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Moltved, Klaus August; Kepp, Kasper Planeta

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O₂-binding to all 3d-, 4d, and 5d-transition metals from coupled-cluster theory

Klaus A. Moltved and Professor Dr. Kasper P. Kepp*

Technical University of Denmark, DTU Chemistry, Building 206, 2800 Kgs. Lyngby, DK – Denmark.

* Corresponding author: Phone: +045 45 25 24 09. E-mail: kpj@kemi.dtu.dk

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Abstract

Understanding how transition metals bind and activate dioxygen (O_2) is limited by experimental and theoretical uncertainties, making accurate quantum mechanical descriptors of interest. Here we report coupled-cluster CCSD(T) energies with large basis sets and vibrational and relativistic corrections for 160 3d-, 4d-, and 5d-metal- O_2 systems. We define four reaction energies (120 in total for the 30 metals) that quantify O-O activation and reveal linear relationships between metal-oxygen and O-O binding energies. The CCSD(T) data can be combined with thermochemical cycles to estimate chemisorption and physisorption energies for each metal from metal oxide embedding energies, in good correlation with atomization enthalpies ($R^2 = 0.75$). Spin-geometry variations can break the linearities, of interest to circumventing the Sabatier principle. Pt, Pd, Co, and Fe form a distinct group with weakest O_2 -binding. R^2 up to 0.84 between surface adsorption energies and our energies for MO_2 systems indicate relevance also to real catalytic systems.

Keywords: O_2 -binding; quantum chemistry; back-bonding; transition metals; catalysis

Introduction

The transition metals of the 3d-, 4d-, and 5d-block, with close-lying diffuse d-orbitals and large variations in effective nuclear charge caused by their gradual occupation, provide a rich diversity of cohesive energies, work functions, redox states, electronegativities, and resulting surface and solution reactivity,^[1–5] and thus are central to catalysis.^[6–12] One of the most important aspects of transition metal catalysis is the binding of dioxygen, O₂, this planet's primary atmospheric electron acceptor, and specifically the strength of the metal-oxygen (M-O) bond and O-O bond. Activation of O₂ defines many transition-metal catalyzed oxidation reactions,^[8,13–16] including vital processes catalyzed by copper^[17–19] and iron enzymes.^[20–22] In oxygen reduction reactions (ORR), the O=O double bond (~500 kJ/mol) is activated, enabling O-O bond cleavage and separation of the oxygen atoms for further chemical reaction.^[1,23–25] The ORR at the cathode is the main restricting step for the efficiency of many fuel cells, with platinum being in practice the most active single-metal catalyst.^[14,16,26] The opposite endothermic reaction of water oxidation, specifically the oxygen evolution reaction (OER), where the O-O bond is being formed rather than cleaved as in photosynthesis,^[27] is of major importance to renewable (sun-based) production of high-energy compounds.^[28,29]

The stronger the metal binds, the more the O-O bond tends to be activated, because of d-back-bonding.^[18,30–34] When O₂ binds, two types of metal d-orbitals are involved, d(σ) and d(π) (**Scheme 1**). With the bond along the z-axis, a metal-ligand σ -bond forms with the d(σ) orbitals, i.e. the z^2 and x^2-y^2 orbitals, whereas π -bonding occurs via the d(π) orbitals, i.e. the xy, yz, and zx orbitals.^[35] The stronger O₂ binds to the metal, the shorter the metal-oxygen (M-O) bond, and the more will the d(π) orbitals contribute. Because of their symmetry, the d(π) orbitals contribute (double) bond character to the M-O bond, but antibonding character with respect to the O-O bond, by overlap with π^* . This produces a linear relationship between M-O and O-O bond strengths. The back-donation controls the O-O bond activation, some metals giving peroxo states, others superoxo states, with a spectrum in-between.^[31]

Scheme 1. Simple illustration of back-bonding leading to O-O bond activation for end-on coordinated O₂. The π -(back) bonding is bonding with respect to the metal-oxygen bond but anti-bonding with respect to the O-O bond at the same time, leading to weakening of the O-O bond.

Back-bonding combined with the linear relationship between activation and reaction free energies^[36] is arguably the cause of the Sabatier principle^[37] that too strong binding of the ligand to the catalyst impairs reactivity, because while it aids the breaking of the inter-ligand bond (e.g. O-O), it simultaneously limits the diffusion and release of O atoms, as required for turnover.^[4,38] This compensation of effects may produce a maximal activity along a series of increasing binding strengths^[39,40], i.e. a “volcano curve”,^[4,41,42] and a central challenge of catalysis is therefore to scrutinize and if necessary, circumvent the limitations enforced by this relationship when it prevails.^[42–44] If back-bonding drives these relationships, understanding it in detail should be of major interest.

Transition metal oxygen chemistry suffers from a critical data noise problem, because both experimental and theoretical O₂-binding energies to transition metals are very uncertain. Experimental errors in both molecular and surface M-O bond energies are perhaps ~20 kJ/mol.^[45–48] In comparison, typical oxygen-bonding errors from density functional theory (DFT) are 50 kJ/mol

both for surfaces^[46] and molecular systems.^[47,49] Best performances do not exceed 30 kJ/mol, even for the cleanest and simplest systems where chemical composition and thermodynamic effects are fully controlled.^[47,48,50,51] Unfortunately, cancellation of errors is modest for these energies due to 1) differences in Hartree-Fock (HF) exchange suitable for different systems (10-40 kJ/mol estimated error contribution);^[47,51–55] 2) “vertical” 4d/5d comparisons (e.g. Pd/Pt) impaired by uncertain relativistic effects (0-30 kJ/mol),^[48] and 3) “horizontal” early-late d-block comparisons impaired by the effective nuclear charge effect on DFT errors (up to perhaps 40 kJ/mol).^[47,48,50,51] Random combinations of these errors produce the typical average errors of 50 kJ/mol (0.5 eV) for absolute O₂-binding when using GGA DFT.^[46] The worst comparisons are those between 3d/4d and 5d periods (e.g. Pd vs. Pt) and early-late groups (e.g. Ti vs. Cu).^[47,48] A widely ignored consequence is that distinct metal separations smaller than 0.2 eV (20 kJ/mol), e.g. in volcano plots, should typically be considered insignificant; spin-orbit coupling alone can produce this magnitude of error for some 5d/4d metals, as implied by M-O bond dissociation energies^[47] and further confirmed below.

Experimentally, the problem is not much smaller: Variations in catalyst structure, solvent, thermodynamic effects, the involved elementary steps (such as secondary binding sites) and O₂-binding geometries make experimental systematic O₂-binding energies very scarce. Oxygen electrocatalysis is very complex and involves many steps, involving proton- and electron-transfer, that may differ between different metals.^[56] Already the O₂-chemisorption enthalpies listed by Toyoshima and Somorjai,^[57] which reflect much simpler reactions, are noisy for the single-crystal data, and the polycrystalline data reflect complex compositions that cannot be modeled in any straightforward way. A handful of single-crystal O₂-adsorption enthalpies from single-molecule calorimetry^[45,58] thus largely define the typical data used to guide theoretical work on O₂-binding, but very often direct relations to quantitative experimental data are completely ignored due to the lack of relevant benchmark data.

The benchmark data problem is thus, in our view, the main problem currently limiting theoretical catalysis. Robust descriptors may aid this problem.^[59,60] Large-system DFT descriptors

are not likely to be successful due to the uncertainties described above, including model-dependent errors and issues with chemical composition and sampling of conformations.^[61,62] Instead, we have argued that small systems are required,^[48,63] because 1) they are the minimal catalytic units relevant to single-atom catalysis;^[9,64–68] 2) their data are less noisy and error-prone in terms of solvent, conformation sampling, and chemical composition; 3) they can be studied by high-quality quantum chemistry; 4) they do not suffer the complex and partly inseparable modulations from large-scale catalyst structure, which can be added systematically to enable rational predictive power;^[69] 5) their trend chemistry transfers to large systems because other modulating effects are secondary in magnitude to the local, very strong metal-oxygen interactions that have the similar d-block trends and physical effects in large and small systems.^[55,69]

The present paper reports coupled-cluster CCSD(T) energies of all the 3d-, 4d-, and 5d-transition MO₂ complexes, and reports the bond strengths of the M-O₂ and (M)-O-O bonds to assess trends in O-O bond activation. As far as we know, this is the only complete coupled-cluster study of this kind, although previous *ab initio* and DFT studies of some dioxygen complexes should be noted.^[70–73] The inserted dioxide complexes are important and well-described experimentally and theoretically^[74–77] as they tend to be more stable,^[71] yet the dioxygen complexes studied in this work are more relevant to catalysis.^[30,78,79] We also compared the widely applied density functional, B3LYP,^[80–84] directly against the CCSD(T) energies for these systems indicating both small and large system-dependent differences between the two methods.

Methods

Spin- and geometry optimizations

The Turbomole software, version 7.0,^[85,86] was used for all computations in this work. In total, we geometry optimized and computed the CCSD(T) energy of 160 MO₂ systems covering all 30 3d-, 4d-, and 5d-metals (see Supporting information, **Table S1** for details). Different geometries of all neutral MO₂ systems for all 30 metals (Sc-Zn, Y-Cd, La-Hg) were optimized using the B3LYP^[81–83] functional and the def2-TZVPP^[87] basis, with energy convergence set to 10^{−6} au. Relativistic effects can potentially change metal-ligand bond lengths.^[88] However, effects will only be significant for soft potential energy curves and/or changes in electronic states.^[69] For most systems of interest, including the systems studied here, nonrelativistic hybrid DFT produces excellent geometries: A benchmark of all 4d and 5d metals found mean absolute errors (MAEs) for B3LYP of 0.03 Å or smaller for all M-O Bond except for La-O.^[54] More importantly, geometric errors in M-O bonds do not scale simply with energy errors, and a method good for one purpose may be bad for another. It is the energy treatment that limits accuracy, not the geometry treatment.^[53] Accordingly, while many functionals, including B3LYP, give poor energies for many transition-metal systems,^[47,53,89–94] the present methodology using relativistic CCSD(T) on non-relativistic B3LYP geometries performs excellently, with near-experimental average accuracy of ~20 kJ/mol for the 60 3d-, 4d-, and 5d- MO BDEs.^[48]

To ensure that the correct MO₂ geometry was found, three starting geometries, side-on (η^2 -O₂), bent, and linear end-on (η^1 -O₂) were studied. Spin states and ground state geometries were taken from the literature when available^[74] or, if not known, we computed the spin state and geometry for all relevant spin states for all three geometries and used for analysis only the lowest CCSD(T) energy.

Coupled-cluster energies

The accuracy of CCSD(T) has been questioned for transition metal systems with strong static correlation where the single HF reference is so inappropriate that the coupled-cluster excitations do not correct the HF bias, which favors high-spin^[95,96] and lower bond strengths.^[69,97] This is particularly the case for diffuse metal hydride states^[52] and some metal-metal bonds,^[98] although considerable experimental errors also obscure evaluation.^[99] However, for the bond strengths of most single-metal systems, including M-O bonds^[48,70], CCSD(T) performs very well, similar to the very best-performing functionals, and much better than typically applied functionals such as PBE, RPBE, and B3LYP.^[47,100–102] Multi-state CASPT2 computations^[103] with relevant-sized basis sets (quadruple-zeta or larger) and identical, saturated (as required for fair comparison) active spaces are not feasible for comparing all 30 metals, although subgroups can be studied.^[104,105] The different correlation treatment of the active and inactive electrons aggravates the HF-bias, giving rise to high-spin and bond weakening biases.^[69,106,107] Recent work is tackling these problems^[108] but currently CCSD(T) is the method of choice for complete d-block trends, as desired here.

Assessment is only meaningful when the correct HF references are identified, which is notoriously difficult for these types of systems, with many local-minima electronic configurations being reported in the literature, as discussed previously.^[48,51] Aware of this issue (and the problem that the reference HF of lowest energy may not give the lowest CCSD(T) energy!) we generally use an extensive fully unrestricted search strategy starting from maximum-possible spin states and down-coupling spins via the alpha and beta occupation keywords in Turbomole, to prevent low-spin instabilities. All ground states used in this work were solely chosen based on having the lowest CCSD(T) energy, with no consideration given to the final behavior in the chemical energy trends. The performance of this protocol against experimental M-O BDEs (20 kJ/mol uncertainty^[48]) and the obtained d-block trends largely show that we have succeeded in identifying the relevant ground states in all cases with very few likely exceptions. Single-point energies were computed for all geometries and spin states using CCSD(T) from a converged HF reference state, with a density and energy

convergence threshold of 10^{-7} au. We applied the resolution of identity approximation^[109] to accelerate the computations, which are very cpu-consuming: After geometry optimization and vibration calculation, each of the 160 CCSD(T) energies on a converged HF reference state took typically between 10-40 hours to compute (cpu times; wall times were longer) using modern cpus at the DTU high-performance cluster, because of the large basis sets (e.g. 354 SCF basis functions for MnO_2), with computing times varying several-fold depending on system.

The electronic energies of the present work are summarized in **Table S1** and were used in connection with the MO and M energies computed by the same method and basis set in previous work (**Tables S2-S3**).^[48] The CCSD(T) energies were computed with all electrons correlated, i.e. without frozen core electrons, using the aug-cc-pV5Z^[110] basis set with diffuse basis functions for the electronegative oxygen (since most basis set effects manifest in the electronegative atoms) and the def2-QZVPPD^[87] basis for all metals to ensure comparability (Sc-Zn, Y-Cd, and La-Hg; larger basis sets were available only for some metals). Although CCSD(T) converges slowly with basis set,^[111,112] this basis set achieves chemical accuracy for strong main-group bond energies such as CO and O_2 relevant to this study^[50] and errors within experimental error bars for MO bond energies,^[48] which we assume resemble the MO_2 systems for which experimental data are only scarcely available. B3LYP energies were also computed using the same basis set and corrections (see below), as summarized in **Table S4**.

Zero-point vibrational and relativistic corrections

Zero-point energies (ZPE) were computed from a frequency analysis of the optimized geometry at the same level of theory as geometry optimizations, as summarized in **Tables S5-S6**. For the 3d systems, scalar-relativistic effects were estimated from the sum of the Darwin term and the expectation value of P^4 using a B3LYP single-point energy calculation, as summarized in **Tables S7-S8**. The scalar-relativistic effects of the 4d and 5d transition metal oxides were estimated by using

default effective-core potentials of Turbomole. Throughout this work, we compared our energies directly to enthalpies of atomization and chemisorption, because the difference of $\sim RT$ (2.5 kJ/mol) does not affect the overall uncertainty in the data of 20 kJ/mol.^[48]

There are many ways but no standard way to treat the relativistic effects of these 3d, 4d, and 5d systems. Some methods are formally better than others. However, choices remain rather speculative since real relativistic state energy corrections for these molecular systems are unknown, and thus, the impact of the various approximations can mainly be evaluated by comparison to actual experimental BDEs. The SOC energies cannot be computed with our CCSD(T)/aug-cc-pV5Z//def2-QZVPP protocol for the 160 MO₂ systems with our available resources as these are extremely cpu time-and disk space requiring. Furthermore as already shown previously, full relativistic (SOC + scalar relativistic) effects are accurately modeled by B3LYP since this give M-O BDEs similar to experiment nearly within experimental uncertainty.^[48] One could also have used CCSD(T) specifically for the scalar-relativistic effects but since the SOC energies must be computed by DFT this would treat the total relativistic perturbation by two different methods, and we favor doing them with one method. Specifically, to know whether a relativistic treatment is accurate, we use errors against a balanced experimental data set for 3d, 4d, and 5d: If the accuracy is similar across all three d-blocks, then the relativistic treatment is balanced. Our previous results^[48] and the sensitivity analysis performed here (discussed below) show that this is the case.

More specifically, the spin-orbit coupling (SOC) energies throughout this work were computed using a Douglas-Kroll-Hess (DKH) B3LYP energy calculation of fourth order for the 3d metal oxides with the dhf-QZVPP-2c basis set. For the 4d and 5d systems, SOC corrections were obtained from a two-component computation including effective core potentials, calling the Turbomole keyword `soghf` again with the dhf-QZVPP-2c basis set to ensure that the basis-sensitive SOC energies are treated in the same way. The SOC energies are available in **Tables S9-S10**. To test the sensitivity of SOC corrections to method and basis set, the SOC corrections were compared for the two-component method implemented in Turbomole (activated `$soghf` keyword in the control file)

using relativistic effective core potentials^[87,113–115], with the basis sets dhf-QZVPP-2c^[116] and the DKH hamiltonian using the basis set by Martins, Jorge, and Machado, which we refer to below as Jorge-TZP-DKH.^[117] This all-electron basis set was designed for the DKH Hamiltonian and obtained from the basis set exchange web server^[118–120]. An excellent description of DKH theory can be found in the account by Reiher^[121]. The two-component formalism implemented in Turbomole allows for fast calculation of the SOC energy.^[122] Finally, the influence of functional choice on the SOC energy was also tested by performing calculations with the hybrids B3LYP^[81–83] and PBE0^[123,124] the meta-hybrid TPSSH^[125,126] and GGA PBE^[124]. The sensitivity analysis of the SOC energies is summarized in **Tables S11–S13**, and the thermodynamic and relativistic correction to O and O₂ are summarized in **Table S14**.

After analysis of the results and sensitivities, despite notable differences and some issues in the absolute SOC energies, the SOC corrections to the chemical energies were quite robust and generally independent of method choice, considering other error sources, and we conclude that the SOC corrections are important for the 5d reaction energies, as applied throughout below. For the 3d metals the corrections are generally too small to be of chemical significance. All the absolute SOC energies are shown visually in **Figures S1–S4**. An irregularity with Ag is evident in the absolute (but not chemical relative) energies of the two-component implemented in Turbomole, and an irregularity in Rh is evident in the absolute SOC energies of the DKH treatment when using the basis set by Martins, Jorge, and Machado. We note that the irregularities occur only in the absolute energies which are of the order of hundreds to thousands of kJ/mol. In the final energies, these irregularities cancel out to provide well-behaved final SOC corrections also for Rh and Ag, as seen in **Figures S5–S6**. For the 5d metals where the effects are significant, the sensitivity to method choice is small compared to the general oscillating trend in the SOC corrections discussed further below, and thus our study provides a robust estimate of the reasonable values and variations in SOC energies for these systems.

Calculating reaction energies

To assess back-bonding and O₂-activation, we calculated the reaction energies of four elementary reaction steps that reflect the M-O and O-O bond strengths. To this end, spin states, ZPEs, CCSD(T) energies, and SOC and scalar-relativistic corrections of the MO and M systems were taken from previous work using the same CCSD(T) method, basis set, and corrections.^[48,52] The reaction energies were obtained from the single-point CCSD(T) energies (**Tables S1-S4**) of the reactants and products, fully corrected by zero-point energies calculated from **Tables S5-S6**, scalar-relativistic corrections (**Tables S7-S8**) and SOC corrections (**Tables S9-S10**). The final, fully corrected CCSD(T) energies for the ground state spin and geometry of each system are summarized in **Table S15**, with associated reaction energies compiled in **Table S16**. Finally, the spin-structure effects were separated out by plotting the equilibrium bond lengths against spin states (**Figure S7**) and final reaction energies (**Figure S8**).

Results and discussion

Structural relationships of O-O bond activation

Figure 1A summarizes the DFT-optimized O-O bond lengths for all spin states of both the linear and bent side-on and the end-on dioxygen structures, compiled for each metal along the 3d, 4d, and 5d series. As can be seen, the geometries depend substantially on the electronic spin states, with variations in the middle of the d-block exceeding 0.2 Å in some cases. However, regardless of the spin-structure relationships, described in full in **Table S1**, a clear trend is seen toward shortest O-O bond lengths, regardless of spin state and geometry, in groups 9, 10, and 11, with Co, Ni, Cu, Rh, Pd, Ag, Ir, and Pt showing particularly short O-O bond lengths. As analyzed in detail below, these short O-O bonds coincide with the smallest extent of O-O bond activation of these metals and thereby constitute a generic scale of single-metal O₂ activation tendencies. It is notable already at this point that the most catalytically proficient metals for the ORR coincide with these metals.

Figure 1B shows the trends in optimized O-O-M angles plotted against the O-O bond lengths. The obtained O-O bond lengths fall within the range from ~1.2 Å to slightly more than 1.5 Å, which is in excellent agreement with the spectrum of bond lengths going from free dioxygen (1.2 Å), via superoxide (1.3 Å) to peroxide (1.5 Å). Despite the major variation in spin states, the side-on peroxo structures (η^2 -O₂), bent, and linear end-on superoxo structures (η^1 -O₂) fall into three distinct groups of linear relationships. The distributions largely justify the common view that the linear and bent structures represent “superoxo” structures with relatively shorter O-O bond lengths resembling those of superoxide, being well spread around an average value close to 1.3 Å. In contrast, the trigonal structures display much larger variation in O-O bonds from dioxygen-like to peroxide-like (1.5 Å), with the majority of structures having longer bond lengths, and an average close to a mixture of peroxide and superoxide (1.4 Å). Accordingly, the extent of O-O bond activation is largely controlled by the geometry of the dioxygen adduct, as is well known, but shown here in a complete way for the full d-block. The behavior is also shown to be similar for the 3d-, 4d-, and 5d metals.

Figure 1. Trends in O-O bond lengths. (A) Box-and-whisker plot of optimized O-O bond lengths of the 3d, 4d, and 5d series for all 160 optimized spin states and geometries, with the medians of all, the top-half, and bottom-half of the data shown as lines, and averages shown as x. Red circulated areas represent the least activated O-O bonds. (B) Relation between optimized O-O-M angles and O-O bond lengths for all geometries and spin states, showing separation of side-on peroxo structures ($\eta^2\text{-O}_2$), bent, and linear end-on superoxo structures ($\eta^1\text{-O}_2$). (C) Relation between optimized O-O-M angles and O-O bond lengths only for the trigonal peroxo structures.

As shown in **Figure 1C**, the relationship between the angle and O-O bond length, which we take to be a proxy of the degree of O-O bond activation, is fairly strong ($R^2 = 0.66$) for the trigonal end-on peroxide coordination mode, considering the mixtures of spin states and metal d-configuration. The length of the O-O bond indicates how much back-donation has occurred into π^*

in order to weaken the O-O bond.^[18,127–129] The O-O-M angle is thus a relevant descriptor of the extent of O-O bond activation in single-metal catalytic systems, because it correlates with the orbital overlap and thereby, efficiency of d-back-bonding; the descriptor obviously cannot stand alone and is only relevant to peroxide side-on coordination modes. Because of the noise of the spin states and geometric differences, the following analysis of the CCSD(T) energies focuses on the ground-state spin states and geometries only, although the overall structural trends of **Figure 1** may be kept in mind.

Spin-orbit coupling effects on M-O bond energies

Before discussing the CCSD(T) energies in full, we wanted to understand how SOC, which is usually ignored in theoretical studies, affects the oxygen binding to the metals across the three periods. **Figure S5** summarizes the computed SOC corrections to the BDEs of the 3d, 4d and 5d neutral and cationic transition metal oxides using the two-component and the fourth order DKH methods. For the 3d metals (**Figure S5, A-B**) the main difference is due to the basis set and except for CrO and CoO⁺ the results are very similar. For the 4d metals, the largest effects and method differences are seen for Ru and Rh. The worst-case uncertainty in SOC contributions to the binding of oxygen to these 4d metals is ~10 kJ/mol (**Figure S5, C-D**). For the 5d metals the effects can reach 30 kJ/mol in several cases, and the SOC corrections show remarkable oscillating trends with both methods, indicating the role of the electronic configuration. The oscillation reaches largest peaks near 30 kJ/mol for Hf, Re, Os, Ir, and Au.

Figure S6 shows the SOC BDE corrections calculated with the dhf-QZVPP-2c basis and fourth-order DKH for the 3d metals and the two-component ECP formalism for 4d and 5d metals. The choice of functional has little influence on the SOC correction, although the correction for TPSSh is typically slightly higher. TPSSh is a meta hybrid parameterized with several exact constraints, including one that removes a divergence in the exchange functional at the nucleus,^[125] which could affect the relativistic core and explain the difference. PBE produces a distinct electronic state for WO⁺

which affects comparison; it was impossible to convert to the ground state of the other functionals despite starting from the same configurations and orbitals. For all other systems, the electronic states are the same for the studied methods. Not surprisingly, for the 4d and 5d metals, the functional effect on the SOC correction is larger. The identified oscillation in the SOC correction is obtained with all four applied density functionals. We conclude that 1) 5d SOC corrections are very important and thus should be computed or estimated; 2) the corrections oscillate across the d-block and are thus not easily predictable without calculation; 3) since these corrections are metal-centered, we can expect our values to represent the magnitude of SOC corrections for M-O bonds also for larger systems, in the absence of alternatives, but for systems with two metal atoms contributing, the effects will differ, but probably have the same sign.

Linear scaling of O₂ binding and activation

In order to make the data obtained from our relativistic corrected CCSD(T) study more useful, we calculated relevant chemical energies that enable estimates of the errors and effects in applied studies of oxygen-binding to transition metals. **Figure 2** describes four reaction energies relating to O₂ binding and activation, computed with relativistic corrected CCSD(T) for all 3d-, 4d-, and 5d-metals. These reactions are the following:

Reaction (1) represents the initial binding of O₂ to the single metal atom. Reaction (2) represents the important elementary reaction where the O-O bond is cleaved and the released oxygen atom is immediately transferred to another metal atom. Reaction (3) represents the O-O cleavage reaction

when there is no second metal atom available for binding the released oxygen. Finally, Reaction (4) represents the M-O bond dissociation energy (BDE), which is experimentally known for almost all 3d-, 4d-, and 5d-metals and was benchmarked in recent work,^[48] showing that the same relativistic corrected CCSD(T) protocol as applied here approaches the average experimental uncertainty of 20 kJ/mol for MO systems. For the other reactions, very few data are available as MO₂ data generally reflect the inserted dioxides. Only the energies for the most stable spin states and geometries were used, with a full list of CCSD(T) energies of all spin states and geometries summarized in **Table S1**.

The similar trend curves of the 3d-, 4d-, and 5d-curves in **Figure 2A-2C** are remarkable and show that the d-electron configuration largely controls the reaction energies, with trends for each reaction type well-preserved and similar across the three d-series. The overall trends follow the oxophilicity of the metals and bear resemblance to many periodic properties of the d-transition metals. As usual in these trends, two effects can be separated, a linear trend due to effective nuclear charge and an orbital occupation effect that produces humps. The linear decrease of M-O binding strength towards the right is caused by the increased electronegativity of the metal which reduces the polar covalent bonding.^[5] Relative to this linear trend, two humps can be observed, which are caused by particularly stable orbital net-bonding at group 5-6 and 10 are notable in the plots, representing higher oxophilicity than the linear trend would imply. In addition to these two humps, the group 4 metals (Ti, Zr, Hf) produce distinct humps in all three periods, due to the O₂-adduct (MO₂) being particularly stable as they achieve the d² M(II) peroxide configuration. The black lines, which denote the actual binding energy of O₂ to the metal, is unfavorable for all the least oxophilic group-11 and group-12 metals. Since entropy also favors O₂ dissociation, this indicates that the real binding of O₂ to the single metals of groups 11 and 12 is unfavorable at standard conditions. We also note that the four metals Pd and Pt, Co, and Fe have the weakest O₂-binding energies among the metals that actually bind O₂. This analysis based on CCSD(T) energies is fully consistent with the structural trends of the O-O bond lengths seen in **Figure 1A**.

Figure 2. Reaction energies computed using CCSD(T) / aug-cc-pV5Z (O) // def2-QZVPP (M), corrected for spin-orbit, scalar-relativistic, and zero-point vibrational energies. **(A)** 3d transition metals. **(B)** 4d metals. **(C)** 5d metals. **(D)** Linear relations between the metal-compensated O-O bond cleavage energy ($M + MO_2 \rightarrow 2 MO$) and the O_2 binding energy ($M + O_2 \rightarrow MO_2$), O-O bond dissociation energy ($MO_2 \rightarrow MO + O$), and M-O bond strength ($MO \rightarrow M + O$).

Figure 2D shows the linear relationships between the reaction energy of reaction 2 and those of reactions 1, 3, and 4. Reaction 2 describes how much energy is gained by moving the oxygen atom from away from the other oxygen (i.e. breaking the O-O bond of the MO_2 complex) and to another metal atom. Evidently, the relationships are quite strong, with some notable outliers. As seen from the O-O bond lengths of **Figure 1**, the linear relationships in **Figure 2D** are due to d-back-bonding: The stronger oxygen binds, the more the O-O bond is elongated and weakened by induction of d-electron density into π^* of O_2 .

Spin-structure effects break linearities of O₂ activation

Because the spin state changes the occupation of the back-bonding $d(\pi)$ orbitals, it also influences the back-bonding propensity of the metal, as perhaps best illustrated by spin-crossover-prone iron.^[35,128] Consistent with this expectation, the spin state and geometry substantially affect each other and the computed CCSD(T) reaction energies (**Figures S7-S8**). The humps of the most oxophilic group-4 metals (**Figure 2A-2C**) lead them to violate the linear energy relationships in **Figure 2D**. This shows that the linear energy relationships between oxygen binding and activation can be broken by specific stereo-electronic variations, in this case the d^2 peroxide state. Deviations from the linear relationships may enhance back-bonding and O₂-activation without binding oxygen too strongly to the metal (i.e. circumventing the Sabatier principle), by favoring specific geometries or spin states, as exemplified by hemes^[127] and platinum clusters.^[130] Changing the coordination geometry and spin state may help to circumvent the Sabatier principle. Although these results for single metals are relevant to single-atom catalysis, but not directly transferable to clusters and surfaces, the fact that geometry and spin state of the O₂-adduct will change the linear relationship between O₂-binding and activation is probably universal. The obvious examples are metalloenzymes, where different spin states change the ligand-metal bond lengths, the energy of the intermediate, the reaction energy profile, and thereby the degree of back-bonding, which controls the linear scaling between binding and activation of a ligand along a reaction energy profile.^[20–22,131] Support for this view is given below where the CCSD(T) data are related to metal surface data by thermochemical cycles.

The spin state plays a major role in enabling back-bonding and O-O bond activation. Perhaps this is best illustrated by the very oxophilic scandium, which forms trigonal (peroxide-type) complexes in both the quartet and doublet spin states, but the doublet features much longer bonds (1.48 Å) than the ground-state quartet (1.35 Å). The low-spin state represents a better spin paired M-O bonding which in turns also enables a larger charge transfer to the π^* system (**Table S1**). In TiO₂ the singlet trigonal ground state is much more stable than the excited states, and except for a highly

excited triplet state it also has the longest O-O bond among the TiO₂ complexes. For VO₂, the doublet and sextet are of similar energy, but the low-spin state has an O-O bond that is more than 0.1 Å longer (1.43 Å vs. 1.32 Å) than the high-spin state. However, the ability of the metal electronic state to adopt the trigonal peroxide structure is critical to the back-bonding as well. The need to form two optimal side-on interactions competes with the tendency towards stronger, spin-paired M-O bonding orbitals so that the two effects become quite complicated in their mutual interaction and consequences (**Table S1**), in particular in the middle of the 3d series (Cr, Mn, Fe) where many spin states come close together, and high-spin tends to be favored. However, these complex structure-spin relationships still translate to remarkably robust energy relationships (**Figure 2**), with the very general tendency of oxophilic early d-block metals of all three periods displaying longer O-O bonds, and the late d-block metals showing O-O bonds as short as 1.2-1.3 Å.

Performance of DFT (B3LYP) vs. Coupled-Cluster

In order to estimate the method sensitivities for reactions 1-4, we computed the reaction energies for all 30 metals also with B3LYP^[80–84], using the same aug-cc-pV5Z // def2-QZVPP basis set, vibrational, and relativistic corrections. B3LYP is a global hybrid functional with 20% HF exchange and a widely used functional together with GGAs such as PBE,^[69] commonly used to study O₂-transition metal chemistry. **Figure 3** summarizes the performance of B3LYP compared to CCSD(T). In **Figure 3A**, all four reaction energies are compared directly for all 30 metals (120 reactions in total). Clearly, the general electronic structures are similarly described by CCSD(T) and B3LYP, i.e. the density functional recovers well most of the electron correlation. It can be seen from **Figure 3A** that the errors in B3LYP scale with the strength of the bonds. This is because the strong-binding limit represents strongly correlated electrons, which are challenging to DFT, and this effect is aggravated by the tight binding differences caused by effective nuclear charge across periods of the periodic table.^[50] For this reason, B3LYP is much less accurate for the oxophilic metals.

Figure 3. Performance of B3LYP vs. CCSD(T). (A) Comparison of CCSD(T) and B3LYP for all four reaction energies 1-4, for all 30 metals. (B) Comparison of the ranked O_2 affinities from CCSD(T) and B3LYP. (C) Radar plot of deviations of B3LYP from CCSD(T) for the reactions noted.

Figure 3B shows the ordered cost of releasing O_2 from the metal atom (i.e. the reverse of reaction 1), of interest to OER and in reverse, to initial O_2 -binding before O_2 activation. Interestingly, Pt and Fe, which are used in catalysts and enzymes, are the two metals that bind O_2 most reversibly according to CCSD(T). Reversible O_2 -binding to iron in hemes is of central importance to oxygen-based life.^[21] Obviously, the other ligands of iron and hydrogen bonding to O_2 change this reversibility,^[127] but the same tendency of the single atoms is still remarkable. CCSD(T) produces a very smooth trend when ordering the 30 metals according to the magnitude of the reaction energy, whereas B3LYP shows several major deviation from this trend, caused by different electronic ground states in some cases (Tc, Cu, Y, Zr). **Figure 3C** shows the main errors in B3LYP relative to CCSD(T) in a radar plot, confirming that the main problems of B3LYP relate to the most oxophilic metals, as

well Cu, probably because of the different correlation treatments of DFT and CCSD(T) for the $4s^2 3d^9$ / $4s^1 3d^{10}$ pure metal configurations.

Relevance of the CCSD(T) data as descriptors

In the above, we have reported our complete relativistic CCSD(T) reaction energies and their relevance for understanding the fundamental interaction between the 30 transition metals and oxygen. In the following, we want to argue that these data will also be useful as descriptors of transition metal oxygen chemistry more generally.

Figure 4A shows the ranking of all the 30 metals of the d-block according to their CCSD(T)-derived dioxygen (reaction 1) and oxygen (reaction 4) affinities in eV. The differences between these two reaction energies are of particular importance, as discussed further below. The reaction energies are also compared to the oxophilicity of each metal derived from a normalized scale of relative experimental M-O and M-S binding strengths,^[5] which explains many trends in activity of larger systems well.^[132–136] As seen, the two reaction energies generally correlate, but there is an important deviation in the middle d-block that metals bind O₂ to a similar extent, whereas the M-O bond strength follows the double hump structure through the d-block due to d-orbital net-bonding as is typical and very similar to e.g. hydration free energies and cohesion energies.^[48] This difference between O₂- and O-binding is very important as discussed in terms of thermochemical cycles below. The O₂ binding is much weaker, typically only half as exothermic as O-binding, because the O-O electronic structure is largely preserved. In the least O₂-activating metals, the O₂ bond is almost fully preserved and the binding becomes reversible. Of the metals that form stable O₂-adducts, these metals are mainly Pt, Pd, Fe, and Co, circled in blue in **Figure 4A**. Their high electronegativity prevents satisfaction of the electron demand of the second-most electronegative element of the periodic table.

Figure 4. Oxophilicity compared to CCSD(T) reaction energies. (A) Relation between affinity for O_2 and O, and oxophilicity. (B) Relation between oxophilicity and energies of reaction 1. (C) Relation between oxophilicity and energies of reaction 2. (D) Relation between oxophilicity and energies of reaction 3. (E) Relation between oxophilicity and energies of reaction 4.

Iron is the most used biological 3d metal for activating O_2 ^[17,34] The reasons could include co-evolutionary constraints and bioavailability, but also chemical optimality. Our CCSD(T) data show that iron, together with cobalt, platinum and palladium, bind O_2 most weakly among those that form stable O_2 adducts at standard conditions. Among the non-biological metals, Pt and Pd are particularly proficient at the ORR, although alloying can improve performance, e.g. 1:1 alloying with Fe.^[137]

Despite their common high electronegativity, a main reason for nobleness in the first place,^[138] gold and silver separate notoriously from platinum and palladium in this aspect, by having no net bonding to O_2 at all (entropy additionally favors O_2 -dissociation), in excellent agreement with their distinctly lower experimental sticking probabilities.^[139] Importantly, the distinct group of Co, Fe, Pt, and Pd tends to have comparatively *strong* M-O bonds relative to the O_2 affinities, because the net-bonding orbital occupation effect plays a larger role in strongly bound oxygen (MO).^[48]

Because of this difference, these particular metals break the linear relationship between M-O and M-O₂ binding, and impair the correlations of the four reaction energies to oxophilicity (which is mainly based on MO binding) as seen in **Figures 4B-4E**. Accordingly, although the oxophilicity captures most of the reactivity effects, as any other single descriptor of M-O bonding it cannot stand alone, whereas descriptors that account for both effects described above (the electronegativity and orbital net bonding effects) will be expected to work substantially better. The fact that it works well for most of the reactions again implies that the back-bonding relationship makes the binding and activating of O₂ linearly dependent, and thus the M-O interaction defines both binding, O-O cleavage, and release of oxygen.

To show that the data presented in this work are relevant to larger systems, we compare our relativistic corrected CCSD(T) data to the benchmark O₂-chemisorption energies obtained from the RPA method by Schmidt and Thygesen, with scalar-relativistic but not SOC corrections.^[140] These data represent complete metal surface models at high coverage to save computer time. The period-wise comparison of the chemisorption and CCSD(T)-computed M-O bond energies is shown in **Figure 5A**. The RPA values are much smaller in magnitude, not so much because they are on full metal surfaces, but because they were carried out at high coverage, which lowers the chemisorption energies by several eV.^[45] Except from this shift, the trend agreement is strong (**Figure 5B**, $R^2 = 0.84$). It increases to $R^2 = 0.89$ when comparing the same method (PBE), but different basis sets,^[48] i.e. system effects describe maximally ~10% of the total trend agreement. Most of this system effect is due to the orbital occupation effect, since the linear effective nuclear charge trend is similar. Specifically, **Figure 5A** shows that the late hump structure is more pronounced for the single metal oxygen affinity, whereas the early hump structure is more pronounced for the surface data, because the net-bonding orbital/band effects differ in the molecular and bulk metal states, as discussed in detail by Van Santen and co-workers.^[141]

Figure 5. Relation between CCSD(T) energies and full-surface O_2 -chemisorption energies. (A) The CCSD(T) oxygen binding energies compared to RPA-computed O_2 -chemisorption energies on high coverage metal surfaces by Schmidt and Thygesen, ordered according to atomic number.^[140] (B) Same comparison in a linear regression plot. (C) Thermodynamic cycles used to illustrate the relationship between high-quality quantum chemical data as presented here and reaction energies of full catalytic systems, exemplified by metal surfaces.

To further argue for the relevance of the present data as descriptors of reactivity, we should note that they are inherently much more accurate than the DFT computations for larger systems. The central question is therefore, if we can separate out the system effects in a meaningful way, to obtain descriptors with better overall accuracy. To this end, **Figure 5C** shows a thermochemical cycle that can be used to relate the reaction energies 1-4 obtained from CCSD(T) directly to large-system bulk metal energies. The rightmost cycle represents the cycle discussed by Van Santen and co-workers.^[141] We note that if the adsorption energy of the single oxygen atom is known, the embedding energy of

MO can be computed at the same level of accuracy, because the atomization heats (cohesive enthalpies) and M-O BDEs are known experimentally at total uncertainties summing to ~ 20 kJ/mol, which is less than that achievable for the two remaining paths of the rightmost cycle. The embedding energy of MO can be considered an equivalent to the atomization energy of the metal M, corrected by the effect that the oxygen-bound atom has on releasing the metal atom from the surface. Thereby, the difference in these two energies measures the impact of the surface metal-metal bonds in modulating the oxygen affinities, which are the energies of reaction 4 and the adsorption energy of O (top and bottom paths of the rightmost cycle of **Figure 5C**).^[141]

To progress further along these lines, we use two additional cycles as shown to the left and middle of **Figure 5C**, which directly explain why the four reaction energies 1-4 have been of particular interest to compute in the present work. The cycles relate these four energies to the physisorption and chemisorption energies of the bulk metal and thereby provides a strict thermodynamic definition of these two processes, discussed e.g. by Fromm and Mayer^[139], as the step where O₂ is bound without or with O-O dissociation, respectively. The energies computed in this work have estimated average errors of ~ 20 kJ/mol,^[48] which is probably at least half that of experimental^[57,58] and GGA/global hybrid-DFT-based energies^[46] of the processes for the large systems (the processes in the bottom of **Figure 5C**). Furthermore, the atomization energies are known at high accuracy. Thus, the limit to predicting accurate chemisorption energies for the real systems is the embedding energy of the MO (and MO₂) systems: If these were known accurately, the full cycle would be obtained at an accuracy that is doubly as high, at least, as current approaches.

Figure 6. CCSD(T)-derived embedding energies and estimated O₂-chemisorption energies. (A) Trends in embedding energy of MO using a coverage effect of 3 or 4 eV, compared to the experimental enthalpy and free energy of atomization. **(B)** Heat of atomization vs. calculated embedding energy using a 4-eV coverage effect. **(C)** CCSD(T)-estimated chemisorption and physisorption energies, vs. experimental single- and polycrystalline chemisorption energies. **(D)** Estimated ($\Delta E_{\text{oo}} = 4 \text{ eV}$) vs. experimental polycrystalline chemisorption energy.

Estimating chemisorption and physisorption energies from CCSD(T) data

Using the thermochemical cycle of **Figure 5A**, we can quantify the magnitude of the real bulk metal's modulation of the molecular single metal energetics by computing the embedding energy (enthalpy) of MO, which can be obtained from reactions 1 and 2. Since the chemisorption energies used are at high coverage, we have to correct for the difference in chemisorption of high and low (0) coverage, caused by the oxygen-oxygen repulsion on the metal surface, which lowers the adsorption energy,^[142]

referred to here as ΔE_{oo} . From the data of Brennan et al. we can estimate ΔE_{oo} for polycrystalline films to be ~ 4 eV for Mn and 5 eV for Ti, for which the curves are best resolved at high and low coverage (Figures 3 and 4 of their paper^[142]). We used values $\Delta E_{oo} = 3$ eV and 4 eV, consistent with the range seen experimentally^[58] and theoretically^[140] for Ni. For simplicity, we assume that the coverage effect is independent of metal, because it reflects only oxygen-oxygen repulsions. Obviously, the lattice constants of the metal will affect the separation between the adsorbed oxygen atoms and thus the coverage penalty, and one can improve the assumption by correcting for the atomic radius or lattice constant of the metals.

As seen from **Figure 6A**, assuming a constant $\Delta E_{oo} = 3$ or 4 eV is enough to produce trends in the calculated MO embedding energies that are in very good agreement with the experimental heats of atomization, with the best fit being $\Delta E_{oo} = 3.8$ eV (values can be found in **Table S18**). Because the ΔE_{oo} values of 3-4 eV are very reasonable, this shows that the embedding energies $\Delta E_{emb}(\text{MO})$ are strongly correlated with the heats of atomization (cohesive enthalpies), as shown clearly in **Figure 6B** ($R^2 = 0.75$). If one compares the same methods for the surface data and molecular data, e.g. PBE, the correlation increases further to $R^2 = 0.83$ (using data in **Table S18**). The physical implication of this finding is that the cost of extracting MO from the metal surface trends very closely with the cost of extracting a metal atom M from the surface, because the oxygen atom is not directly interacting with the other metal atoms that modulate the cohesive energies. On the other hand, we do not expect perfect agreement, since the surface structure, nature of the binding site (top, hollow) and lattice constants will affect ΔE_{oo} and thereby the embedding energies, which may thus be improved in further work. The purpose here was mainly to show that the thermochemical cycle of **Figure 5C** can be used to relate high-accuracy quantum-mechanical data to low-accuracy experimental and DFT-based data and ultimately help to provide less noisy estimates of chemisorption and physisorption energies.

An additional advantage of the thermochemical cycle is that reaction 1 and 2 enable us to estimate the physisorption energy, i.e. the energy of adsorbing O_2 without O-O bond dissociation, which is often hard to obtain experimentally, although secondary binding sites of higher or lower

affinity are well-known. Separating the two processes should be of major interest and is directly possible with the proposed thermochemical cycle if we use the assumption that the embedding energy of MO_2 is the same as that of MO , $\Delta E_{\text{emb}}(\text{MO}_2) = \Delta E_{\text{emb}}(\text{MO})$, which, in the low-coverage range of interest here should be a quite good approximation. If so, we can compute the physisorption energy from the leftmost thermochemical cycle of **Figure 5C**.

The chemisorption and physisorption energies thus estimated from the CCSD(T) data using the RPA/CCSD(T)-based embedding energies (**Table S18**) are shown in **Figure 6C**, compared to experimentally available room-temperature single- and poly-crystalline chemisorption energies.^[57,58,142] The polycrystalline data were taken for all reported film samples measured by Brennan et al.^[142] and also reported by Toyoshima and Somorjai,^[57] summarized in **Table S17**. Agreement is very good with the polycrystalline data for the 4d and 5d metals and the middle 3d metals, but is bad for Ni, Cu, and Ti. The reasons for the discrepancy is not currently clear. For the single-crystalline data, the agreement is bad for Ni, Mo, W, and Ir. We note that the experimental polycrystalline and single-crystalline data differ markedly as well for these metals, and that our estimated chemisorption data show strong trends across the d-block, which could indicate that they are more accurate than experiment, which we tend to believe. However even the differences, the polycrystalline and estimated chemisorption energies correlate with $R^2 = 0.77$ (**Figure 6D**), which is remarkable considering the heterogeneity in the experimental data alone, and the simple approximations used when applying the thermochemical cycles, most notably the assumption of a constant coverage penalty.

As also seen from **Figure 6C**, the coinage metals display the weakest binding, in excellent agreement with the very low experimental sticking probabilities of these metals.^[139] Au and Ag display endothermic chemisorption, with physisorption being *less* endothermic than chemisorption, largely explaining why these metals are not active in the ORR (**Figure 6C**). From this, we conclude that high-accuracy quantum-chemistry data for small systems can be important descriptors both of single-atom catalysis but also for large catalytic systems.

Conclusions

Understanding how transition metals bind and activate O₂ is important to many areas of catalysis. We have reported the first complete study, using high-quality relativistic and vibrationally corrected coupled-cluster energies, to compute the O₂-affinity and the O-O bond activation of all the 3d-, 4d-, and 5d-single metals. The obtained data, the first of this kind for the full d-block, are useful as descriptors of single-atom catalysis.^[9,64] and large catalytic systems, as argued from thermochemical cycles that relate the CCSD(T) data directly to chemisorption energies. Since the same methodology achieves near-experimental accuracy (~20 kJ/mol, similar to experimental uncertainties) for the 60 3d-, 4d-, and 5d- MO bond energies where experimental data are known,^[48] we can expect similar accuracy for the present systems, where experimental data are generally not available.

One might think that small molecules offer little trend predictive power and thus catalytic relevance. There are two reasons why they do, as shown in this work:

1) Theoretical catalysis requires predictive power, which comes from full error control of the chemical composition, conformation sampling, method quality, basis set effects, relativistic effects, solvent effects etc. The final trend energies across the d-block should be accurate without unknown error cancellations. The noise in experimental and theoretical data of O₂-binding to larger systems^[45,46] obscures error control and leads to a relying on unknown error cancellations, which again limits predictive power. Trends obtained from DFT studies of large systems are impaired by extra-DFT effects (such as spin orbit coupling, which affects some 4d/5d comparisons by 20 kJ/mol, conformation sampling, and solvent effects) and intrinsic imbalances in DFT itself, with different HF exchange required across the p- and d-block.^[50–52] The small systems do not suffer the noise of solvent treatment and conformational sampling (the possible trigonal, linear, and bent geometries are fully accounted for) and can be treated *ab initio* with large basis sets as required for electronegative oxygen. Thus, small-molecule benchmarks are necessary as increasingly recognized.^[53,69,90,98,100–102]

2) The small systems carry most of the trend chemistry of the large systems, and are thus catalytically relevant, since the most important effects scale to the larger systems. This is why the same functional effects and extra-DFT effects are seen for diatomic and large enzymatic models.^[55] In the present work, it is perhaps best seen from the squared correlation coefficient $R^2 = 0.84$ between computed O₂-adsorption energies for full-surfaces and our CCSD(T) reaction energies in **Figure 5B**. The local M-O and O-O bonding dominates other modulating effects: Across the d-block, the M-O bond energies vary from 100-800 kJ/mol, dwarfing the modulation effects of additional ligands or metals, which often tend to be systematic. Our systems represent the universal minimal models of O₂ binding and O-O breaking on all 3d, 4d, and 5d metal atoms and thus holds a special place in the hierarchy of chemical models, not studied before in their entirety at this level. Adding systematically to these models may ideally enable tailoring and understanding of chemical and catalytic systems bottom-up, in a fully rational sense, with considerable error control and thus predictive power.

Beyond the database itself, which can be compared to DFT, the main new findings of physical insight are that i) We find that single-atom properties describe most ($R^2 \sim 0.7-0.8$) of the O₂-chemistry of larger transition metal systems; ii) consistent linear energy relationships between the binding energy and O-O bond activation are caused by d-back-bonding and probably explain the relevance of Sabatier's principle^[37] to O₂-activation chemistry as this local bonding effect prevails in larger systems^[127]; iii) we show that spin states and geometries of the O₂ adducts can break these relationships as also seen for heme proteins^[21], providing possible means of circumventing the Sabatier principle; iv) some geometric descriptors such as the O-O-M angle are relevant descriptors of O-O bond activation in the peroxide coordination modes ($R^2 = 0.66$); and may be of value since they can be obtained with theory at lower computational cost than energies; v) the CCSD(T) data identify as a special group of metals Pt, Pd, Fe, and Co as the weakest oxygen binders among metals that form stable O₂ adducts, consistent with their use in ORR under various specific circumstances; vi) we provide a quantitative separation of the chemisorption and physisorption energies for the metals by using thermochemical cycles; vii) we find that our computed cost of extracting MO from

the metal surface (the MO embedding energy) is strongly correlated ($R^2 = 0.75$) with the experimental cohesive energy (heat of atomization). These embedding energies enable us to directly relate high-accuracy quantum mechanical gas-phase reaction energies to surface energies, thereby potentially reducing errors of these via thermochemical cycles.

Perhaps most importantly, we have demonstrated that simple generic reaction energy descriptors obtained from high-quality quantum-chemistry (the upper part of the thermochemical cycle in **Figure 5C**) can help to circumvent the “noise wall” of transition metal oxygen chemistry when combined with thermochemical cycles. Briefly speaking, in terms of d-trend predictive power (arguably the essence of theoretical catalysis), the errors in large system treatments with more precise chemical composition but less accurate physics seem to exceed the errors of small systems with more precise physics but less precise chemical composition, at least for O₂-chemistry. This lends promise to a bottom-up approach adding composition gradually to minimal catalytic units during effective error control. As an example, more accurate embedding energies of MO, which were crudely estimated in the present work, should allow substantially more accurate chemisorption and physisorption energies to be obtained.

Conflicts of interest

The authors declare that they have no conflicts of interest associated with this work.

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Supporting information available

The Supporting information file contains all the electronic energies and corrections in a.u., as well as the final used, fully corrected energies.

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TOC entry

Transition-metal bonding to O₂ is of major biological and catalytic importance. We report a complete coupled-cluster CCSD(T) study of all 3d-, 4d-, and 5d metals bonding to O₂. Our CCSD(T) data should aid DFT benchmarks and give insight into linear energy relations and O-O bond activation upon metal-oxygen bonding.