0.33}MnO_3$ film: (A) above $T_C > 321$ K and (B) below $T_C < 320$ K. (C) Magnetic properties of $La_{0.67}Sr_{0.33}MnO_3$ thin films with a thickness of 10 and 13 uc. (D) Ordered inter-atomic QSEI reduce the overpotentials in the FM active sites. Adapted from the open access article distributed under the terms of the Creative Commons CC BY license.[39]

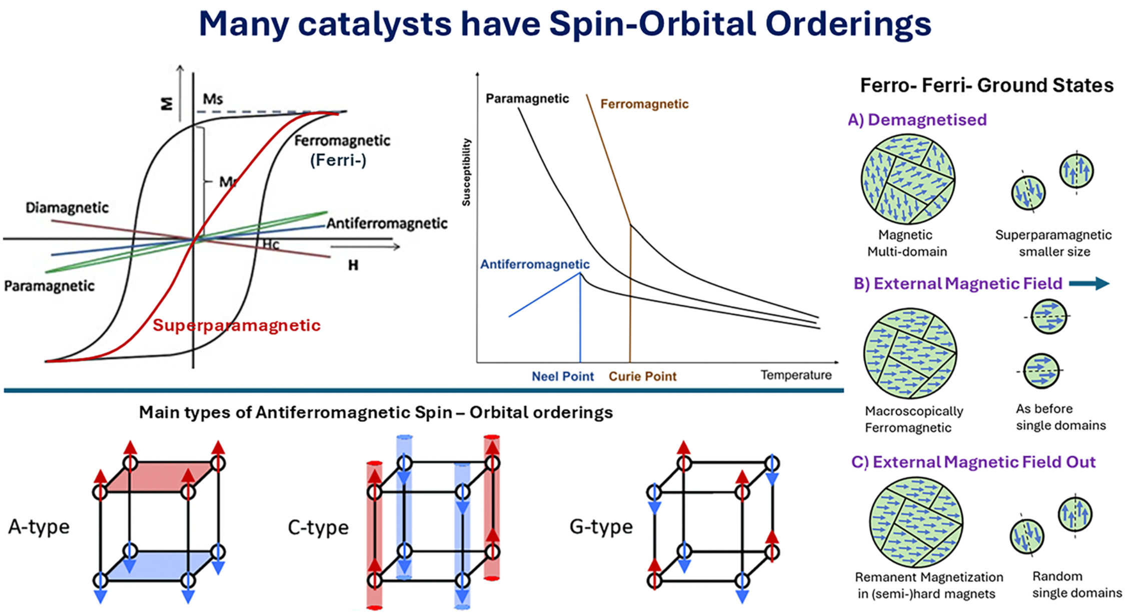

Fig. 5 Various types of catalysts *versus* their response (magnetization) to an external magnetic field and ground-state spin–orbital ordering. Any theoretical study on catalysts with open-shell orbitals should specify the use of the correct spin–orbital ordering, such as ferro-, ferri- or antiferromagnetic orderings; here, some common examples of AFM orderings are presented.

abundant experimental evidence, namely, theory applicable to any branch of catalysis and integrated with the physics of quantum materials. For researchers more acquainted with many-body physics, our fundamental point of view is an extension of the Hartree–Fock (H.-F.) wavefunction method as the only alternative that incorporates the true nature of non-classical quantum interactions and explanation related to quantum entanglement and superposition. Our work aims to make the concepts more accessible for experts and non-experts in orbital physics; also, to relate the character of the electron correlations with chemical concepts, *e.g.* discussing the imaginary self-energy is not an option in catalysis.[3] Generally, imaginary numbers are a conceptual obstacle, and thus we attempt to provide a plausible, but hypothetical alternative. Also, the application of chemical concepts to quantum materials will give physics another point of view, given that all approaches should be merged to explain the same reality.

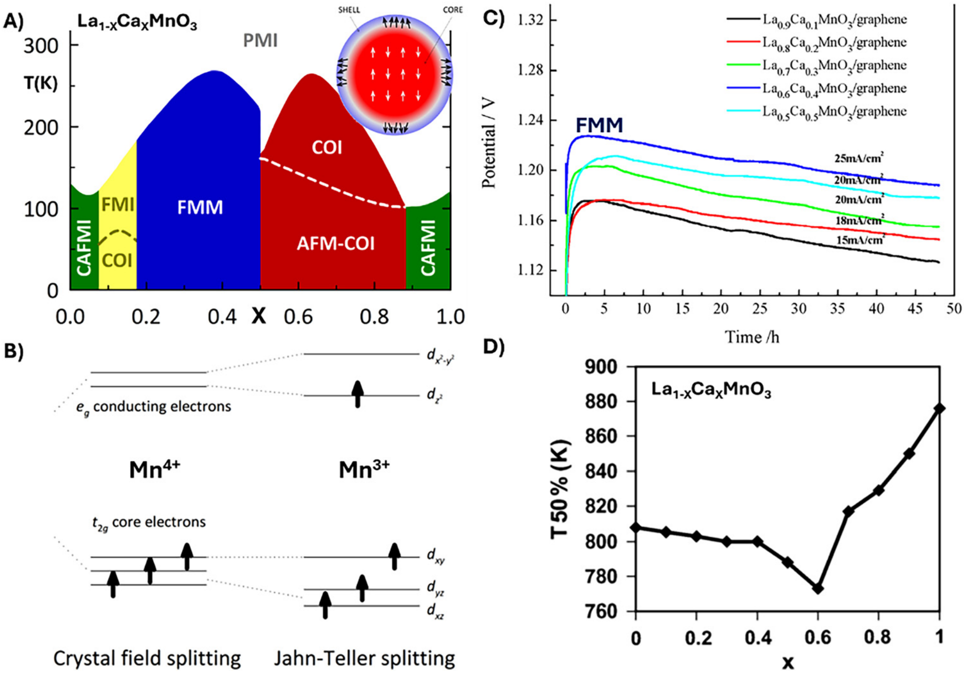

Fig. 6 (A) Conventional phase diagram of $La_{1-x}Ca_xMnO_3$, where surfaces have higher tendency for FM ordering (smaller nanoparticles are topological insulators). PMI stands for paramagnetic insulating phase, FMM for ferromagnetic metallic, COI for charge-ordered insulating, AFM for antiferromagnetic, FMI for ferromagnetic insulating and CAFMI for canted antiferromagnetic insulating state. (B) Splitting of the Mn 3d levels into e_g and t_{2g} orbitals using crystal field and Jahn–Teller distortions, for instance metallic conductivity *via* e_g electrons is the key for electrocatalytic activity of the abundant 3d-metals, as shown in Fig. 7. This figure is adapted using data from ref. 48, open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license. As a function of *X*, (C) ORR electrocatalytic activity, reproduced with permission from ref. 49, Copyright © 2014, Elsevier B.V. (D) Temperature for 50% conversion of CH_4 to CO_2; reproduced with permission from ref. 50, Copyright © 2005, Elsevier B.V.

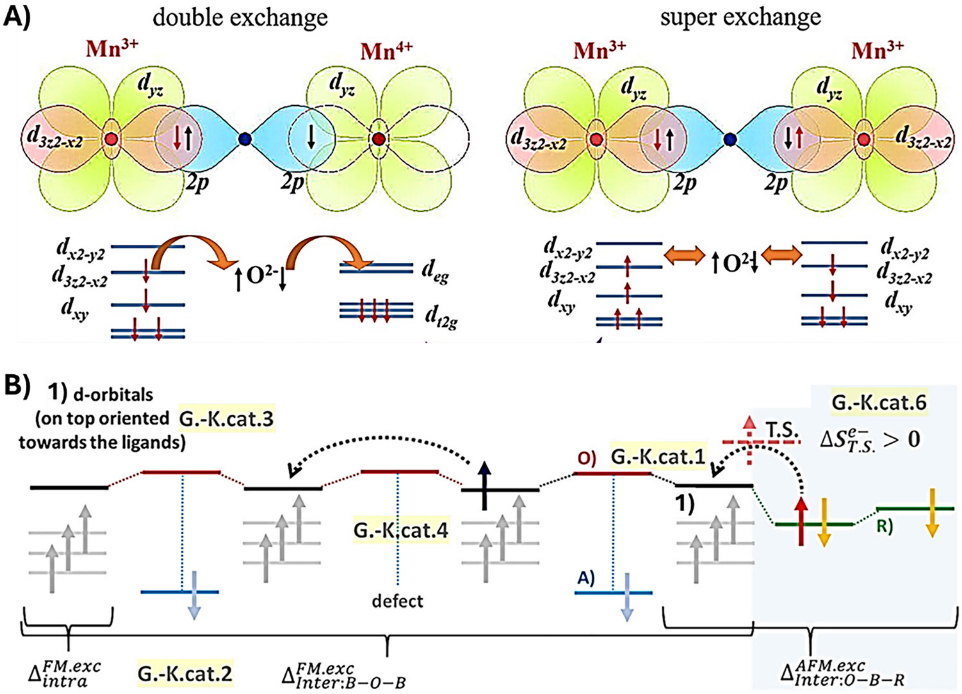

Fig. 7 (A) Example of the 180° mechanism of double-exchange spin-delocalization and super exchange localization, which participates in the modulation of phase diagrams;[51] open access article licensed under a Creative Commons Attribution 4.0 International License. (B) Representation of the double-exchange guidelines in spintro-catalysis, where every G.K.cat. label corresponds to qualitative electrocatalytic rules, leading to favourable spin-dependent electron delocalization. Reproduced with permission from ref. 42, Copyright © 2018, Elsevier B.V.

We should also briefly highlight that a complete direct quantum framework in catalysis is highly relevant for the economy and industry

It is needed, as shown in Fig. 8, for understanding and designing lower-cost and highly efficient (electro-) catalytic technologies. Fig. 8B is neither original nor of high scientific interest, but it helps to group the vast number of alternatives in catalysis and show the need to squeeze quantum mechanics to cover all cases, which is a future challenge for the next generation. Because these catalysts are acceptably described by uncorrected mean-field approximations to electron–electron interactions or simplified descriptors, weakly correlated closed-shell (WCCS) metallic structures, are in many cases, an expensive minority in nature. The growth in articles on all branches of catalysis reporting the active role of spin potentials has indeed considerable economic interest. Both in acid, as shown in Fig. 9, and basic, as shown in Fig. 10, media, magnetic catalysts are under techno-economical evaluation for advanced water electrolysis and fuel cells. Considering their abundance in nature,[74] our future greener economy is dependent on the optimum use of abundant elements in correlated electron materials, accurately with more examples of recognised quantum catalysts in electrocatalysis,[75–77] fuel cells (triplet-state oxygen reduction reaction (ORR)),[78–80] water electrolysis,[81–85] dual OER & ORR catalysts,[86] hydrogen evolution reaction (HER),[87–90] efficient photocatalysts,[91–100] batteries,[101–108] metalloenzymes,[109–111] enzyme-mimics,[112–114] chiral-catalysts,[30,115,116] ammonia[58] and Fischer–Tropsch (FTS) synthesis,[117] CO_2 and nitrate electro-[118–121] photo-[122,123] reduction, novel applications in biomedicine,[124–127] and others.[128–131] These theoretical and experimental advances are already amazing, and the biggest unification with an impact on all aspects of catalysis, this field can only be completely understood by directly addressing quantum correlations.[1,2,14,42,53]

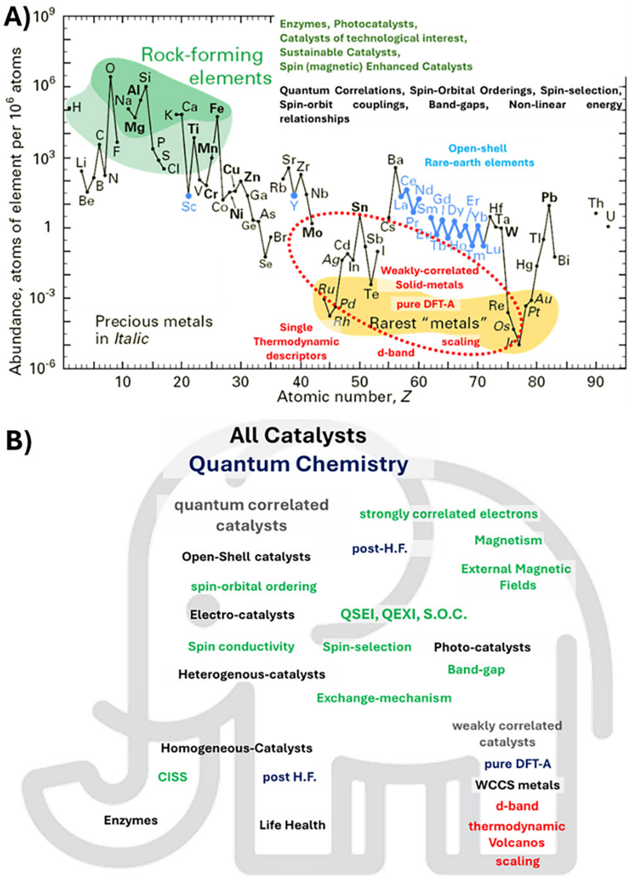

Fig. 8 (A) Quantum-correlated catalysts with open-shells, QCC-OS, are the most abundant on earth. Weakly correlated solid metallic catalysts are typically expensive and less abundant in nature. (B) Inclusive perspective on catalysis based on all the electronic interactions.

Challenging the *status quo*, not everything depends/occurs on the top surface atoms of catalysts

In 2020, Pt_3M magnetic alloys showed sub-surface alterations in their spin-density with the chemisorption of reactants.[60,62] Later, in 2022, similar results were observed by Cinchetti.[132] Specifically, ferromagnetic Pt_3Co structures were observed to have double the mass activity for ORR compared to Pt/C.[133] These intermetallic open-shell alloys are examples of structures that are neither strongly correlated nor weakly correlated,[134] and thus a compromise definition is (non-weakly) quantum-correlated compositions with open shells (QCC-OS). In 2024, the results reported by the group of Prof. Chhowalla on OER again provided evidence that the transmission of both quantum mechanical and electrochemical information initiated by sub-surface QSEI leads to an enhancement in catalytic performance.[37] The current densities are very low, but the results are particularly interesting because no d-orbitals are directly involved, *e.g.* the active surface is a layer of graphene with magnetic Fe_5GeTe_2 (FGT5) below. As ''non-local'' interactions, QSEI can be mediated over longer distances, such as through conduction electrons, which is seen in phenomena such as the RKKY interaction (Ruderman–Kittel–Kasuya–Yosida),[135] where QSEI, mediated by conduction electrons, can extend over several atomic distances. The technological interest in spin spin/magnetic enhanced water electrolysis became clear in 2021, where long-range ferromagnetic order was observed to double the OER and ORR current densities, as shown in Fig. 9. These results also prove that the intrinsic magnetic properties of oxygen electrocatalysts are the main driving activity-enhancing factor due to QSEI. There are many works in the literature about intermetallic nanoparticles based on open-shell 3d-metals, *e.g.* $PtM_X^{open\text{-}shell}$, QCC-OS used in catalytic applications; however, they failed to identify the key role of the magnetic features in the activity. The OER activity and stability of ferromagnetic RuO_2 doped with Mn are among the best, making it of technological interest although Ru is a platinum group metal.[36] Some of the principles of spin-enhanced catalysis extend to all reactions, and thus can be used to develop dual (industrially competitive) electrodes for water electrolysis, as shown in Fig. 10, with the advantage of being resistant to reverse currents for use with renewable energy. Overall, these works demonstrate that the distant transmission of quantum interactions is not only important, but can be the main factor, which are nowadays one of the most outstanding examples of QCC. Fig. 9 also proves that

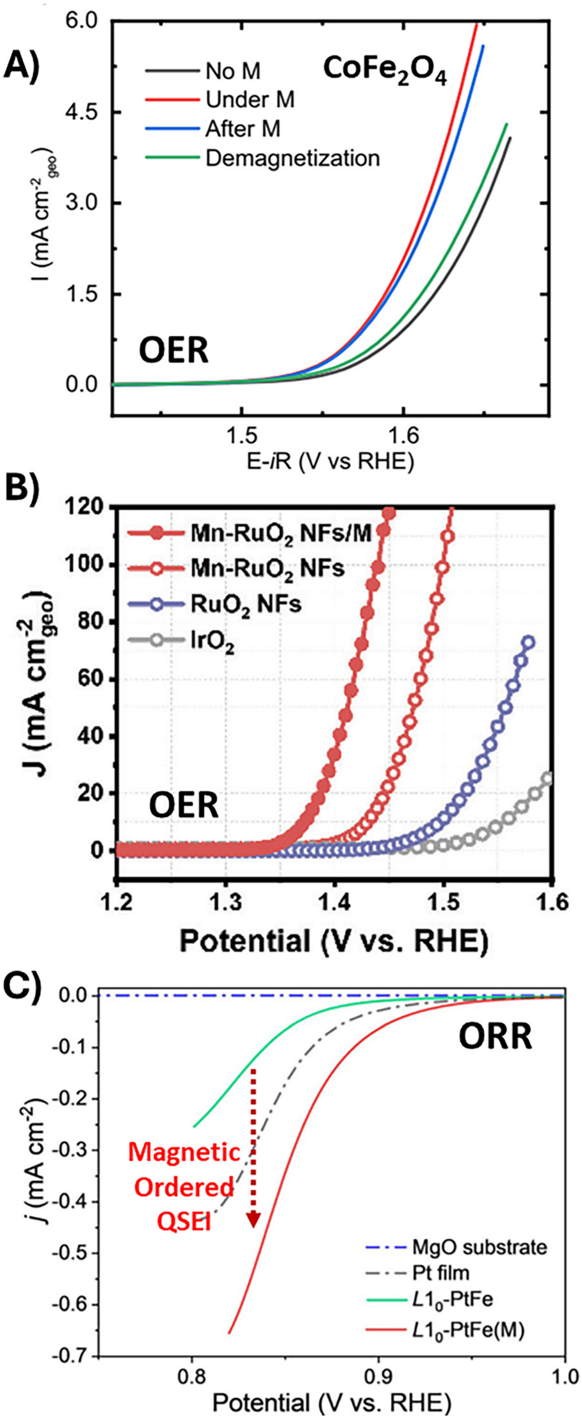

Fig. 9 Linear sweep voltammetry curves of: (A) ferrimagnetic $CoFe_2O_4$ at a scan rate of 10 mV s^{-1} in O_2-saturated 1 M KOH with and without a constant external magnetic field (*M*) (10 000 Oe), after *M* is removed (after *M*), and after demagnetization.[34] Image from the author's referenced under a Creative Commons Attribution 4.0 International License. (B) $Mn-RuO_2$ plus EMF, $Mn-RuO_2$, RuO_2, and IrO_2 in 0.5 M H_2SO_4 at a scan rate of 5 mV s^{-1}.[36] Image adapted with permission from the author's reference, Copyright @ 2023, John Wiley & Sons, Inc. (C) ORR polarization curve of MgO substrate, Pt film, L10-PtFe NF, and L10-PtFe(M) NF. Image adapted with permission from the author's ref. 41, Copyright © 2020, Elsevier B.V.

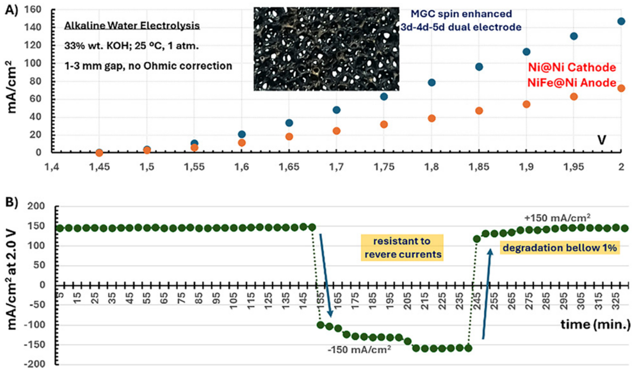

Fig. 10 (A) Activity and (B) stability of a dual OER and HER high-entropy 3d–4d–5d block metal spin catalyst deposited on nickel foam in basic media, reproduction of the result in acid media.[36] Developed by **https://www.magnetocat.com** using the principles of quantum catalysts as industrial solution to the degradation of electrocatalysts using reverse currents, especially when powered with intermittent renewable energy sources.

single-structure-sensitive catalytic activity plots and selectivity maps are not generally true, as shown in new superior studies.[80] This is because they are an oversimplification assuming that the electronic structure varies consistently/linearly/equally for all compositions with hypothetical structural descriptors. Similarly, descriptors based on counting the number of outer electrons must include a proper basis of the alterations of properties with the actual orbital fillings, depending on the spin–orbitals orderings. Logically, the conclusion from these imperfect works is still an unknown characteristic of active OER electrocatalysts because in many incomplete models, the true relevant quantum properties of catalysts were overlooked.

Endothermic electro- and photo-catalysis

Photons, as electromagnetic energy packets vibrating in space and time, are absorbed and emitted by electrons in photocatalysts by altering the energy of their quantum state. Endothermic electro- and photo-catalysis start from the initial increase in electronic energy, and subsequently energy transfers to the lattice surface vibrations, causing electron–phonon scattering to activate atomic movements, and also *via* many-body large-hole (magnon) polarons.[136] The increase in electronic energy in an environment with preferential cooperative spin–orbital orderings *via* QSEI in atoms with unpaired electrons also means that in the separation of an entangled electron pair (↑↓) towards the formation of intermediates or T.S. with net spin density, the orientation of one of the spins will be parallel and the other perpendicular to the resident spin polarization. This indicates that according to momentum conservation rules, during their departure at equilibrium, the electrons remain entangled (↑···QSEI···↓),‡ with energetic consequences. In any electron transfer, charge and

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‡ Entanglement refers to a quantum state where two or more particles become linked, causing the state of one particle to almost instantly influence the other, regardless of the distance between them. When particles are entangled, their properties are non-locally interdependent, and measuring the state of one particle instantly determines the state of its entangled partner.

spin move, and given that T.S. has at least a higher radical character than one or both of the initial and final stationary states, non-bonding stabilizations are more relevant. In the presence of ferri- or ferro-magnetic bonds *via* QSEI, EMF or CISS, spin entanglement carries energy, which can be a crucial component in processes where energy transfer occurs with efficiency, reducing the activation barriers and overpotentials in electro- and photo-catalysis.

Quantum non-locality

The observed influence/response of the open-shell sub-surface atoms on the chemisorption on the surface-active sites indicates the possibility of quantum non-locality in catalysis. Postulated in most cases *via* quantum entanglement, virtual orbital teleportation is implied as the phenomenon of a group of electrons interacting in such a way that the quantum state of each electron of the group cannot be described independently of the state of the others, including when the electrons are in atoms separated by a large distance. Quantum energy teleportation has the paradox to be described as a virtual process where the quantum state of an electron is transferred from one location to another, but without having a way to check if the particle itself has physically moved. Thus, in some cases, we wonder if the catalytic activities in multiparticle entangled and superimposed quantum systems carrying energy need an interpretation with non-local realism, *e.g.* do the results in Fig. 9 and some others imply non-locality? This speculation is part of our perspective for future investigations, as it is in physics.[3] Here, a more educated postulate is presented, given that is has been known since 2016 that the double-exchange mechanism allows spin selection in $^3O_2$ electrocatalysis.[13] The double-exchange mechanism implies cooperative inter-atomic QSEI interactions, where electrons transfer between neighbouring ions, aligning their spins to minimize energy. Also, this coherent transport regime occurs when electrons move in a collective and wave-like fashion, maintaining phase coherence over long distances, where spin transport is mediated by distant metals. This introduces a layer of complexity because this scenario can involve quantum coherence and entanglement, which are hallmarks of quantum non-locality. Quantum non-locality arises when entangled particles exhibit correlations that defy classical explanations, even across distances. If the spin transport in the catalytic scenario maintains coherence over long distances and involves entanglement, lowering the activation energies, it essentially implies quantum non-locality.

Non-locality in catalysis in the quantum sense is an uncertain but interesting conjecture§ because there is a medium surrounding the active sites, *i.e.*, a coordination sphere, which effectively influences the activity. The coordination sphere is fundamental to adjust the electronic and steric characteristics of catalysts,[137] or needed in the cooperation between the active sites and supports.[138] Accordingly, many examples of a coordination environment that produces a distinctive optimum electronic structure regulation *via* quantum correlations, EMF and CISS, are being identified, *e.g.* in batteries,[139–141] enzymes,[142] or enhancement by aligned magnetic domains.[34,38,39,46,143] A related observation is that most high-entropy catalysts exploit QSEI and QEXI in a complex coordination environment.[144] It is difficult to find high-entropy catalysts that do not include open-shell metals, given that based on their precise definition, most of them are QCC-OS. Unfortunately, the obvious role of intra- and inter-QSEI, coupled with QEXI in spin-polarized metallic ground states and partially occupied d-orbital shells are frequently not yet identified/discussed. In contrast, the clear importance of quantum correlations is now emerging, indicating that on-site static properties and local interactions do not reveal everything; a statement that will not probably be a surprise for the developers of the CISS effect.[30,31,145–151] A valid question is if in some cases, can the energy carried by the quantum correlations, especially in electro- and photo-catalysis, stabilize the transition states (T.S.) entangled-superimposed with the spin–orbital of the transferred electron? The key stabilization may be due to any non-classical potentials (QSEI, QEXI, CISS, and EMF) outside the atomic structure of the active sites, a possibility represented in Fig. 11. Local, semi-local or non-local, the peculiarities in the electronic structure of T.S. is a key topic for the future, which has barely been studied in detail for most solid catalysts, in particular QCC-OS.

Nowadays, they are starting to be common, but in 2017, not even in the most cited theoretical/computational articles on $^3O_2$ electrocatalysis, the words "spin", "triplet", "exchange interaction" and "spin–orbital ordering" appeared. When we started our research, almost no one in solid catalysis was talking about the enormous importance of quantum correlations, *i.e.*, spin–orbital orderings of correlated electrons in general. Oxygen

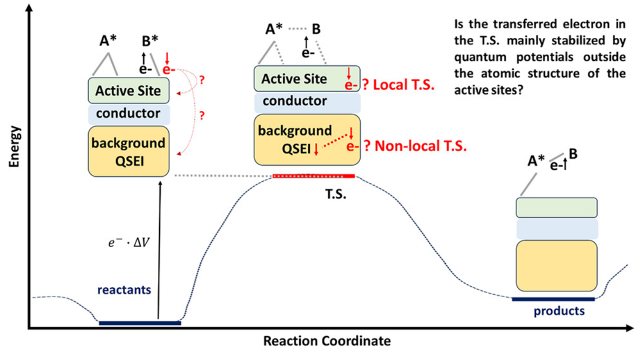

Fig. 11 By nonlocality in catalysis, we raise the question about the possibility of the stabilization of the electronic structure of T.S. significantly depending on the distant quantum entanglement with electrons–holes outside the bonds of the atomic structure of the active sites. This conjecture implies that the transferred electron advances the activation of the nuclear coordinates of the T.S. and stabilizes it but *via* distant quantum correlations. Thus, QSEI teleportation and/or the QEXI superposition with states non-local to the atomic structure of the active sites are key to reducing the overpotentials.

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§ Non-locality describes the phenomenon where these entangled particles seem to influence each other instantaneously over large distances. Although entanglement often implies non-locality, they are not strictly the same concept. Entanglement is a broader phenomenon, and non-locality is one of its intriguing implications.

electro- and photo-catalysis, including metal–air batteries, are the most important topic in catalysis of our generation, and the reemergence of the spin started in 2016 in a first novel contribution anticipating spin conduction, accumulation and selection, associated with the double exchange mechanisms, as shown in Fig. 12,[13] on strongly correlated magnetic oxides. Spin selection is possible in bonds with extended preferential ferromagnetic spin–orbital orderings, where intensification of spin entanglement, chemical potential and mobility of more stable but less bonding electrons become spin-dependent, which will facilitate the reaction kinetics. Similarly, it is helpful to recognise that photosynthesis starts in quantum photocatalysts,[8,74] with similar fundamentals. Specially, in the case of ferro- and ferri-magnetic photocatalysts, we should discuss spin-polarized electrons and holes (electron–hole quasiparticles); another subject to develop in the future, despite the already existing interest.[152] For example, in outstanding photoanodes with open-shells, such as NiFe-LDH/Co_3O_4/$BiVO_4$,[153] the potential role of the spin is still typically neglected.

Spin selection-accumulation associated with polarized metallic bands/bonds indicates significant thermodynamic effects in catalysis. In 2016, there were a few works in catalysis discussing spin–flip and Zeeman splitting,[154] but these effects, similar to direct spin–spin interactions, are usually too weak. In the works about the CISS effect, the changes in chemisorption enthalpies and activation barriers are challenging to quantify.[155] Alternatively, the computational works by Escaño on ferromagnetic metallic surfaces[20–23,156–160] show clear thermodynamic effects. Quoting this author: "the potential energy curves for the reaction of Pt with O_2 as a function of O_2 center-of-mass distance from the platinum layer and O–O interatomic distance show that PtML/Fe(001) produces a combination of lower activation barrier for O_2 dissociation and weaker O-atom binding, which are both beneficial for easier O_2 dissociation".[160] We needed to generalize and further clarify these thermodynamic spin polarization effects in any type of spin–orbital ordering and composition, presenting a general broad view directly connecting the interactions with chemisorption and the activation barriers. Indirect analysis *via* the overall consequences of quantum interactions, such as the changes in the density of states, was not ideal. It is necessary to individually understand and quantify the source of how quantum potentials compete with each other in catalysis, *e.g.* "stabilizing FM interactions enhance the rate of spin-selective steps by reducing the Coulomb repulsions between the electrons at the expense of the Coulomb attractions by the nuclei".[14] The quantum nature of QSEI makes them strong, affects the kinetics and thermodynamics, and can also disrupt the other electronic potentials and non-linear effects.[1,2] In 2018, a cobalt oxide OER catalyst also showed deviations from the Bell–Evans–Polanyi (BEP) principle,[64] as shown in Fig. 16 and observed by Dr Escaño on bimetallic ferromagnetic interlayers.[25] According to non-classical quantum potentials, the attempts to linearize catalysis are not universal, which is most likely limited to the weak chemisorption in weakly correlated closed-shell catalysts (WCCS).

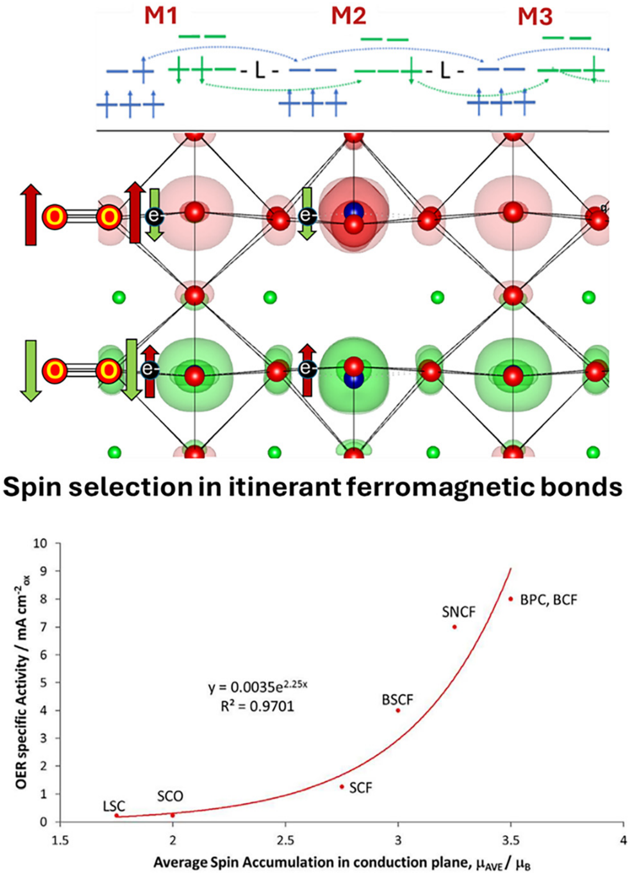

Fig. 12 In layered antiferromagnetic OER electrocatalysts with ferromagnetic planes, parallel magnetic channels allow easier accumulation and selection of spin moments at the interphase, anticipating $^3O_2$ evolution. Adapted with permission from ref. 13, © 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The construction of a wavefunction in relation to entanglement and superposition is a fundamental aspect of quantum mechanics

QSEI is a non-classical spin-dependent potential that emerges from the anti-symmetry of the wavefunction, as will be shown later, where its makes it strong. It will also be probed that local or semi-local DFT-A and other non-wavefunction approximations are not a general theoretical background for the complete understanding of catalysis. The previous sentence may not be acceptable by some researchers working on DFT-A based mapping approximations to study complex systems; thus, we will attempt to prove why we expect that wavefunction methods beyond the non-local Hartree–Fock approximations will expand in the future. Progress in advanced catalysis moved slowly between 2015–2018, and it took years to relate and understand the works of Goodenough on oxides, *i.e.*, why double-exchange and super-exchange mechanisms are of importance in catalysis? In 2018, explanations appeared for OER based on the decisive role of cooperative intra- and inter-atomic QSEI;[14,42] the first experimental verifications appeared gradually in 2019.[161,162] Later, in 2020, these concepts were also reproduced computationally in the laboratory of Professor Xu,[163] and the main enhancement due to the intrinsic magnetism of catalysts, extended ferromagnetic bonds, in 2021,[34] as shown in Fig. 9. Nowadays, the private sector is developing industrial water-electrolysers, planning the world giga-plants that will reduce global warming and create a more sustainable economy; all the optimum electrodes incorporate QSEI- and QEXI-enhanced catalysts for OER, including open-shell 3-4-5-d metals in quantum materials with double-exchange spin conduction, as shown in Fig. 12. Alternatively, cathodes for HER with the best stability and/or even dual activity, resistance to contaminants and reverse currents also benefit from spin-enhanced catalysts with open-shell orbitals, as shown in Fig. 10.

An advantage of age is the luxury to walk the path in 12 years from having almost no clue to developing the most fundamental quantum level, defending the new ideas to most of the community, laboratory verifications, general scientific acceptance, and industrial scale application. However, after 2021, it became common to find reports on $^3O_2$ electrocatalysis with open-shell active sites not discussing QSEI (spin exchange), despite the abundant experimental and theoretical literature. In general, in all branches of catalysis, there are QCC-OS compositions with unpaired electrons everywhere, established with QSEI and QEXI, but still many works do not discuss or identify them properly. Advances take time to be accepted, for example, all solid catalysis, independently of their electronic structure, were traditionally attempted to be described as weakly correlated metals with simplifications assuming/adopting partial views. For instance, in OER and ORR with incomplete thermodynamic profiles (see Fig. 13A),[164] or *e.g.*[165] non-catalytic and partial because the chemisorption and rupture of H_2O (H_3O^+ and OH^-) on the catalysts were not included, neither the catalytic formation/rupture of the O···O spin-polarized bond at some point,[166] nor the chemisorption and desorption of $^3O_2$. It was frequently ignored that the $^3O_2$ molecule is in a triplet state, and at some point, the spin must play a role, or the activation barriers (transition states) between steps, or if the electrocatalyst is an insulator or a conductor. The present article agrees with M. Lingenfelder *et al.*, "the role of electron spin, as an intrinsic property of electrons, has commonly been overlooked in solid catalysis",[167] and Sun *et al.*[80] Overall, past conceptual and computational simplifications in electrocatalysis overlooked the overpotentials, as shown in Fig. 14. Logically, oversimplified approaches, even in their methodology, are incomplete and unable to reveal the general features of $^3O_2$ electrocatalysts.[168] Fig. 13C and D show a good, more complete work by Song *et al.* in 2019,[169] or Lin *et al.* in 2023.[170] Nowadays, there are hundreds of theoretical and experimental articles identifying QSEI in quantum catalysts, with some of the more recommended ref. 171–175; also the connection with the observed CISS effect is more evident.[30,145–147]

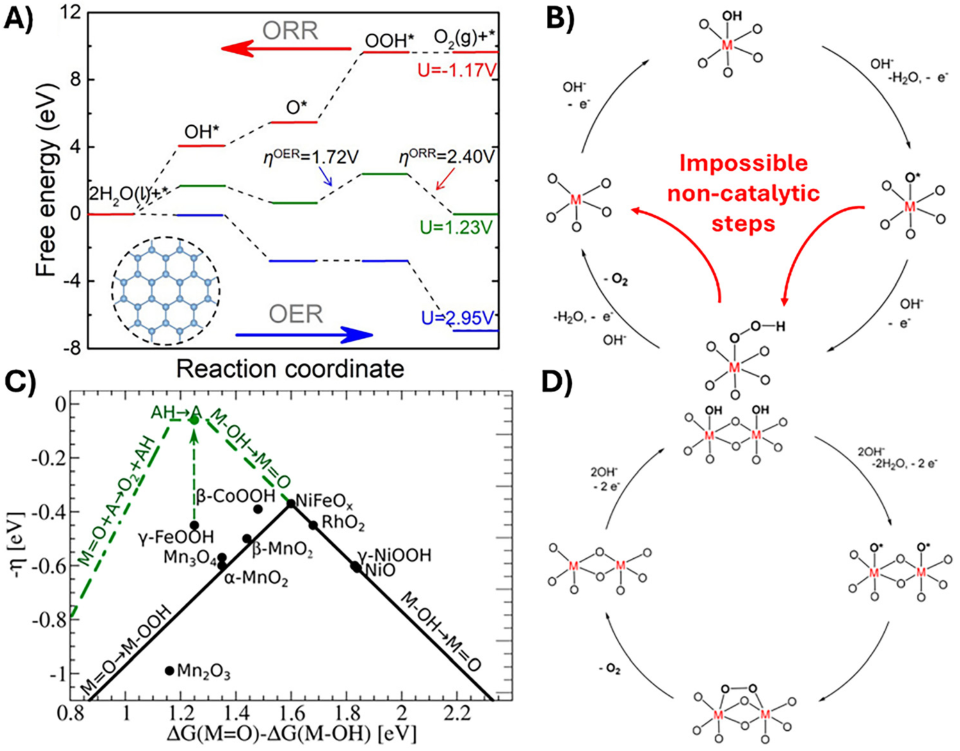

Fig. 13 (A) and (B) Examples of the traditional incomplete thermodynamic profile frequently believed to describe OER and ORR in 2021, adapted from ref. 164. Copyright © 2021, The Authors. Published by the American Chemical Society. This publication is licensed under CC-BY-NC-ND 4.0. (C) One example of the imprecision of single thermodynamic descriptors in $^3O_2$ electrocatalysis and (D) some improvements by recovering some catalytic steps, at least for the formation $^3O_2$ chemisorption, adapted from ref. 169. This is an open access article published under an ACS Author Choice License, which permits copying and redistribution of the article or any adaptations for non-commercial purposes.

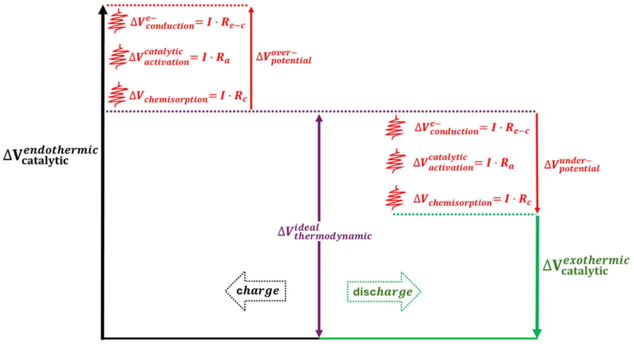

Fig. 14 In electrocatalysis, over- and under-potentials contribute to the loss of useful energy and added resistances; (left) endothermic reactions (*e.g.* OER or battery charge) and (right) exothermic reactions (*e.g.* ORR or battery discharge).

In electrocatalysis, the over- and under-potentials account for the irreversible work done at the catalytic interphase, which dissipates to its surroundings as energy losses *versus* the useful reversible thermodynamic potential, $|\Delta V_{\text{Electro-catalysis}}| = |\Delta V_{\text{Reversible}}| \pm |\Delta V_{\text{Irreversible}}|$, as shown in Fig. 14. Similarly in heterogeneous catalysis, the activation barriers in endothermic reactions determine that excess irreversible thermal energy is needed, as shown in Fig. 15. Alternatively, in exothermic reactions, some of the thermodynamic (reversible) heat generated will be also used in irreversible interactions with the surroundings, which is less useful energy, and also related with the activation barriers, as shown in Fig. 15. In electrocatalysis, similar to any catalytic reaction, only ideal barrierless steps will be energetically fully reversible. Thus, it is a good exercise to check how the different theoretical models attempt to explain the underlying kinetics and activation barriers and their (quantum) nature to ultimately distinguish good catalysts from bad catalysts.

Spin–orbital orderings in open-shells stabilize because electrons have overall lower orbital energies, which is a general effect for any reaction/catalyst

The spin-metallic conduction in magnetic bonds[11–13] also has significant thermodynamic consequences, namely, typically weaker chemisorption and lower activation barriers.[42,64,74] According to the electronic alterations based on the comparison among conducting FM bonds, AFM insulators and weakly correlated catalysts, the Bell–Evans–Polanyi (BEP) principle,[176] as shown in Fig. 16 from Prof. R. van Santen, is not universal. Quantum correlations are stabilizing non-bonding interactions;[1,2] considering this idea, we can understand the outstanding results reported by Li *et al.* in 2023,[36] or identify other QCC-OS examples, such as the excellent ^{2}NO oxidation activity on complex open-shell oxides.[177] Again, intermediate oxidation states in 3d-metals, *i.e.*, the partial occupation of orbitals, is the signature of inter-atomic ferromagnetic bonds.[2,14,36,42,57]

From 2018, ideas expanded, given that the modulation of QSEI potentials is present in industrial ammonia catalysts,[58] and in nitrogen fixing in soil bacteria,[2] our work was obviously followed and experimental verifications appeared in 2024.[144,178] Considering the historical relevance of ammonia synthesis, these fundamental works have upgraded our view on heterogeneous catalysis. For instance, in relation with the greener energy transition, efficient electrocatalytic nitrogen reduction has been achieved *via* spin polarization.[179,180] The rationalization and generalization of most aspects of spin-enhanced (quantum) catalysis[1,2] are the most influential advances, and the successful theoretical prediction of solid catalysts of our time has already appeared in several reviews.[174,175,181–184]

The electronic structures at transition states (T.S.) for the activation of bonds remain in equilibrium between the potential curves of the reactants and products, as shown in Fig. 2 and 19, where T.S. are the minimum energy bridge.[185] In these

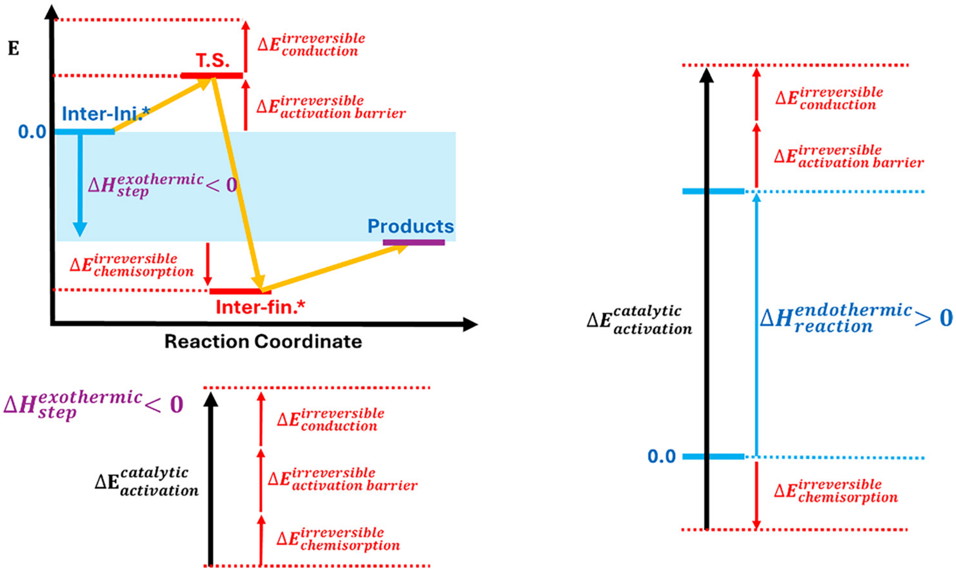

Fig. 15 Similar to electrocatalysis, irreversible energy factors always contribute to catalytic reactions. The amount of less useful energy needed, associated with excess in chemisorption, activation barriers, and even charge-spin transport, distinguishes between good and bad catalysts.

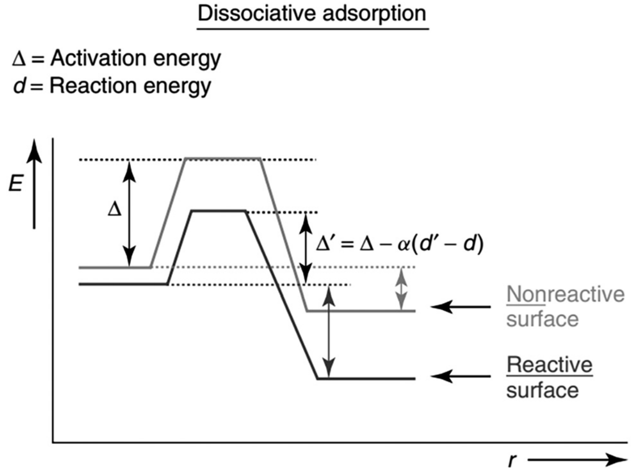

Fig. 16 Illustration of the BEP relation, as extracted from an excellent chapter by Prof. Rutger A. van Santen, with permission from ref. 176, Copyright © 2010, Wiley-VCH Verlag GmbH & Co. KGaA.

equilibrium states of many-body systems, the persistence of quantum coherence influences the thermodynamics during electron transfer/relocation. Compared to the more stable end points, T.S. (activation energies) are more anti-bonding electronic structures.[1] This is because they represent a high-energy configuration, where bonds are partially broken, and new bonds are forming. The electronic structure of transition states involve molecular orbitals that have significant antibonding contributions along the reaction coordinates, which make them less stable. The Bell–Evans–Polanyi (BEP) approximation assumes that for certain electronic structures, the difference in activation energy for a reaction step is proportional to the difference in their enthalpy of reaction, as shown in Fig. 16. Thus, the BEP principle supposes a linear energy relationship to approximate the energy of T.S. from the chemisorption enthalpy of the intermediates. In the comparison of catalysts, the BEP approximation assumes that the pre-exponential factor of the Arrhenius equation and the position of the T.S. along the reaction coordinates are the same for all active sites, independently of the possible considerable differences of the contributions of quantum potentials between different catalysts. Scaling relationships can be seen as an extension of the BEP approximation to estimate, for instance, the chemisorption of a double bond, such as X═*, from a related single bond, such as HX–*, which is typically weaker. The important point is to recognize that BEP and scaling relationships are not general, given that many of the most active catalysts do not follow common linear tendencies (approximated parametrizations). Scaling relationships combined with BEP are not universal approximations in catalysis because changes in the composition, structure, oxidation state, size, *etc.* of different active sites do not produce common linear energy changes for all compositions; in both cases, quantum correlations, as intrinsic properties of catalysts, are frequently responsible. Actually, it becomes apparent that the best catalysts are those that deviate, the compositions not expected in the simplifications, and those that follow the principle of reducing all the less useful energy steps, namely, lower chemisorption and activation barriers.[1,25,64] Recurrently in many of the examples and references herein, the following observations are noted for the optimum quantum catalysts: (1) lower (exothermic) chemisorption energy occurs because the stabilizing quantum correlations lower the chemical potential of electrons in the catalysts. (2) The endothermic energy barriers of the T.S. decrease because quantum correlations can relatively stabilize these less covalent electronic distributions. (3) The valence active electrons are not paired or trapped, or in the ground-state inter-atomic ferromagnetic bonds, associate with spin-dependent electronic mobility and QEXI, with higher orbital flexibility.

The advantage of a complete quantum description of catalysis is that it reveals what is inside the activation barriers, as part of our future perspective. Preliminary thermodynamic activity indicators are a good idea initially, but to advance, more information is needed. The intention of the previous long reiterative introduction is to familiarize readers with the concepts and show that studies on quantum catalysts are rapidly advancing because to really understand the experimental results, we must go deeper. Quantum correlations were incorrectly not explicitly interpreted in most studies on solid catalysts; thus, the amendment in the future is to incorporate explicit quantum correlations. Possibly it is helpful to state that quantum correlations are part of the information/disorder that is intrinsically hidden in the system. They are a quantum entropic energy correction; considering that entanglement and superposition mean electrons participating in many different individual states at the same time.

2. It is all about the wavefunction

The wavefunction, $\Psi(t,x_1,x_2,\ldots,x_n)$,¶ is the representation of a non-deterministic reality that reveals the probability of observables, such as the electron $\rho(r)$, spin $\rho_{\text{spin}}(r)$, densities or the energy. This indicates that any observable $\rho_{\text{spin}}(r)$ is a consequence of $\Psi(t,x_1,x_2,\ldots,x_N)$, and not the other way around. In the case of stationary states, where $\Psi = \varphi(t)\cdot\Phi_R(x_1,x_2,\ldots,x_n)$ is the product of the time and real spatial part, observables do not carry all the information implicit in the non-directly observable $\Psi(t,x_1,x_2,\ldots,x_n)$. The integral construction of spin-densities, $\rho(r) = \rho_\alpha(r) + \rho_\beta(r); \rho_{\alpha(\beta)}(r) = n\int|\Phi_R(r_1 + \alpha(\beta), x_2, \ldots, x_n)|^2 d^4 x_2 \ldots d^4 x_n$,[186] prevents them to directly carry the QSEI and QEXI, and these interactions are imported from the non-local symmetry of $\Phi_R(x_1,x_2,\ldots,x_n)$. To match the experimental observables, symmetry-constructing rules are available for the electronic spin-spatial part, $\Phi_R(x_1,x_2,\ldots,x_n)$, which is not intuitive, but needed to create valid quantum solutions in catalysis. The construction and consequences of $\Phi_R(x_1,x_2,\ldots,x_n)$, just the logic are as follows:

(a) If electrons do not lose their particle identity. If electrons maintain their fundamental identity as fermions, and thus a multielectron wavefunction combines individual monoelectronic ($\phi_i(x_i)$) spin–orbitals, $\Phi_R = f(\phi_1(x_1),\phi_2(x_2),\ldots\phi_n(x_n))$. The total spatial wavefunction is a superposition of the individual amplitude of probabilities of all electrons. The first simplest

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¶ t, time, and x_i, spatial (r_i) and spin (α or β) coordinates of electron i.

possible approximation for Φ_R is the Hartree product, $\Phi_{\mathrm{Hartree}} = \prod_i \phi_i(x_i)$.

(b) Electrons are fermions and there cannot be two identical, with equal quantum numbers *e.g.* $\phi_1(r_{1(2)}\alpha)$, or $\Phi_R = f(\phi_1(r_1\alpha), \phi_1(r_2\alpha),\ldots\phi_n(x_n)) = 0$. Thus, the Pauli exclusion principle appears, *i.e.*, two electrons with the same spin cannot occupy a common orbital, in the example $\phi_1(r_{1(2)}\alpha)$. The Pauli repulsion as a classical force does not exist, it is a condition in the shape of Φ_R. The Pauli restriction is not true for the Hartree product; thus, the proposed solution must improve.

(c) Electrons are undisguisable, where if we exchange the spatial coordinates ($r_i \leftrightarrow r_j$) of two electrons with the same spin, the response (experiments) should be the same. Wavefunctions must respect this indistinguishability, or $|\Phi_R(r_1\alpha,r_2\alpha,\ldots,x_n)|^2 = |\Phi_R(r_2\alpha,r_1\alpha,\ldots,x_n)|^2$; furthermore, to satisfy the Pauli exclusion principle, in the exchange of any two electrons with the same spin, $\Phi_R(r_1\alpha,r_2\alpha,\ldots,x_n) = -\Phi_R(r_2\alpha,r_1\alpha,\ldots,x_n)$. Now, the simplest candidate solutions are Slater determinants,‖ $\Phi_{\mathrm{Slater}} = 1/\sqrt{(n!)}\left|\prod_i \phi_i(x_i)\right|$, or single electronic configurations based on the Hartree–Fock method.[52] The forced restrictions in the anti-symmetry of the solution (indirectly) will introduce the non-classical quantum spin exchange stabilising energy terms (QSEI). It is hoped that it is clearer now why we prefer to use its longer name. Φ_{Slater} expresses the reality that (entangled) electrons with the same spin are virtually interchanging their orbitals, reducing the expected classical Coulomb repulsions. The implications of QSEI for reality are enormous including spin–orbital orderings, magnetism, quantum computing, spin liquids, superconductors, and chemical bonding. Spin exchange interactions bridge the quantum and classical realms, and it is impossible to understand catalysis without properly describing QSEI, and the advances since 2016 are without doubt the most influential in solid catalysis of the decade. Regarding any theoretical discussion on catalysts with open shells, for it to be complete, intra- and interatomic QSEI should be specifically discussed/quantified.

(d) As a fix set of always occupied orbitals, $\phi_i(x_i)$, in a single Slater determinant, which is a unique electronic configuration, does not include the possibility of spontaneous (virtual) orbital excitations (QEXI) or participation of other orbital configurations at 0 K. A complete space-time representative solution is multiconfigurational, $\Phi_{\text{full CI}} = \sum_j c_j\left(1/\sqrt{(n!)}\left|\prod_i \phi_i^j(x_i)\right|\right)$, including multiple Slater determinants. Any two electrons at 0 K can virtually scatter into empty (conduction) orbitals at that time, moving away from Coulomb repulsions. These are undetectable virtual excitations because there is no emission of information, namely photons. Thus, multiconfigurational wavefunctions add/involve the superposition of all possible electronic configurations to describe the electronic state of a system. The intrinsic possibility, which is undetectable, is that as two electrons come together, their electronic repulsion grows, and this repulsion potential is the source to incite the probability to any virtual excitations (QEXI) to avoid an increase in Coulomb repulsions. QEXI are more essential for accurately describing systems with non-weak electron correlation, such as excited states, transition states, and compositions with metallic open-shell bands. QEXI open the possibility for the electrons to temporarily and virtually occupy any place in their configurational space because any method to detect/observe them *via* interchanging energy/information would destroy the mechanisms. I also hope it is clearer why we prefer QEXI as a clearer name than "correlation energy", especially for the chemistry community more used to electronic configurations, and to make a clear connection with the more general concept of quantum superposition.

In chemistry, electrons are one of the main playgrounds of quantum physics, which are stranger than fiction, defying our everyday intuition and challenging classical notions of reality. In this case, increasing the quantum correlation/entropy energy of catalysts can make them more active.

The energy and Hamiltonian operators extract information from $\Phi_{\text{full CI}}$ to get the final shape and energy observables

The quantum reality has imposed a certain shape for $\Phi_R = \Phi_{\text{full CI}}$, and we cannot completely reverse this construction from the observables, such as $\rho_{\mathrm{spin}}(r)$. The wavefunction includes information about the phase and the correlations between electrons, which are not directly accessible from the electronic density alone. For example, the wavefunction can describe the spin state of electrons and their entanglement, while the electronic density is a scalar quantity and lacks this level of detail. In chemistry, we chiefly need the time-independent Born–Oppenheimer Hamiltonian of the system, $\hat{H}_{e-}$, which is composed of operators with a classical correspondence, to establish the relevant stationary electronic space equations to solve: $\hat{H}_{e-}\Phi_{\mathrm{Re-}} = E_{e-}\Phi_{\mathrm{Re-}}$. The energy responses, E_{e-}, are observables. At a fix position of the slow nuclei: $\hat{H}_{e-} = \widehat{\mathrm{K.E.}}_{e-} + \widehat{\mathrm{CORE}}_{e-} + \widehat{\mathrm{COAT}}_{e-n+} + \widehat{\mathrm{SOC}}_{e-}$, kinetic energy, Coulomb repulsion and attraction and spin–orbit coupling can be determined, respectively. Now, the gradual construction of Φ_R will explain the appearance of non-classical (quantum correlations) energy terms, as follows:

(a) $\Phi_{\mathrm{Hartree}} = \prod \phi_i(e_i)$: E(Hartree) = K.E.(Hartree) + CORE(Hartree) + COAT(Hartree) + SOC(Hartree).

In the Hartree model, each electron interacts with the average local potential created by all other electrons. The interaction is local because it depends on the position of the electron and the electron density around it. In the Hartree approximation, the identical electrons are incorrectly described as energetically distinguishable particles, and the quantum state of this non-entangled system can be factored as a product of the functions of individual orbitals. The absence of indistinguishability means that there are no quantum correlations that span the entire system, which are responsible for non-local energy terms. The improper construction of Φ_{Hartree} overlooks both quantum energy correlations, QSEI and QEXI; Φ_{Hartree} is inherently a mean-field

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‖ A Slater determinant is a mathematical expression used in quantum mechanics to describe the wavefunction of a multi-fermion system, while ensuring it obeys the Pauli exclusion principle. It is built from single-particle wavefunctions (spin-orbitals) arranged in a determinant form.

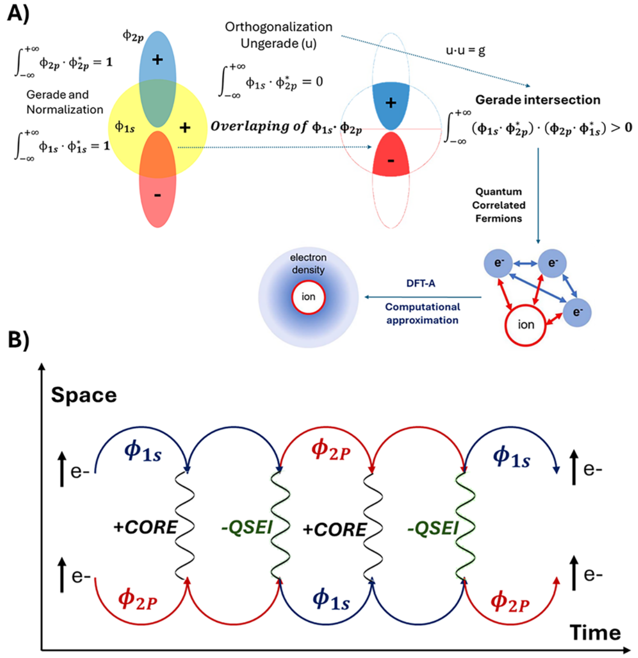

Fig. 17 (A) Orthogonalization of orbitals creates "ungerade"-type intersections; thus, the multiplication of two intersections is a "gerade"-type probability. Local-pure DFT-A tries to mimic fully quantum many-body interactions *via* the addition of approximated fitting functionals of the spin density to non-correlated wavefunctions. The DFT-A attempt is more applicable for simple quantum matter and conventional closed shell compositions, where electronic interactions are dominated by the potentials with a classical interpretation. (B) Quantum correlations imply additional Feynman diagrams in the description of the interactions between electrons. Thus far, this is one of the most clear visual descriptions of virtual quantum teleportation of electrons with the same spin between two different orbitals in the QSEI entanglement.

(non- or improper-wavefunction) approximation, incorrectly assuming non-correlated electrons.

In relation, the Kohn–Sham density functional theory approximation (DFT-A) tries to use effective local or semi-local invented potentials to approximate the true non-local QSEI and QEXI. Although this simplifies the calculations, it is an approximate treatment of the interactions, and electrons remain distinguishable given that the non-locality is a consequence of quantum mechanics and the indistinguishability of particles. The numerical simplifications of (semi-)local DFT-A use fictitious distinguishable single-electron orbitals, as in the Hartree model, to represent non-entangled electrons that try to reproduce the same electron density as the real quantum system. Because pure DFT-A adds fictitious potentials to the Hamiltonian, DFT-A is constructed to fit the electron density of the real system, and in this case, a surprising mathematical trick is done by adding fabricated (local or semi-local) QSEI ($\hat{V}(\rho_{\mathrm{spin}})_{\mathrm{QSEI}}$) and QEXI ($\hat{V}(\rho_{\mathrm{spin}})_{\mathrm{QEXI}}$) unreal operators, which are mathematical functions of $\rho_{\mathrm{spin}}(r)$, to impose the appearance of approximated energy quantum corrections. DFT-A is a clever numerical approach to accelerate numerical solutions, starting from an incomplete method of non-correlated electrons, which will be corrected by another imperfect $\hat{H}(\text{DFT-A})_{\mathrm{e-}}$ to try to mimic the observed real quantum system, as shown in Fig. 17.

Reasonably, the shortcut of DFT-A does not always work,[187–190] and there is no universal form for $\hat{V}(\rho_{\mathrm{spin}})_{\mathrm{QSEI}}$ and $\hat{V}(\rho_{\mathrm{spin}})_{\mathrm{QEXI}}$, revealing a considerable fundamental oversight in solid-catalysis, *i.e.*, DFT-A is not the fundamental general basis of the electronic interactions in catalysis.

Pure (DFT-A) $\Phi_{\mathrm{Hartree}} = \prod_i \phi_i(e_i)$ plus fitting $\hat{H}(\text{DFT-A})_{\mathrm{e-}} = \widehat{\mathrm{K.E.}}_{\mathrm{e-}} + \widehat{\mathrm{CORE}}_{\mathrm{e-}} + \widehat{\mathrm{COAT}}_{\mathrm{e-}} + \widehat{\mathrm{SOC}}_{\mathrm{e-}} + \hat{V}\left(\rho_{\mathrm{spin}}\right)_{\mathrm{QSEI}} + \hat{V}\left(\rho_{\mathrm{spin}}\right)_{\mathrm{QEXI}}$: $E(\text{DFT-A}) = \text{K.E.}(\text{DFT-A}) + \text{CORE}(\text{DFT-A}) + \text{COAT}(\text{DFT-A}) + \text{SOC}(\text{DFT-A}) + \text{QSEI}(\text{DFT-A}) + \text{QEXI}(\text{DFT-A})$.

A proper wavefunction is essential to fully account for non-local correlation effects in quantum mechanics. The wavefunction of an entangled system cannot be factored into independent components for each particle. This makes the wavefunction essential for describing the interconnected nature of these particles. Non-wavefunction methods, or other mean-field approaches, can neither fully account for all quantum correlation effects, nor explain the fundaments of these interactions.[2]

(b) Slater determinant $\Phi_{\mathrm{Slater}} = 1/\sqrt{(n)}\left|\prod_i \phi_i(e_i)\right|$: $E(\text{Hartree–Fock}) = \text{K.E.}(\text{Hartree–Fock}) + \text{CORE}(\text{Hartree–Fock}) + \text{COAT}(\text{Hartree–Fock}) + \text{S.C.}(\text{Hartree–Fock}) + \text{QSEI}(\text{Hartree–Fock})$.

The Φ_{Slater} wavefunctions reveal the first type of non-classical correlation energy, QSEI(Hartree–Fock), because electrons are indistinguishable. For only two electrons in a singlet state $\Phi_{\mathrm{Slater}}^{\mathrm{singlet}} = 1/\sqrt{2}[\phi_{\mathrm{A}}(r_1)\phi_{\mathrm{A}}(r_2)]\cdot[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$, because the anti-symmetry the spin part is undecided; in this case, reality does not distinguish the label of which spin every electron has. Due to this spin entanglement, the individual spins are inherently unknowable, and if we measure one of them immediately (instantly) no matter where it is, the other collapses to be in the opposite spin. This spin-momentum conservation reflects the symmetry of the system and adheres to the rules of quantum mechanics, but in this case, the entangled spin conservation does not have direct energy consequences. Alternatively, for a triplet state, $\Phi_{\mathrm{Slater}}^{\mathrm{singlet}} = 1/\sqrt{2}[\phi_{\mathrm{A}}(r_1)\phi_{\mathrm{B}}(r_2) - \phi_{\mathrm{A}}(r_2)\phi_{\mathrm{B}}(r_1)]\cdot[\alpha(1)\alpha(2)]$, it is undecided in which orbital each electron stands. Due to this space-time entanglement, the individual orbital of each electron in inherently unknowable, which a Feynman's diagram will associate with virtual tele-transport between orbitals, as shown in Fig. 17B.[2] The first true non-classical, non-local energy term associates electrons with the same spin, which appears due to the undistinguishable-antisymmetric Ψ_{Slater}: stabilizing quantum spin exchange interaction (QSEI).

The steady-state spatial anti-symmetric wavefunctions, *e.g.* $\Phi_{\mathrm{Slater}}^{\mathrm{singlet}}(r_1,r_2,\mathrm{spin}_1,\mathrm{spin}_2) = 1/\sqrt{2}[\phi_{\mathrm{A}}(r_1)\phi_{\mathrm{B}}(r_2) - \phi_{\mathrm{A}}(r_2)\phi_{\mathrm{B}}(r_1)]\cdot[\alpha(1)\alpha(2)]$, mean that the electrons are entangled because it is not possible to describe the complete system as a superposition of states of the individual electrons, as in $\phi_{\text{non-entangled}}^{\mathrm{trial}}(r_1,r_2) = c\cdot(\gamma_1\phi_{\mathrm{A}}(r_1) + \delta_1\phi_{\mathrm{B}}(r_1))\cdot(\gamma_2\phi_{\mathrm{A}}(r_2) + \delta_2\phi_{\mathrm{B}}(r_2)) = c\cdot\gamma_1\gamma_2\cdot\phi_{\mathrm{A}}(r_1)\phi_{\mathrm{A}}(r_2) + c\cdot\gamma_1\delta_2\cdot\phi_{\mathrm{A}}(r_1)\phi_{\mathrm{B}}(r_2) + c\cdot\delta_1\gamma_2\cdot\phi_{\mathrm{B}}(r_1)\phi_{\mathrm{A}}(r_2) + c\cdot\delta_1\delta_2\cdot\phi_{\mathrm{B}}(r_1)\phi_{\mathrm{B}}(r_2)$. The conditions to try to make $\phi_{\mathrm{Slater}}^{\mathrm{triplet}}(r_1,r_2) = \phi_{\text{non-entangled}}^{\mathrm{trial}}(r_1,r_2)$ are: $\gamma_1\gamma_2 = 0$, $\delta_1\delta_2 = 0$, $\gamma_1\delta_2 = 1$ and $\delta_1\gamma_2 = -1$. But if $\gamma_1\gamma_2 = 0$, or $\gamma_1 = 0$ or $\gamma_2 = 0$, and then or $\gamma_1\delta_2 = 0$ or $\delta_1\gamma_2 = 0$, and thus it is impossible to obtain valid solutions only based on separable electrons, which is the mathematical meaning of entangled electrons. Given that DFT-A essentially means $\phi_{\text{DFT-A}}^{\mathrm{trial}}(r_1,r_2) = \phi_{\text{non-entangled}}^{\mathrm{trial}}(r_1,r_2)$, we also proved that all DFT-

A non-wavefunction mapping attempts are non-entangled numerical approximations, which are fundamentally incomplete and never exact.

Entanglement is fundamental to quantum mechanics itself, given that it underpins concepts such as non-locality and quantum coherence to be discussed in catalysis, which is mainly revealed through spin–orbital orderings. In the actual $\Phi^{\text{anti-symmetric}}_{\text{wavefunction}}$, no matter how far apart $\phi_{\mathrm{A}}(r)$ is from $\phi_{\mathrm{B}}(r)$, if we detect an electron in orbital $\phi_{\mathrm{A}}(r)$ with a spin, then instantaneously, the other electron collapses superluminally to be in the complementary orbitals and spin. This collapse of the quantum states is based on our observable measurements apparently instantaneous and independent of the distance. Nonetheless, the energetic effect of the entangled $\Phi^{\text{anti-symmetric}}_{\text{wavefunction}}$ solutions, the QSEI part of the correlation energy, depends on the separation between electrons because it corrects the Coulomb potentials, $\mathrm{QSEI} \propto -\iint [(\phi_{\mathrm{A}}(r_1)\cdot\phi_{\mathrm{B}}(r_1))\cdot(\phi_{\mathrm{A}}(r_2)\cdot\phi_{\mathrm{B}}(r_2))]/r_{12}\mathrm{d}r_1\mathrm{d}r_2$. Within this framework, we cannot explain much more about the mechanism of entanglement, but some additional details can be gained from the time-dependent part of the wavefunctions. In any case, for a stationary state, the real time-dependent part is real$[\varphi_i(t)]$ = cos$(\nu\cdot t)$, with $\nu = E/h$ being an oscillating frequency in time. The whole real part of the wavefunction, real$[\Psi^{\text{stationary}}_{\text{state}}]$ = cos$(\nu\cdot t)\cdot\Phi^{\text{anti-symmetric}}_{\text{stationary state}}$(space,spin), breath in time; before it changes sign, it pass periodically through instances with real$[\Psi^{\text{stationary}}_{\text{state}}]$ = real$[\varphi_i(t_{\text{vanish}})]$ = 0, where in all points of space, the real wavefunction has the unique value of zero. The energy and momentum are conserved but there are instances in space-time, t_{vanish}, where the real amplitude probability of the wavefunction is zero everywhere, and the electrons lose track of any spatial distinction. Soon after, the real wavefunction starts to increase again with the opposite sign, and again with distinctive probabilities in space-time to find the particles, but not conserving (revealing) the information of the previous sites of the electrons if we want to agree with entanglement (indistinguishability).

Articles about spin effects in catalysis should be clear because there is more than one type, what it is? QSEI (spin exchange), spin–orbit coupling,** CISS effect, direct spin–spin interactions. Typically, the most relevant is QSEI; plus, it may be something else. To better visualize the nature of QSEI, and the meaning of the integrals that determine their value, we can do some more orbital physics, as shown in Fig. 17. The steady-state orbitals of electronic configurations are orthogonal eigenfunctions, $\int\phi_{\mathrm{A}}(r)\cdot\phi_{\mathrm{B}\neq\mathrm{A}}(r)\mathrm{d}r = 0$, meaning that $\phi_{\mathrm{A}}(r)\cdot\phi_{\mathrm{B}\neq\mathrm{A}}(r)$ is imposed to be an odd ("ungerade") function. Also, the multiplication of two ungerade functions gives even ("gerade") functions, $u\cdot u = g$. Thus, the QSEI integrals are gerade $K_{ij} = -\iint\left[\left(\phi_i(r_1)\cdot\phi_{j\neq i}(r_1)\right)\cdot\left(\phi_i(r_2)\cdot\phi_{j\neq i}(r_2)\right)\right]\Big/r_{12}\mathrm{d}r_1\mathrm{d}r_2$, which are related with the improbability of finding two electrons with the same spin at the same time in the intersection zone. Two electrons with the same spin cannot be at the same time in the Pauli exclusion zone, where the quantum energy space-time reality forbids that any observation will place two electrons with the same spin in the orbital gerade intersections, thus being non-local for both electrons. The classical CORE does not anticipate this quantum correlated restriction in the energy space available for electrons with the same spin. The true stabilizing nature of QSEI appear from the appropriate anti-symmetric wavefunctions, and its value depends on the overlapping of orbital pairs and how many electrons there are with each spin. QSEI are two electron integrals, the value of which is always relevant, which might correspond with two vertex representing Feynman type diagrams.[2] This perspective deliberately pays a lot of attention to QSEI because they are the main quantum correlations, which are always important for any composition but even more for open-shell orbital configurations (main origin of quantum catalysts and materials). In any catalyst with unpaired electrons, computational studies must explain how they tried to properly reproduce the correct experimental spin–orbital orderings of the ground state, bulk and surface, treating intra- and inter-atomic QSEI the best they can. DFT-A in the proper open-shell orbital configurations, if needed with additional parametric Hubbard penalties for double occupancy (+*U*), is not ideal but it can be a first approximation to QSEI. However, if studies do not explain how they have tried to do this properly, then it may be suspected that the popular DFT-A calculations might be too erroneous because this was often the case in all types of QCC-OS compositions before 2021. Sometimes DFT-A on real open-shell orbital configurations was even fictitiously forced to be closed-shells to accelerate the calculations, and thus all those studies should be revisited.

(c) Multiconfigurational solutions, $\Psi_{\text{full CI}} = \sum_j c_j \left(1/\sqrt{(n!)}\left|\prod_i \phi^j_i(e_i)\right|\right)$, E(exact) = K.E.(exact) + CORE(exact) + COAT(exact) + S.O.(exact) + QSEI(exact) + QEXI(exact).

Another non-classical stabilizing energy terms appears associated with multiconfigurational $\Psi_{\text{full CI}}$, QEXI; in the literature starting from the Hartree–Fock (H.-F.) approximation, it is indeterminately just called "quantum correlation". We prefer to use quantum excitation interactions (QEXI), given that QEXI are the part of quantum correlations due to a superposition of diverse electronic configurations with different probabilities. Quantum superposition is one of the fundamental principles of

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** Spin–orbit coupling and spin–orbit ordering are related but distinct concepts in physics. Spin–orbit coupling refers to the interaction between the spin of a particle and its orbital motion due to relativistic effects. This interaction is particularly significant in atomic physics, where it leads to energy level splitting in atoms, known as fine structure. It also plays a crucial role in condensed matter physics, influencing electronic properties in materials such as semiconductors and topological insulators. Alternatively, spin–orbit ordering describes a collective phenomenon, where spin–orbit interactions (intra- and inter-QSEI) lead to a specific ordered state in a material. This can manifest in systems where spin–orbit coupling drives the formation of exotic quantum phases, such as spin–orbit-induced magnetism and topological states. In essence, spin–orbit coupling is the fundamental interaction, while spin–orbit ordering refers to the resulting organized state that emerges in certain materials due to this interaction. Any article that properly tried to explain spin effects in chemisorption and catalysis must explain intra- and inter-quantum spin exchange interactions because they are the fundamental quantum mechanical origin, and any other approach is an incomplete indirect view. At the personal level, I give my honest opinion about the future perspective, hoping for the best in this field. It is time to disentangle the individual quantum effects in catalysis.

quantum mechanics, which is like the electrons can see/feel/use instantaneously all their energy space-time available, *i.e.*, the Hilbert space.†† $\Psi_{\text{full CI}}$ is the mathematical representation of the reality that electrons respond to the energy interference of multiple states, or probability of virtually being in different orbital configurations at the same time. The term "quantum correlations" alone is not sufficiently defined to refer to a specific a phenomenon related with superposition. The energy space/volume available for the electrons increase by adding additional configurations, and then electronic repulsions can decrease, again non-locally. The energy ligated with QEXI is related with how $\widehat{\text{CORE}}_{\text{e}-\text{e}-}$ propels the interference mainly between the ground-state single configuration and excited configurations,[2] *i.e.*, virtual‡‡ quantum excitations (QEXI), and it is the most difficult part to calculate for solid catalysis, making it a topic for the future.

Again, we must remember that DFT-A is not multiconfigurational and can only approximate numerically from a non-entangled simplification the quantum superposition point of view. DFT-A does not identify the true meaning of QEXI and tries to approach this energy correction with variational added fictitious-fitting local (semi-local) potentials. The computational speed of DFT-A is useful, which is based on approximated solutions non-entangled and without superposition. In the original paper by Hohenberg and Kohn in 1964,[191] the foundation of (non-wavefunction) density functional approximations, we consider that there is a fundamental misunderstanding. The authors of eqn (1), page B865, place the correct basic electronic Hamiltonian $\hat{H}_{\text{e}-} = \widehat{\text{K.E.}}_{\text{e}-} + \widehat{\text{CORE}}_{\text{e}-} + \widehat{\text{COAT}}_{\text{e}-\text{N}+}$. Thus, in the classical $\widehat{\text{COAT}}_{\text{e}-\text{N}+}$, $\nu(r)$ in their notation, evolves as a unique functional of the electronic density, $\rho(r) = \rho_\alpha(r) + \rho_\beta(r)$ or $n(r)$. However, as we have explained, $\widehat{\text{CORE}}_{\text{e}-} \cdot \Psi_{\text{real}}$ is not a functional of $\rho(r)$, the true quantum correlations require information beyond the electron density, given that they depend on the detailed structure of the many-body wavefunction. This means that the main statement of the authors on page B865 is not true, "thus $\nu(r)$ is (to within a constant) a unique functional of $n(r)$; in turn, given that $\nu(r)$ fixes H, we see that the full many-particle ground state is a unique functional of $n(r)$". Accordingly, to correct this paper, we must add before the sentence: "let's make the non-entangled and without superposition simplification of approximating the real $\widehat{\text{CORE}}_{\text{e}-} \cdot \Psi_{\text{real}}$ as a functional $\rho(r)$. Thus $\nu(r)$ is (to within a constant) a unique functional of $n(r)$; in turn, given that $\nu(r)$ fixes H, we see that the full many-particle ground state can be approximated as a unique functional of $n(r)$." In addition, every time in that paper authors state "universal", just change it to "approximated", and thus we can continue and understand the origin and limitations of the great (semi-)local density functional approximation (DFT, DFA or DFT-A).

We can resume and further clarify the context of computational studies for the multitude of catalysts that are inherently quantum materials. DFT-A implementations are neither exact nor equally precise for all compositions, but are good local (semi-local) approximations computationally in terms of cost/quality, and more accurate for weakly correlated closed-shell electron systems (WCCS). Pure DFT-A serves to compare reasonably WCCS, where QSEI and/or QEXI are not the differential factors in their catalytic properties.[1] More importantly, DFT-A is not the fundamental theory in materials science, surface chemistry and catalysis because $\rho_\alpha(r) + \rho_\beta(r)$ does not directly carry any anti-symmetric (entanglement) and multiconfigurational (superposition) quantum information. In the so-called (advanced) hybrid DFT-A implementations, $\hat{V}(\Phi_{\text{Slater}})_{\text{QSEI}}$ is not a function of the electronic density anymore but Φ_{Slater}, essentially is not a DFT-A anymore, but a variational extension of the H.F. method. 100% hybrid DFT-A is a corrected post H.-F. wavefunction numerically improved with an extra fitting $\hat{V}(\rho_{\text{spin}})_{\text{QEXI}}$. To study better transition states in any catalyst, we aim for a near future with at least 100% non-local QSEI plus some approximated QEXI variational correction, hybrid post H.F. wavefunction implementations, which are hopefully more equally precise for WCCS, and the opposite, non-weakly correlated open-shells (QCC-OS).

Our proposed updates in notation for chemistry, nomenclature and amendment of some explanations compared to other many-body works may cause some discontentment. In the literature, works talk about static and dynamic correlations, which are essentially partial approximated views to QEXI. The quantum energetic corrections must be related with the general non-classical reality of (spin) entanglement (QSEI) and superposition (QEXI). Conceptual approaches in catalysis to study systems with many interacting quantum electrons by mapping a many-body problem to a single-site problem with a self-consistently determined bath do not allow the advancement, isolation and differentiation of the true nature of the quantum correlations. This is not an opinion, given that nowadays there is experimental evidence of quantum entanglement and superposition of states. It is a reality, not a hypothesis, that there are many quantum catalysts in the literature, and we need to start identifying them, which is a path that has already begun, *e.g.*, the recent work by H. Sudrajat about topological quantum materials in catalysis.[192] Also, in the new quantum biology, the attention has shifted to the discussion of wave-particle duality, superposition, and entanglement.[8]

The quantum potentials influence and compete, they are not independent, especially in transition states, where the electronic structure is less stable and depends more on non-local + QSEI(exact) + QEXI(exact).[1]

The time-dependent part of the wavefunction might also be real and have a closer relation with photons. The transition of wavefunctions between stationary states with different energy

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†† Quantum states are represented as vectors in a Hilbert space. It is an infinite-dimensional vector space, and in quantum mechanics is the space of square-integrable functions with specific symmetries. Operators acting on the Hilbert space, such as the Hamiltonian, are often expressed as a differential equation, defining measurable quantities such as energy, spin, and momentum.

‡‡ Although virtual interactions cannot be directly observed, their effects are measurable and play an essential role in quantum chemistry. Virtual interactions refer to temporary exchanges of energy between quantum particles, and these interactions involve virtual particles that mediate forces but do not exist as observable entities.

emits or adsorbs photons. Also, the energy of a photon is directly proportional to its frequency, $E = h\cdot\nu$ (s^{-1}), as if a real periodic event, repeating occurrence per unit of time, is changing in the wavefunction in the emission or adsorption of a photon.

Quantum mechanics is less intuitive from the Schrodinger formulation, $\hat{E}_i(t)\Psi_i(x,t) = \hat{H}(x)\Psi_i(x,t)$, because the energy operator, $\hat{E}_i = i\cdot h\cdot d/dt$, is complex, making the wavefunctions imaginary (i), $\Psi_i(x,t)$. In the case of stationary states, $\Psi_i = \varphi_i(t)\cdot\Phi_R(x)$, the spin-spatial part is real (R), $\widehat{H(x)}\cdot\Phi_R(x) = E\cdot\Phi_R(x)$, being $\phi_R(r)^2$ the spatial probability. Alternatively, the $\hat{E}_i(t)$ operator forces the time-dependent part, $\varphi_i(t)$, to be imaginary. The shape of $\hat{E}_i$ appeared thinking that a desired mathematical solution was $\varphi_i(t) = e^{i\cdot\nu\cdot t} = \cos(\nu\cdot t) - i\cdot\sin(\nu\cdot t)$, with frequency $\nu = E/h$. Thus, ν in the Schrodinger formulation controls the rotation speed of Ψ_i with time in a complex plane. Also, here the issue starts, what does it mean? Is Ψ_i a mathematical solution with imaginary numbers or a physical energy reality? This is a question that made Schrodinger hesitate.

Supposing that there is a complementary real $\Psi_R(x,t) = \mathrm{real}(\Psi_i)$, we must also find the corresponding real $\hat{E}_R$. Attempting to start from $\hat{E}_R = \mathrm{real}(i\cdot h\cdot d/dt)$ does not help much. To be related with actual oscillation frequencies in time, $\varphi_R(t)$ should be a derivable periodic function, and $d/dt\cdot\varphi_R(t)$ must similarly be a periodic function; however, there is no periodic real function that solves $d/dt\cdot f(t) = \mathrm{cte}\cdot f(t)$. The condition $d/dt\cdot f(t) = \mathrm{cte}\cdot f(t)$ forces $f(t)$ to be proportional to its derivative, when both evaluated at the same time, t. It is less restrictive to think that the equivalency with the derivative is not instantaneous, but it might be delayed, $d/dt\cdot f(t) = \mathrm{cte}\cdot f(t + \Delta t)$, or translated in time. Thus, an alternative is $\hat{E}_R(t) = h\cdot\hat{T}(\Delta t)\cdot d/dt$, where $\hat{T}(\Delta t)$ is a time translation operator. Δt should be related with ν^{-1}, under the condition $\varphi_R(t) = \mathrm{real}(\varphi_i(t)) = \cos(\nu\cdot t)$, and then $\Delta t = 3\pi/2\nu$:

$$\begin{aligned}\hat{E}_R(t)\cdot\cos(\nu\cdot t) &= h\cdot\hat{T}(3\pi/2\nu)\cdot(d/dt\cdot\cos(\nu\cdot t))\\ &= h\cdot\hat{T}(3\pi/2\nu)\cdot\nu\cdot{-\sin(\nu\cdot t)}\\ &= h\cdot\hat{T}(3\pi/2\nu)\cdot\nu\cdot\cos(\nu\cdot t - 3\pi/2)\\ &= h\cdot\nu\cdot\cos(\nu\cdot(t + 3\pi/2\nu) - 3\pi/2) = h\cdot\nu\cdot\cos(\nu\cdot t).\end{aligned}$$

The hypothesis that $\hat{E}_R(t)\cdot\Psi_R = \hat{H}_R(x)\cdot\Psi_R$ is possible and real improves our understanding, which is the main idea behind this perspective. Stationary quantum energies will imply a vibration in time, $\cos(\nu\cdot t)\cdot\Phi_R(x)$, an oscillation of the intensity and sign of the whole amplitude of probability with frequency ν, in still this non-relativistic approach. A change in the quantum energy of a state implies a change in the actual vibration frequency of the electron density, *i.e.*, overall (Hilbert) space, which translates in the emission or adsorption of the complementary frequency change, or photon $\nu_{\mathrm{foton}} = |\nu_{\mathrm{final}} - \nu_{\mathrm{initial}}|$, a conservation of the time vibrational breath.

Photons are a way to transport/interchange quantum energy/information and energy vibrational changes using all the quantum Hilbert space. Even when we use the correct Lorentz invariant (LR) form of the stationary wave equation, $\hat{E}_{LR}\cdot\Psi_{LR} = \hat{H}_{LR}\cdot\Psi_{LR}$, the construction rules for Ψ_{LR} will maintain antisymmetric and multiconfigurational, entanglement and superposition of all possible states. The complete quantum wavefunction for multiple interacting fermions will always be $\Psi_{LR}(\text{anti-symmetric \& full CI}) = \sum_j c_j\left(1\big/\sqrt{(n)}\psi_j(\mathrm{LR})\right)$, and the superposition c_j coefficients, expand the wavefunctions to any place at the fundamental level. The virtual probability of finding electrons and their energy, mass, charge and spin far from their confining potential (in a remote orbital) is very low, but it is not absolutely zero, where the influential available energy Hilbert space expands to infinity. Now, please take this conjecture with caution, if we add the hypothesis that the remote multiconfigurational energy relevant expansion may be related with the quantum vacuum. According to our hypothesis from quantum chemistry, the superposition causes the quantum vacuum to not be empty, *i.e.*, it has a Hilbert structure, and it does not have an absolute zero mass, charge and energy (because of the virtual participation of all the states available for electrons in the superposition). Imagine virtual electrons like flying fishes swimming in their confined ocean, but sometimes they jump briefly to the air to escape, before always returning superluminally to their waters; of course, we cannot directly detect these virtual flights without significantly modifying the quantum state.

A deeper quantum understanding of solid catalysts, unified with any branch of catalysis and with advanced materials science.[1,2] Looking at the (non-weakly) correlated materials, *e.g.* those studied by Professor Zunger,[188,193–199] authors describe a rich physics for compositions such as in many catalysts. Fig. 18 shows, from a chemistry wavefunction point of view, how the main quantum potentials divide catalysts/materials into two big groups. (right) WCCS with closed-shell orbital configurations, meaning maximum Coulomb interactions and minimum QSEI and S.O.C., or in other words maximum covalence for that composition (orbital filling). (left) The opposite QCC, mainly with open-shell orbital configurations or QCC-OS, diminishing the role of Coulomb interactions (reducing covalence) increasing the stabilizing quantum correlations, QSEI and sometimes QEXI, or other spin dependent potentials (S.O.C., CISS, EMF). Non-linear behaviours in chemistry/catalysis, with changes in composition or oxidation state, start because it is not possible to maximize the stabilizing Coulomb attractions and quantum correlations at the same time.[1,2] The classical and non-classical potentials compete and interact. *E.g.*, as shown in Fig. 6 for the QCC-OS $La_{1-x}Ca_xMnO_3$ as x varies at the frontier between different phases, different ground-state spin–orbital orderings appear, and we should expect non-linear catalytic behaviours,[49,50] despite the fact that their compositions/structures are very similar. Intermediate oxidation states appear at the same time as holes and electrons in the more antibonding orbitals, avoiding the more extreme AFM insulating phases, and indicating more active catalysts.

All potentials are always present and influential, as shown in eqn (1), where essentially all compositions are quantum catalysts but some more than others. In Fig. 18, the round corners qualitatively have the compositions that their properties primarily depend on the optimization of one potential. Most materials are in the connection lines with multiple differentiating potentials. All the optimum catalysts for OER, ORR, batteries, industrial Fischer–Tropsch and ammonia synthesis, most high-entropy catalysts, V, Cr, Mn, Fe, Co, Ni, Cu and some Ru-based catalysts, and many enzymes are around the centre of the rhomboid, slightly displaced towards the QSEI ←→ QEXI side of the QCC-OS. Vanadium oxides are another great QCC-OS family,[200,201] with vast catalytic interest. Optimum photocatalysts, due to the need for a band gap, have low QEXI in the ground state and appear in the QSEI ←→ S.O.C. connection.[202–205] Natural materials (metalloproteins) frequently appear in the QSEI(CISS) ←→ QEXI, or in the centre-top associated with chiral helical wavefunctions,[8,145,206] but still untreatable by *ab initio* computational chemistry. If S.O.C. in 4d and 5d transition metals generates magnetic insulators,[207] then S.O.C. does not seem optimum for catalysis. In contrast, spin–orbit interactions and interlayer ferromagnetic coupling in metallic conductors, *e.g.* Co/Pt structures,[208,209] are of high interest.[210]

In the WCCS area, on the Coulomb ←→ QEXI connection, there are also excellent catalysts based on closed-shell orbital configurations, *e.g.* Ti, Cu, Zn, Mo, Rh, Pd, Ag and Cd. If the S.O.C. is not strong enough to be significant in a composition/reaction with closed-shell 5d-metals, Rh, Pd, Ir, Pt and Au, then their behaviour will also be like WCCS. There are great WCCS catalysts, *e.g.* silver, industrially used in multiple selective oxidation reactions. In the case of metallic WCCS, DFT-A, parametric and linear simplifications or single thermodynamic catalytic descriptors seem to be more reasonable approximations. The importance of Fig. 18 is that we can see all compositions as part of the same physics, a universal view that is necessary in solid catalysis. Fig. 18 also helps to see the connection, and another point of view, to quantum materials science, *e.g.* heavy fermion materials are a specific type of intermetallic compound containing elements with 4f or 5f electrons, increasing QSEI in unfilled electron bands.[211,212] Inside the green triangle, the heavy fermion metallic systems reside, in which localized magnetic moments and itinerant electronic conduction coexist, where the potential interesting catalysts in this family include $CeCu_{6-x}Au_x$, $UCu_{5-x}Pd_x$, $YbRh_2Si_2$, $Ce_3Pd_{20}Si_6$, $Cr_{1-x}V_x$, and UPt_3. Topological materials with superior carrier mobility are also interesting catalysts in the centre of the QCC.[192,213–217]

Gradually, more researchers start to follow non-weakly correlated electrons in catalysis, as explained in 2021,[2] realizing the more quantum correlated character of many active catalysts.[218] Considering that right now we are trying to outline generalized statements, in the future there will be particular cases.

Overall, catalysis is a quantum phenomenon

According to the literature, that are many QCC and QCC-OS, making it impossible to mention them all, with some examples in ref. 219–223, or chiral catalysts for the spin-dependent electron transfer in the OER.[216,224–226] Also, ferromagnetic catalysts in this single domain exhibit similar water oxidation performances in the absence of an external magnetic field their multi-domain counterparts under magnetization.[35] A unified theoretical perspective in catalysis, from single atoms to solid materials, comes from the proper construction of $\hat{H}\cdot\Psi$. Most of the optimum catalysts create lower activation barriers (overpotentials) by optimizing quantum correlations, and the nature of the rate-limiting step (r.l.s) can be different between compositions, as follows:

(r.l.s.1) Chemisorption energy when the intermediates bind too strongly to the active sites.

(r.l.s.2) Chemisorbed transition state for the rupture/formation of bonds in reaction intermediates.

(r.l.s.3) In electro- and photo-catalysis and batteries, an extra-overpotential for charge-spin conduction, *e.g.* to access the conduction band in insulators.

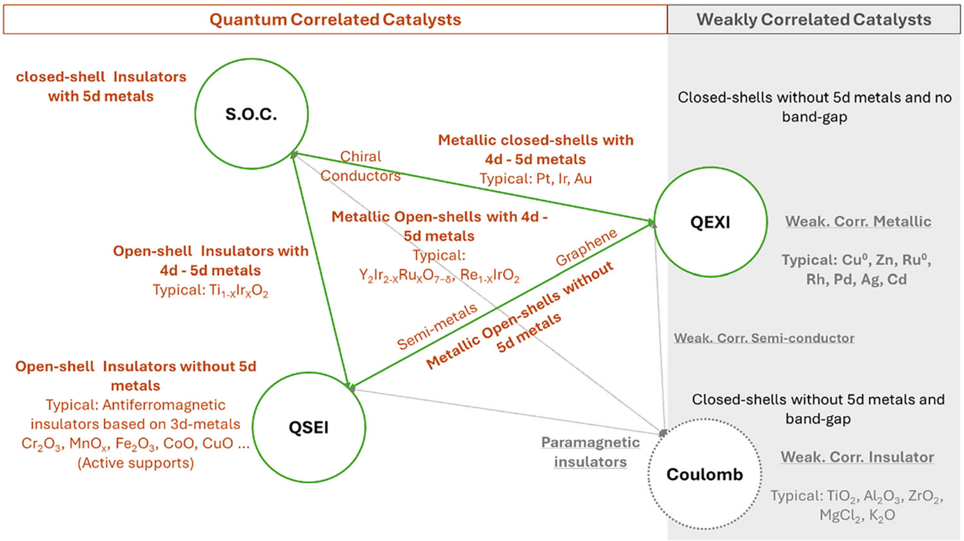

Fig. 18 The main quantum potentials divide catalysts/materials into two big groups; (right) WCCS with closed-shell orbital configurations and minimum QSEI and S.O.C.; (left) just the opposite QCC, mainly QCC-OS. All the potentials compete and interact. In the round corners there are the materials which differentiated properties due to the key significance of one potential, and in the connection lines materials with multiple distinctive influential potentials.

Between catalysts, the reaction mechanisms and rate-limiting steps (r.l.s.) do not need to be the same, they can be more than one competing, *e.g.* the Mars–van Krevelen (MvK)[117,227,228] and Langmuir–Hinshelwood mechanisms.[229] The energetics of the r.l.s. appear in the transition state theory (T.S.T.) with the Arrhenius expression, rate $\propto A\cdot e^{-E_a/k_B\cdot T}$. The value of the activation barrier depends on all competing quantum potentials[1] through of activation energy $E_a = \Delta H^\# - T\Delta S^\#$, as follows:

$$\begin{aligned}\Delta H^\# \sim \Delta E^\#_{\mathrm{e-n+}} \approx \frac{1}{2}\cdot\big[&\Delta\mathrm{CORE}^\#_{\mathrm{e-e-}} + \Delta\mathrm{COAT}^\#_{\mathrm{n+e-}} \\ &+ \Delta\mathrm{QSEI}^\#_{\mathrm{e-}} + \Delta\mathrm{QEXI}^\#_{\mathrm{e-}} + \Delta\mathrm{SOC}^\#_{\mathrm{e-}}\big] \\ &+ \Delta\mathrm{CORE}^\#_{\mathrm{n+n+}}.\end{aligned} \tag{1}$$

Eqn (1) reveals the almost complete quantum chemistry, an energy decomposition analysis where experiments cannot reach.[1] In future, we will need to understand catalysts by decomposing $\Delta E^\#_{\mathrm{e-n+}}$ for the r.l.s., which is a direct approach. Frequently, in solid catalysts, we presently do not know what specific interactions make certain compositions outstanding, namely the explicit key potentials that lower the r.l.s. At the practical level, we can imagine future attempts of improved volcano plots with the experimental activity *versus* the true activation energy of the r.l.s. Because the scientific literature is abundant presently, our advice when reading computational studies in solid (electro-) catalysis is to look for the actual calculation of the transition states and proper discussion of the characteristics of the r.l.s.

The degrees of freedom in materials/catalysts, charge, spin, orbital and lattice, are interconnected *via* the potentials in eqn (1). Phonons and electron–phonon scattering are media that materials use to exchange thermal energy with the environment *via* $\mathrm{CORE}^\#_{\mathrm{n+n+}}$ (nuclear repulsions) coupled first with $\mathrm{COAT}^\#_{\mathrm{n+e+}}$, acting as a link with the purely electronic $[\mathrm{CORE}^\#_{\mathrm{e-e-}} + \mathrm{QSEI}^\#_{\mathrm{e-}} + \mathrm{QEXI}^\#_{\mathrm{e-}} + \mathrm{SOC}^\#_{\mathrm{e-}}]$, which are crucial interconnections in catalysis.[8,230] Also, equivalently, magnons and spin-magnon scattering, a collective excitation of the spin structure of a crystal lattice, transmit energy. The understanding of QCC-OS compositions, the most frequent type of quantum catalysts, needs experimental research including magnetic characterization of their catalysts/surfaces. In the future, it will be beneficial to have some magnetic atomic force microscopy images of the active sites, neutron-scattering studies, regular magnetometer characterization and Mössbauer spectroscopy. Here, some reflection about *operando* characterization in catalysis is presented; these techniques provide real-time insights into the structure, composition, and behaviour of catalysts during chemical reactions. However, it is necessary to remember that observing catalysts and the interchange of energy in their active state will alter the quantum correlations (entanglement and superposition). For instance, due to the strong interference from electron transmission microscopy, the non-local quantum correlations of the transition states on QCC will be severely altered.

Enriching concepts

According to the equations in quantum chemistry, eqn (1), catalysts/materials possess considerable intrinsic complexity and inter-connected degrees of freedom. In physics and materials science, non-weakly correlated compositions (QCC) are a vibrant field, with the need for theoretical/computational updates.[72,189,231,232] Reactivity patterns in organometallic and bioinorganic chemistry often critically depend on the spin states, which have been acknowledged for decades.[8,233–236] Enzymes and homogeneous catalysis are modulated by chirality and QSEI.[237] In batteries, Goodenough demonstrated the key role of spin–orbital orderings;[54] Naaman discovered the CISS effect;[30] spintronics use spin currents in technology;[238] and superconducting materials liberate vibrationally strongly correlated electrons.[239–241] We must also include all the grey/overlapping zones between strongly and weakly correlated electrons, which include insulators and electronic materials with more unusual electronic and magnetic properties, such as metal-insulator transitions, heavy fermion behaviour, half-metallicity (semi-metals), topological materials, and spin-charge separation.[232,241–243] In the future, both fields of quantum catalysts and quantum materials will benefit from studies using extensions of the non-local Hartree–Fock scheme, focusing on wavefunction methods. However, none of this is new, *e.g.* in 1955, Lowdin was already working on that as part of the quantum theory of many-particle systems.[244]

The formal definition of covalence is "in chemistry, covalence refers to the type of chemical bond formed when two atoms share one or more pairs of electrons. This shared bonding allows each atom to achieve a more stable electron configuration, typically resembling that of the nearest noble gas." Covalence is a partial qualitative description for bonds taking closed shell configurations as a reference. If we quantify covalence as the amount of spin-electron density shared between two atoms; quantum correlations, chirality, spin-/magneto-enhanced catalysis decrease covalence. The main types of chemical bonds are as follows: (1) ionic bonds: formed when one atom donates an electron to another, typically between a metal and a nonmetal. (2) Covalent bonds: occur when two atoms share electron pairs. (3) Metallic bonds: found in metals, where electrons are shared among a lattice of atoms, generating properties such as conductivity and malleability. (4) Hydrogen bonds: a type of weak bond that occurs between a hydrogen atom and an electronegative atom. Maybe it makes sense to consider a sub-category (5): QSEI open shell bonds with unpaired electrons more localized on the atoms, not between. For example, we can live on earth because of the stabilization of $^3O_2$ molecules by an additional QSEI ferromagnetic non-covalent bond, which does not belong to any of the main 1–4 categories.

Main contributors to the overpotentials in catalytic electron transfer

Analysing the theory of electron transfer, also considering electrocatalysis, one of my preferred scientists, Prof. Fletcher[245–247] helped to focus on some parts in (2010) page

708:[247] "then the system energy may be calculated uniquely for every possible position of the atomic nuclei (assumed motionless). This then allows one to construct a plot of total energy as a function of all the nuclear coordinates, yielding a multidimensional "potential energy surface" for the system under study. The contributing factors to this potential energy surface are: (1) the Coulomb attractions between the electrons and the nuclei. (2) The Coulomb repulsions between the electrons. (3) The Coulomb repulsions between the nuclei. (4) The kinetic energy of the electrons. It is immediately clear that this is not a true potential energy at all because it contains a mixture of potential energy and kinetic energy terms." Firstly, quantum correlations are missing, which is not a surprise, given that before 2021, in general nobody was talking about correlated electrons in electrocatalysis or in electron transfer. Additionally, given that we can omit the kinetic energy with the Virial theorem, then we can derive a true complete potential energy, eqn (1), and decompose the chemisorption and activation energies, as shown in Fig. 19, which is also applicable to electron transfer.

Electrocatalytic steps speed up when the reactants chemisorb on the active sites, significantly altering their electronic structure. Representations where the interaction with the active sites are assumed to be weak, such as in Marcus-type models,[248] are not the main factor to distinguish most catalysts. When species are strongly chemisorbed, as is in the most cases of electrocatalysis or enzymatic reactions, all the quantum factors in bond formation and electronic reconfiguration are more important and outside the classical Marcus theory. In other words, simple Hamiltonian Marcus-type models are severely incomplete in electrocatalysis, where all the interphases are influenced by quantum correlations, which is the future perspective to have a true general theory. This is especially true to develop catalysts beyond platinum group metals. Reactions are accelerated by the significant electronic interaction of the reactants with the active sites, and familiar concepts in the Marcus inner and outer sphere electron transfer are background common energy factors, but no longer of prime importance to distinguish electrocatalysts. Of course, the nearby ions in the media, in the immediate external coordination sphere, interact and stabilize the chemisorbed and transition states;[249] and there is a Marcus solvent reorganization energy. However, this interfacial double layer structure is external to the electron transfer (ET), where electrocatalytic ET occurs between the chemisorbed reactants and the conduction band/orbitals of the active sites inside the catalytic interphase (Fig. 11).[250] Fig. 14 and 19 show that mainly the direct analysis of the overpotentials at the internal interphase, where electron transfer couples with transition states, will allow to completely understand/differentiate electrocatalysts. Marcus theory helps to describe how reorganization energy and solvent dynamics influence electron transfer rates, and this relevant background effects in electrocatalysis also in future need to be analysed under the influence on quantum correlations. However, the key factors to distinguish most electrocatalysts go beyond the Marcus models, and in any case, non-weekly chemisorbed catalytic interphases depend on the potentials described in eqn (1).

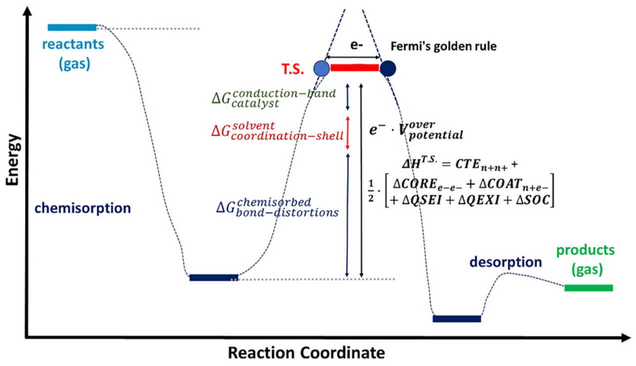

Fig. 19 Decomposition of the activation barriers *versus* the contribution of different interphases/resistances and different quantum potentials to free energies.

Challenges in theoretical/computational solid catalysis

The latest results have proven that solid catalysts need a more complete fundamental approach to align with homogeneous and enzymatic catalysis, besides advanced materials physics. Our perspective for the future cannot be brighter, unification of catalysis is here. Quantum potentials are the electronic fundaments of catalysis/chemistry/nature/physics. However, the challenge in the necessarily more complex studies will be in maintaining some conceptual and tangible rules, which will help to find better catalysts and understand them. This exercise started in 2018 with spintro-catalysis rules in open-shell oxides for electron transfer reactions,[42] where the experimental success in oxygen electrocatalysis is outstanding; in OER/ORR, all the optimum catalysts[36,80,133,251,252] follow those rules, being the most successful proven guidelines, also including solid oxide cells[253] and polymers.[254] We can extend these qualitative construction rules to any QCC-OS composition in any reaction, as follows:

Quantum rule (1) open-shell orbital structures allow QSEI to increase their relative relevance *versus* the other potentials and relocate electrons, diminishing bonding interactions, and at the same time stabilizing the higher radical character of the transition states. This first rule optimizes the use of abundant open-shell elements. Practical indications: perform magnetic characterization of the catalyst; how precise is its electronic configuration? dope a WCCS metal with open-shell atoms/defects to create a QCC-OS (semi-) metal. Try to get spin-polarized photocatalysts.[255]

Quantum rule (2) ferromagnetic bonds, in the active states, with itinerant spin-electrons allow inter- and intra-atomic QSEI, moreover enhancing QEXI in structures more conductive, and if needed spin selective. The underlying principle of this rule is the population in the FM bonds of QCC-OS of more antibonding orbitals with migrant electrons (majority spin), and more bonding orbitals with mobile holes (minority spin), thermodynamic and kinetic effects. For example, the asymmetry in the mobility of charge carriers seems to differentiate OER from ORR catalysts. Consider that insulators show the opposite effect due to anti-ferromagnetic spin–orbital orderings; unless a bandgap is needed for photocatalysis, Mott and charge-transfer insulators (AFM insulators) typically do not enhance reactions because of the localization of electron pairs due to inter-atomic Coulomb attractions. Practical indications: Does your catalyst have a band gap and how big? Explain the specific spin–orbital ordering; look for intermediate, mixed, oxidation states, and partial orbital occupations that favour (double exchange) the mobility of charge-spin carriers.[256] Besides AFM type-G, all the open-shell extended spin–orbital orderings, ferro-, ferri- and AFM-type -A, -C, -E have ferromagnetic directions and spin-polarized bonds. Active surfaces/edges may be magnetic conductors, but the bulk is not, or in other words, is your quantum catalyst a topological insulator (see Fig. 20B)?

Quantum rule (3) the addition of 4f–4d–5d metals to previous rules allows the constructive introduction of non-bonding and stabilizing S.O.C. and/or additional QSEI. Specially 4d and 5d orbitals can help improve electronic conduction, and thus also QEXI to moderate the chemisorption energies and lower transition states, while adding stability. The danger of strong S.O.C in bigger orbitals is the destruction of the ferromagnetic itinerancy, *i.e.*, the loss of the energetic degeneracy in the active orbitals, and thus the appearance of less active insulating phases. Practical indications: the presence of 4f–4d–5d metals enhances a positive magnetic or conductive and catalytic response.[257–259] Does the introduction of Kondo-type impurities[260,261] improve the activity? Does your catalyst have a chiral space-group inducing S.O.C.?

In relation with the previous rules, if possible, perform specific characterization experiments, magnetometry, Mössbauer spectroscopy, bulk and surface conductivity, magnetic atomic force microscopy, spin-polarized scanning tunnelling microscopy or neutron scattering.[262] At the computational level, always look for the most stable spin–orbital orderings and try to reproduce the experimental results to see if the method is accurate. The fastest option is typically DFT-A plus *U* corrections, but you must calibrate the *U* to check if you obtained the correct magnetic ordering and still remember the limitation of this method. Ideally, start a transition towards post-H.F. methods, which include 100% hybrid DFT-A as the most feasible alternative. Also, be aware that the surface spin–orbital ordering may be different in the bulk and on diverse surfaces. In catalysis, always include the full calculation of transition states, detailing the rate-limiting step, otherwise you cannot talk about activation barriers or overpotentials.

Quantum rule (4) quantum correlations are short- and long-range cooperative interactions, adding a ferromagnetic subsurface phase (permanent magnet), maximum 3–4 nm below, can

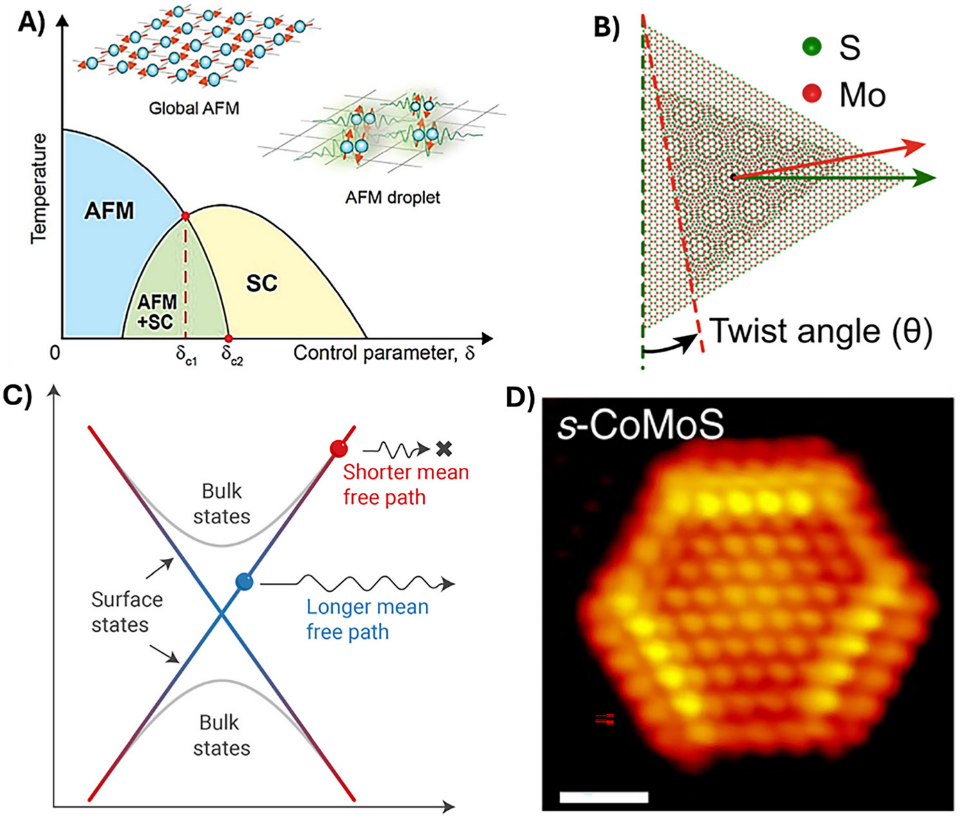

Fig. 20 (A) Starting from the left, in hole-doped cuprates, a small number of carriers suppresses antiferromagnetism and induces superconductivity, adapted from ref. 280 and 281. (B) Schematic atomic configuration of twisted bilayer MoS_2 with a twist angle owing to the relative lattice alignment between two layers.[282] (C) Topological insulators are a unique class of materials that act as insulators in their interior but have conductive surfaces or edges,[283] as in (D) MoS_2 enhanced with open shell Co in hydrodesulphurization catalysts.[284] Open access articles distributed under a Creative Commons Attribution 4.0 International License.

also significantly enhance the activity. Not to add more rules, lets include here the role of external magnetic fields or the CISS effect as spin-polarizers of the active sites. Practical indications: deposit some nanolayers of catalysts on top of a hard magnet[263–265] or add CISS effects. In superparamagnetic nano-catalysts, the EMF will barely have any effect, but for ferro-(ferri-)magnetic catalysts with multiple domains, the EMF (CISS) helps to reach a magnetized state, with aligned magnetic domains, which are more active and stable.[36]

Quantum rule (5) the classical Coulomb potentials are always the leading interactions and can also drive optimum WCCS catalysts, especially in metallic phases with enhanced QEXI. Not everything needs spin-polarization, or if the bonding interactions are already too weak, a reduction of quantum correlations in favour of Coulomb attractions will help. Practical indications: doping with open-shell metals can worsen the activity, even on the subsurface. Sometimes the addition of close-shell atoms augments the bonding nature of open-shell phases, enhancing the activity of catalysts.[58] Doping a too non-bonding open-shell catalyst with closed-shell elements, defects, which act as electron donors, but still maintain spin polarization.

There is a lot to learn and do, and we need new voices to individually quantify the quantum electronic interactions in relation to the activity and selectivity of catalysts, besides decomposing all the factors in the true r.l.s., T.S. mostly, as shown in Fig. 19. Our aims have gradually moved forward from our initial goals, until the development of a general framework to understand and compare any composition, or *ab initio* calculation; the future of catalysis, as a united field, is in quantum correlations.

Quantum correlations add new dimensionalities to catalysis, starting from the competition and interaction between them.[1,2,14,42] For example, it is good to consider the cooperative behaviour of the electrons in the magnetic active centres with partial orbital open-shell occupations, which is consistent with the few works by Goodenough on electrocatalysis.[67–71] The increasing appearance of modern experiments evidencing the importance of double-exchange mechanisms in catalysis has been observed.[266–268] We are at the end of the beginning in solid catalysis, in my opinion a postmodern regeneration has started. The explanation of the interplay of quantum correlations in catalysis, especially in solid catalysts, is growing as the most influential successful theoretical advance. About half of the articles in catalysis include open-shell orbital fillings, unpaired electron typically originating from 3d and 4d metals, or in carbon nanostructures,[5–7,269–272] in challenging chiral-induced magnetic materials;[30,31,145–151,155,273–277] however, only a few works properly recognize the role of QSEI (symmetry entanglement) and its connection with QEXI (superposition of configurations); QCC-OS are the Rosetta Stone of abundant catalysts.

A quick wavefunction (chemistry) view to quantum materials.[278,279] In any composition, the quantum fundamentals of entanglement and superposition produce the energetic electronic responses QSEI and QEXI, which correct the classical Coulomb potentials. Fig. 4, 6, 9, 10, 12 and 13 include examples of quantum materials used in catalysis in most references here, indicating that Fig. 18 is also relevant in the quantum physics of any composition. $\text{COAT}_{\text{N+e}-}$ connects the lattice degree of freedom with the electronic potentials, charge $\text{CORE}_{\text{e}-\text{e}-}$, spin QSEI + SOC and additional states in QEXI. As part of SOC, we can include chiral wavefunctions. At the microscopic level, behind the four observed degrees of freedom, charge, spin, orbit and lattice, which become particularly intertwined in quantum materials, moving the electronic strings, such as in catalysis, with the quantum potentials in eqn (1) establishing a particular orbital state *versus* others, locally or globally. This is not an assumption or hypothesis, it is a reality to be developed further, and soon we can indicate what it looks like. This field will also benefit the use of a more chemical terminology, slightly different to the typical computational studies in the field of quantum many-body physics, to explore the same emergent properties of many interacting quantum particles.

High-temperature superconductors

Antiferromagnetic Mott insulators appear because intra-atomic QSEI stabilize on-site open-shell orbital occupations; simultaneously, COAT prefers to open a bandgap, facilitating inter-atomic orbital overlapping, and thus antiferromagnetic paring.[1,2] Inter-atomic electron repulsions increase and the bond distances elongate, which are signatures of Jahn–Teller distortions and global AFM orbital order where electron pairs are localized and trapped,[57] as shown in Fig. 20A. In hole-doped cuprates, a controlled number of orbital vacancies creates carriers that can destabilize the antiferromagnetic inter-atomic blockage of electron pairs and induce superconductivity,[280,281] and a challenge is to relate this mechanism with the vibrational motion of the zero-point energy. The removal of electrons in AFM insulators means a relative loss in the relevance of inter-atomic COAT, holes shorten some bonds, and there are available empty orbitals (holes near the valence band). In some cases, as shown in Fig. 20A,[285] it seems that the loss in COAT plus gain in QEXI due to the presence of holes allows phonons to couple the structural distortions with the cooperative movement of electron pairs to longer bonds or holes to shorter bonds. Already at 0 K, the zero-point energy vibrations and increasing QEXI create a superposition of equally possible configurations in the ground state, where electron-pairs swap sites with holes as coherently, frictionless dynamic paired, or partially paired charge carriers.

Typically, with the excess doping of holes in an AFM insulator, at some point the number of empty orbitals allow inter-atomic QSEI to increase *versus* COAT, shifting to directional extended ferromagnetic orbital orderings. In ceramics (oxides, sulphides, *etc.*), the typical examples are associated with the double exchange mechanims.[54] Phonons also relax, losing the Jahn–Teller elongations, and the geometrical symmetry of the system recuperates with more degenerate orbitals (electronic states) and more homogeneous vibronic coupling; another point of view is to understand why typically superconductivity (SC) and ferromagnetism (FM) are mutually antagonistic collective phenomena in solids.[286] It makes sense to plan quantum calculations including the electronic response in the always present ZPE vibrations, and also in catalysis. There is also an energy side, where it can be imagined that the COAT reduces its value in compositions, maybe in the presence of holes, and for the electrons at the Fermi level, COAT + CORE + QSEI ~ 0. Electrons seem to be a type of a simulated free space, but they are stabilized by the ZPE vibrations and QEXI.

Topological materials

Topological insulators[287,288] are a class of materials that have conductive surfaces or edges but in their interior are insulators. A three-dimensional (3D) topological insulator supports novel spin-polarized Dirac fermions§§ on its surface, as shown in Fig. 20C. In two-dimensional topological insulators, this effect results in edge states, where electrons with opposite spins move in opposite directions, creating a spin current. Inside the bulk, all the bonds are more saturated, and the orbitals maximize the stabilized overlapping by maximizing 3D COAT, resulting in small bandgaps. On the surface or edges, atoms are less coordinated, and some orbitals do not have neighbouring atoms to ambush electron pairs with inter-atomic COAT. The logical alternative is to further exploit other potentials looking for stabilization, including QSEI, QEXI and spin–orbit couplings, what results in conductivity, and also sometimes in unpaired electrons. From our perspective, topological insulators are a hybrid, having an insulator as their bulk and a QCC-OS conductor on their surface-edges.

Topological materials are indeed interesting catalysts,[213,215,289,290] for example, the outstanding MoS_2 hydrodesulfurization quantum catalysts, as shown in Fig. 20D, where bulk MoS_2 is a semiconductor, but its catalytically active edges are metallic/magnetic.[87,284,291] MoS_2-based compositions are highly important catalysts, the activity of which still needs to be clarified based on eqn (1). Topological insulators as catalysts are magnetic Schottky junctions given that they combine spintronics and semiconductor physics,[292] enabling spin-polarized charge transport. Topological materials have been studied for electrocatalysis, particularly in CO_2 reduction[293–295] and hydrogen evolution reactions (HER),[296–303] and QSEI are the key factor.[304,305] $Cu_2C_2N_4$ is another 2D topological quantum catalyst that exhibits nodal line states, making it highly efficient for HER.[306] Sb_2Te_3 is a topological insulator that has shown promise in photo-electrocatalysis, leveraging its surface states for improved charge transfer. Transition metal dichalcogenides (TMDs): some TMDs, such as $MoTe_2$, exhibit topological properties and have been investigated for water splitting and oxygen reduction reactions, with some more examples.[307,308] Topological semimetals are gaining attention in catalysis as QCC-OS with electronic properties, allowing efficient charge-spin transport and efficient robust surface states.[264,299]

Moiré superlattices

In twistronics in 2D materials, the angle (twist) between layers of two-dimensional materials can change their electrical properties. For instance, layer constructions, typically involving graphene, have been shown to exhibit superconductivity, insulation and ferromagnetism.[309–314] The tuneable source of strong-correlation physics is most likely related to the mechanical (twist) control of the overlapping of orbitals, as shown in Fig. 20B, driving the observed motorized regulator of the local dominance of the different quantum potentials in eqn (1). Experimenting with strong correlations and interlayer coupling works to obtain advanced catalysts, as observed recently in outstanding works.[37,315] The competition between non-classical potentials and lattice responses (in this case mechanically controlled) allows the strength of the electron–electron interactions to be locally varied.

3. Conclusions

The wavefunction is the fundamental concept in quantum mechanics and materials; it encapsulates all the available information about a quantum system, and it is still both central and enigmatic to explain non-classical phenomena such as superposition, where electrons exist in multiple states at once, and entanglement, where electrons remain connected even when separated by long distances. The understanding of the interplay between classical and non-classical quantum potentials in atomic structures is already a considerable advancement in the comprehension of quantum catalysts/materials. Although we are just starting, experiments prove that this path is needed in the field of solid catalysis, which is a challenging, critical and valiant perspective forward. According to the already abundant rapidly increasing literature, the following points can be summarized:

In catalysis, the energetic responses of quantum entanglement and superposition of states are in the QSEI and QEXI. Many catalysts are quantum materials and *vice versa*. Electrons carry charge and spin. Quantum correlations are always relevant in catalysis. Overall, catalysis is a quantum phenomenon. Nature exploits quantum correlations in enzymes. Stabilizing quantum correlations compete with Coulomb attractions. Quantum spin exchange interactions (QSEI) are more relevant in catalysts with unpaired electrons (open shells). Catalytic steps involving reactants with unpaired electrons, such as $^3O_2$, ^2NO molecules, transition states, and radical intermediates cannot be explained without QSEI. Ferromagnetic bonds stabilized by QSEI and quantum excitation interactions (QEXI) allow spin selection and transport in catalysts. Only antiferromagnetic (AFM) type-G spin–orbital orderings, in open-shells, do not have any direction with extended ferromagnetic bonds. Many catalysts do not follow the common Bell–Evans–Polanyi principle in their reaction steps. The activation barriers and overpotentials can only be accurately estimated by properly calculating the transition states. Quantum correlations reduce the covalent character of bonds. Transition states have at least higher radical character than one of the reactants. Abundant catalysts have (non-weakly or strongly) quantum correlated electrons. Mean field approximations are more imprecise for non-weekly quantum correlated catalysts. In (non-weakly)

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§§ Electrons behave as massless (Dirac) fermions, leading to high conductivity and unusual quantum Hall effects.

quantum-correlated catalysts, the behaviour of their electrons, or spinons, cannot be described effectively in terms of non-interacting entities. Local and semi-local density functional theory approximations (DFT-A) within the Kohn–Sham scheme are not the fundamental basis of catalysis. Spin–orbital orderings are very important in catalysis. AFM insulators, especially type-G, show typically higher activation barriers. Microscopic and macroscopic spin–orbit and domain magnetic ordering are important in catalysis. QEXI are essential to place the energy of the conduction band. QSEI and QEXI can transmit over long distances. Electro- and photo-catalysts use the conduction band for electron transfer. Electrocatalysts cannot be completely understood with thermodynamic descriptors, such as the chemisorption of some intermediates. It is only possible to comprehend oxygen electrochemistry by explaining the spin-dependent chemisorption of the triplet state, $^3O_2$ and activation of the O$\cdots$O spin-polarized bond. All optimum catalysts for the oxygen evolution reaction (OER) have ferromagnetic bonds due to inter-atomic QSEI in the spin–orbital orderings of the ground states of ferro-, ferri- and many antiferromagnetic conductors. Consider any study in computational/theoretical $^3O_2$ electrocatalysis that does not explicitly explain the role of QSEI severely incomplete or incorrect. Consider any computational study including catalysts with unpaired electrons (typical of V, Cr, Mn, Fe, Co, Ni, Ru and others depending on their oxidation state and the magnetic environment) that does not explain the role of QSEI in the correct open-shell spin–orbital orderings severely incomplete or incorrect. *Ab initio* studies of reactions are only complete after resolving the whole reaction mechanism, including all transition states; or at least they should completely treat the rate-limiting step (r.l.s). Mott insulators are not correctly described by the band theories of solids due to their strong electron–electron interactions. Quantum potentials interact and compete with each other. Coulomb attractions allow the electronic quantum potentials to couple with structural distortions and phonons. Many enzymes are non-weakly quantum correlated catalysts. Quantum correlations explain non-linear energetic behaviours in catalysis, and thus parametric and linear relationships are not universal. The double-exchange spin transport mechanism, which may arise between ions in different oxidation states, is very important in catalysis. Double exchange is widely used by enzymes. Spin orbit couplings, including the CISS effect (chiral wavefunctions), are important in catalysis. External magnetic fields coupled with QSEI can enhance catalysts with several magnetic domains. Spin-selective channels enable fast cathodic kinetics of Li–O_2 batteries. Magnetic supports, such as $Fe_xO_yH_z$, trigger spin polarization, transport, and selectivity effects on the active sites. Perform magnetic characterization of your catalysts and explain the orbital filling, open (unpaired) or closed (paired) shells (valence electrons). Structural descriptors are largely qualitative activity indicators, and only acceptable for restricted families of compositions. Oversimplifications do not allow the understanding of advanced catalysts. The unification of catalysis as a field is possible by differentiating the role of all quantum potentials. Quantum potentials are responsible for the charge, spin, orbit and lattice interplay in the exceptional properties of quantum materials.

Data availability

No primary research results, software, or code have been included in this review. Additionally, no new data were generated or analysed as part of this work.

Conflicts of interest

There are no conflicts to declare.

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