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Performance of Density Functional Theory for Transition Metal Oxygen Bonds

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Abstract

The accuracy of Density functional theory (DFT) limits predictions in theoretical catalysis, and strong chemical bonds between transition metals and oxygen pose a particular challenge. We benchmarked 30 diverse density functionals against the bond dissociation enthalpies (BDE) of the 30 MO and 30 MO⁺ diatomic systems of all the 3d, 4d, and 5d metals, to test universality across the d-block as required in comparative studies. Seven functionals, B98, B97-1, B3P86, B2PLYP, TPSSh, B3LYP, and B97-2, display mean absolute errors (MAE) < 30 kJ/mol. In contrast, many commonly used functionals such as PBE and RPBE overestimate M-O bonding by +30 kJ/mol and display MAEs from 48-76 kJ/mol. RPBE and OPBE reduce the over-binding of PBE but remain very inaccurate. We identify a linear relationship (p-value $7.6 \cdot 10^{-5}$) between the *precision* and *accuracy* of DFT, i.e. inaccurate functionals tend to produce larger, unpredictable random errors. Some functionals commonly deviate from this relationship: Thus, M06-2X is very precise but not very accurate, whereas B3LYP* and MN15-L are more accurate but less precise than M06-2X. The best-performing hybrids have 10-30% HF exchange, but this can be relieved by double hybrids (B2PLYP). Most functionals describe trends well, but errors comparing 5d to 4d/3d are ~10 kJ/mol larger than group-wise errors, due to uncertainties in the spin-orbit coupling corrections for effective core potentials, affecting e.g. Pt/Pd or Au/Ag comparisons.

Keywords: DFT, transition metals, oxygen, catalysis, bond dissociation enthalpy

Introduction

Chemical bonds between d-transition metals and oxygen play a central role in mineralogy^[1–4], biological management of oxygen by iron and copper,^[5–8] and chemical catalysis^[9–12], including numerous energy-related applications^[13–16], specific examples being metal-catalyzed water splitting^[17], conversion of methane to methanol^[18], and epoxidations.^[19]

The simplest possible transition metal oxygen system is the diatomic molecule (MO), which in a pure way probes the ability of the metal (M) to bond to oxygen, without any modulating, potentially noisy effects from other ligands or metals in a catalytic or chemical system. These systems have long been important as benchmark systems for theory^[20–22], in astrochemistry, high temperature inorganic chemistry, and spectroscopy^[23,24]. Major interest in them has emerged with the increasing focus on very small catalytic systems approaching the limit of single-atom catalysts which can exhibit many-fold increased efficiency relative to conventional catalysts^[11,25,26].

Inspired by the push towards minimal catalytic systems, we envision a *de novo* approach to catalysis starting from the “minimal catalytic units” such as MO, and rationally adding components in a fully understood manner to reach the complete, tailored catalyst. We expect that complete insight into the electronic structure of the minimal catalytic units such as M, MO, MO₂, and M₂O₂ enables the building of the maximally efficient catalyst by adding chemical components bottom-up. The success largely relies on the observation that many chemical properties of small molecules are periodic, leading e.g. to the early concept of a periodic table of diatomics^[27–29].

A major advantage of this strategy is the existence of many more systematic experimental data for small molecular systems than for larger homogeneous and heterogeneous catalytic systems. For the diatomic MO and MO⁺ systems studied in this work, almost all of the 60 bond dissociation enthalpies (BDE) are available for all the 3d, 4d, and 5d systems, enabling full account of the periodicities and trends needed for rational catalyst design^[30]. In contrast, experimental data for larger catalytic systems are very protocol-dependent,^[31] they are incomplete along the 3d, 4d, and

5d series and are sensitive to defects, solid crystal structure, surface coverage, solvent, pH, and temperature. Even if experiments could sort out these confounding system- and condition-dependent factors, it is beyond the capability of current theoretical methods to model these effects accurately, producing likely random errors of the order of 20–50 kJ/mol, in addition to the errors in the functional itself, the thermodynamic and relativistic corrections, and the dispersion effects.^[32] Claims of higher accuracy than 30 kJ/mol between DFT and data such as chemisorption energies on surfaces should thus be considered with substantial skepticism. Fortunately, some errors are systematic and affect different systems in the same direction, inducing partial cancellation of the systematic errors in comparisons, which is good enough for catalyst design but not for understanding the processes absolutely.

For small systems, accurate quantum-chemical methods can compute the energies of bond formation and bond breaking, which enables a test of the accuracy of DFT methods used for specific systems. In particular, the use of the BDEs of metal-ligand bonds are receiving significant attention as best-practice benchmark properties for chemical reactivity across the d-block^[30,33–40]. The success largely relates to the fact that the diatomic M–O BDEs correlate better than any other known single descriptor to the chemisorption energies of pure metal surfaces, with R^2 approaching 0.89 when computed with the same methods^[30], across a range of more than 500 kJ/mol in both O_2 chemisorption energies and M–O BDEs within the d-block. Coordinative saturation, metal-metal modulations and solvent effects contribute smaller errors to the DFT-modelled process than the local M–O bond, because the relative M–O bond energies vary by an order of magnitude more than the metal-metal modulating influences, or correspondingly, the trend in cohesive energy changes upon ligand dissociation from different metal surfaces. Diatomic M–O BDEs display a residual error of 46 kJ/mol against full surface chemisorption energies when computed with the same method^[30], i.e. the total modulating effects contribute less than 46 kJ/mol to the trend prediction, consistent with the smaller variations in enthalpies of metal atomization relative to M–O bond energies. For comparison, PBE itself has an MAE of 76 kJ/mol for the M–O BDEs, as shown below.

We recently^[30] established a data set of curated experimental BDEs for diatomic transition metal oxides, using experimental trends and state-of-the-art CCSD(T) computations, which reproduce experimental values excellently^[30]. We have also shown how CCSD(T) can be used to evaluate full, simple catalytic cycles^[41], again utilizing the fact that the energy errors of the bonds broken and formed during catalysis dominate the energies of the overall catalytic reaction and thus the errors of theoretical catalysis. Using such “full-cycle benchmarking”^[41], the difficulty of modeling each step of a process with DFT can be assessed directly. It turns out, unfortunately, that different density functionals have problems with different steps of a catalytic cycle due to their distinct electronic changes, with particular problems emerging in the non-universality of DFT when simultaneously studying early and late transition metals^[40], metals with variable coordination number^[39], and metals with variable types of ligands binding^[40], with particular problems arising for self-interaction-error-prone metal-hydrogen bonds.^[39,41]

Although progress in the use of coupled-cluster theories to larger systems is promising and will accelerate *de novo* strategies^[42,43], they remain too computationally demanding for larger catalytic systems. Accordingly, in this work we benchmark the ability of state-of-the-art DFT to describe the MO and MO⁺ BDEs, using curated experimental data set that include 28 of the 30 possible neutral diatomic MO molecules and 27 of the 30 possible diatomic cationic MO⁺ systems of the 3d, 4d, and 5d transition metal series^[30]. Importantly, these data do not suffer from errors due to the modeling of solvent, dispersion, and entropy effects as they are gas phase enthalpies with dispersion effects substantially smaller than 1 kJ/mol^[40], and the data set is balanced across the 3d, 4d, and 5d metals and thus prevents system-biased conclusions common to many studies of both large and many small systems with over-representation of some *nd^q* electronic configurations.^[39,40]

Many of the 60 diatomic systems have been studied before at various levels of theory^[20,21,46–50,22,23,30,34,35,40,44,45]. However, this paper presents the first systematic benchmark of DFT for all 3d, 4d, and 5d MO and MO⁺ systems as required to evaluate system dependencies and universality across the groups and periods of the d-block. To probe DFT broadly, we compared 30 different

diverse functionals, including local, gradient-corrected, local and global hybrids, meta functionals and range-separated functionals, giving the most systematic and complete picture so far of the ability of DFT to describe M-O bonds.

Methods

Experimental data. Based on analysis of the trends of experimental BDEs, a recommended experimental data set for BDEs of MO and MO⁺ systems was established in previous work(**Table S1**)^[30]. The data set contains BDEs for 55 of the 60 systems and is well-balanced across all three d-transition metal periods and groups.

Computational details. All computations were performed with the Turbomole software, version 7.0^[51] and the Gaussian 16^[52] software. All computations were performed using unrestricted Kohn Sham orbitals without symmetry (C1 point group). BDEs were calculated for the 30 neutral M-O and 30 cationic M⁺-O systems of the 3d, 4d and 5d transition metals (Sc-Zn, Y-Cd and La-Hg). BP86/def2-TZVPP optimized geometries were taken from our previous work^[30] (**Table S2**) and used for all energy calculations. This method provides some of the best geometries for these systems, with average errors below 0.02 Å^[30]. For 15 of the diatomic molecules, experimental bond lengths are available (**Table S3**). To ensure that BDEs and conclusions are not sensitive to reasonable variations in geometry, we computed the B3LYP single-point energies of these 15 systems both at the experimental and optimized geometry (**Tables S4-S5**). As seen, the energy is affected by less than 1 kJ/mol in all cases except LaO (8 kJ/mol) which is a particular difficult system. Considering that the BDEs span from 100-800 kJ/mol (**Table S1**) and errors exceed 25 kJ/mol, the uncertainties in geometry do not contribute substantially to the results and conclusions presented below.

Zero-point energies (ZPE), relativistic corrections to electronic energies, and used spin states for the 60 diatomics were taken from previous work where these parameters were carefully evaluated against the best experimental data and CCSD(T)^[30]. Thus, for example, the previously observed uniform accuracy of CCSD(T) across the 3d, 4d, and 5d series shows that the applied spin orbit coupling and scalar relativistic corrections capture accurately (errors of ~5 kJ/mol) the full d-block as a whole as required for DFT applications across all three periods^[30,40]. For convenience

these corrections are summarized in the supporting information **Tables S6-S9**. The ground state spin states for atoms and atomic ions used for computation were taken from NIST^[53] and can be found in **Table S10**.

Single point DFT energies. Single point energies were computed using the 30 density functionals of **Table 1**, with references, functional type, HF exchange percentage, and software used (Gaussian or Turbomole) given. These 30 functionals include many of the most popular used in computational chemistry and theoretical catalysis such as PBE, RPBE, and B3LYP, but also many newer functionals and representing all the major classes of design type. The basis set used for single-point energies was def2-QZVPPD^[54] for the metals (Sc-Zn, Y-Cd and La-Hg) and aug-cc-pV5Z^[55] for the very electronegative oxygen. This basis set is saturated to within 2-3 kJ/mol in terms of errors in BDEs as shown from previous work^[40,56].

Calculation of BDEs. The BDEs were calculated from the computed electronic energies as:

$$BDE(M-O) = E(M) + E(O) - E(MO) - E_{ZPE} + E_{scalar} + E_{SOC} + 3.7 \text{ kJ/mol} \quad (1)$$

Here, $E(M)$, $E(O)$ and $E(MO)$ are the electronic energies of the metal, oxygen atom, and MO or MO⁺ molecule, as tabulated in **Tables S11-S20**. E_{ZPE} is the computed zero-point energy of the molecule (**Table S7**). E_{scalar} is the scalar-relativistic energy correction (**Table S8**), E_{SOC} is the computed spin orbit coupling (SOC) correction (**Table S9**), and 3.7 kJ/mol corresponds to 3/2 RT at 298 K which converts the BDEs from 0 K to 298 K. The 60 BDEs calculated for the 30 functionals (1800 BDE values in total) are compiled in **Tables S21-S25**. Signed errors (SE) were calculated according to Equation 2:

$$SE = BDE(MO)_{comput} - BDE(MO)_{exp} \quad (2)$$

where $BDE(MO)_{comput}$ is the BDE calculated from Equation 1, and $BDE(MO)_{exp}$ is the experimental BDE from **Table S1**. The absolute errors (AE) reported in this work are the absolute values of the SE, whereas the mean signed errors (MSE) and mean absolute errors (MAE) discussed

below are the averages of the SE and AE, respectively; these errors for the full data set are summarized in **Table S26** and in **Table S27** (excluding the main outlier, LaO⁺). **Tables S28-S40** show errors for various subsets of the overall data set to test the sensitivity of results to variations in the data by dividing them into groups and periods, and MO vs. MO⁺ systems. The overall five largest errors for all functionals are compiled in **Table S41**, whereas **Table S42** shows the properties of the linear regression analysis.

Table 1. 30 Exchange-correlation functionals used in this work, with references, amount of HF-exchange, functional type and program used for calculations.

Functional	Type	% HF	References	Software
APFD	Hybrid GGA	23	[57]	Gaussian16
B2PLYP	Double Hybrid	53	[58]	Turbomole
B3LYP	Hybrid GGA	20	[59–61]	Turbomole
B3LYP*	Hybrid GGA	15	[59–61]	Turbomole
B3P86	Hybrid GGA	20	[62,63]	Turbomole
B97-1	Hybrid GGA	21	[64]	Gaussian16
B97-2	Hybrid GGA	21	[65]	Gaussian16
B97-D	GGA	0	[66]	Gaussian16
B98	Meta hybrid	22	[67]	Gaussian16
BHLYP	Hybrid GGA	50	[68]	Turbomole
BLYP	GGA	0	[62,63]	Turbomole
BP86	GGA	0	[62,63]	Turbomole
CAM-B3LYP	Range-separated	19-65	[69]	Gaussian16
HSE06	Range-separated	0-25	[70–76]	Gaussian16
M06	Meta hybrid	27	[77]	Gaussian16
M06-2X	Meta hybrid	54	[77]	Turbomole
M06-L	Meta GGA	0	[78]	Gaussian16
MN15	Meta hybrid NGA	44	[79]	Gaussian16
MN15-L	Meta NGA	0	[80]	Gaussian16
O3LYP	Hybrid GGA	12	[81]	Gaussian16
OLYP	GGA	0	[60,82]	Turbomole
OPBE	GGA	0	[83,84]	Turbomole
PBE	GGA	0	[84]	Turbomole
PBE0	Hybrid GGA	25	[84,85]	Turbomole
PW6B95	Meta hybrid	28	[86]	Turbomole
RPBE	GGA	0	[87]	Turbomole
SVWN	LSDA	0	[88,89]	Turbomole
TPSS	Meta GGA	0	[90]	Turbomole
TPSSh	Meta hybrid	10	[90]	Turbomole
wB97XD	Range-separated	22-100	[91]	Gaussian16

Results and Discussion

Accuracy and precision of density functionals. **Figure 1A** and **Figure 1B** show the mean absolute error (MAE) and mean signed error (MSE) for the 30 functionals describing the BDEs of **Table 1**. The MAEs describe the overall absolute accuracy of the functionals and the MSEs describe the accuracy in terms of systematic over- or under-binding; a negative value implies under-binding, and a positive value implies over-binding. We also speculated that the *precision* of DFT applied to M-O bonds is of interest in addition to the normally assessed *accuracy*. The precision tells us about the spread in estimated values regardless of how accurate the numbers are. We estimated the precision from the standard deviation (STD) of the SE, which is shown as black lines in **Figure 1B**.

From **Figure 1A**, the MAE ranges from 26 to 178 kJ/mol and the MSE from -121 (BHLYP) to +178 (SVWN) kJ/mol. The STD can be found in **Table S26** and ranges from 33 kJ/mol to 56 kJ/mol. The most accurate functional B98 also has an acceptable MSE of -8 kJ/mol and a STD of the SE of 34 kJ/mol, i.e. the functional is expected to produce an SE of -8 ± 34 kJ/mol for 68 % of the studied MO BDEs, assuming a normal distribution of the errors. Considering that CCSD(T) with the same type of vibrational and relativistic corrections has a MAE of 25 kJ/mol and MSE of 3 ± 32 kJ/mol for the same data,^[30] the performance of the best functionals is almost on level with CCSD(T), which is highly encouraging. Since the average experimental uncertainty is ~17 kJ/mol for the data where these uncertainties are reported (assuming similar uncertainty for the remaining data) a “perfect” method can never achieve a MAE smaller than ~20 kJ/mol, and we note that several of the best functionals perform not far from this threshold.

Figure 1. A) Mean absolute error (MAE) B) Mean signed error (MSE) (red bars), for the 30 functionals of **Table 1**. The black lines show the standard deviation of the error. C) Relation between overall numerical accuracy as measured by MAE and systematic binding error as measured by MSE. D) Relation between precision (measured as standard deviation of the error) and accuracy (measured as MAE) of the functionals. Tabulated errors are available in **Table S26**.

The most accurate functionals measured by the MAE of **Figure 1A** are B98, B97-1, B3P86, B2PLYP, B3LYP, TPSSh, and B97-2, with MAEs of between 26 and 30 kJ/mol, MSEs between -16 and 0 kJ/mol, and standard deviations of the errors of 34-37 kJ/mol (**Figure 1B**). These functionals are all hybrids. B98, B97-1, B3P86 and B3LYP have 22, 21, 20 and 20% HF-exchange, respectively, whereas TPSSh is a meta-hybrid with 10% HF exchange. This meta-hybrid requires less HF-exchange to be accurate, possibly due to its kinetic energy gradient. It is notable that the MSE and MAE are not always fully correlated, and thus some functionals, e.g. B3LYP, have a surprisingly low MAE despite a consistent tendency to under-bind. Because of the substantial

diversity of the 30 investigated functionals, such variations are expected. B98, B97-1 and B2PLYP have previously^[92] been found to predict the thermochemistry for 3d transition metal species excellently, as is also the case for the transition metal oxides (**Figure 1A** and **1B**). The success of the B98, B97-1 and B97-2 functionals is remarkable considering that their parameterization was based on the G2 test set or slight modifications thereof^[64,65,67].

The good performance of B2PLYP with 53% HF exchange shows that the “requirement” of 10-20% HF exchange can be relaxed by compensating correlation energy from MP2 perturbation theory, which works very well. The performance of B2PLYP for the M-O bonds of both 3d, 4d, and 5d transition metals is promising as this functional is also accurate for both coordinately saturated and unsaturated M-H bonds, which are intrinsically hard to model simultaneously with a global hybrid or GGA.^[39] Since theoretical catalysis requires uniform accuracy across both 3d, 4d, and 5d systems, often involves both hydrogen and non-hydrogen ligands and common changes in coordination number at the metal site, we recommend B2PLYP for use in d-transition metal catalysis due to its uniform (transferable) high accuracy and precision. Other well performing functionals are the meta hybrids PW6B95 (12% HF exchange) and MN15 (44%). It is interesting that the higher-order derivatives included in the more mathematically complex meta functionals reduce the need for HF exchange. Kulik and co-workers have noticed a similar effect on spin state energies^[93], favoring the more atomic state (weakening bonding and favoring higher spin), which is also the reason why TPSSh (10%) commonly performs similar to the 15%-HF hybrid B3LYP*^[94,95]. The good performance of MN15 with 44% HF-exchange probably relates to its careful parametrization vs. data that include metal-ligand bond strengths^[79].

The performance of the range-separated hybrid CAM-B3LYP is also reasonable (**Figure 1A, 1B**). In contrast to many global hybrids and meta functionals, this range-corrected functional performs well for both unsaturated and saturated transition metal systems^[39] and for spin splitting energies^[96]. It is notable that the more complex double hybrids and range-separated hybrids uniquely show ability to model all these types of bonds as required for an accurate theoretical catalysis.

Energetic effects of varying the HF exchange fraction in global hybrids is commonly linear, with high HF fraction causing under-binding and low HF fraction leading to stronger bonds^[97,98]. For BHLYP, B3LYP, B3LYP*, and BLYP, the MSEs are -122, -16, -1, and 54 kJ/mol, respectively. This shows that an increase of 1% HF-exchange affects the MSE by approximately 3 kJ/mol, which is typical also for the high-spin low-spin energy gaps.^[96] A similar conclusion can be drawn when looking at the TPSS (0% HF) and TPSSh (10% HF) functionals where the MSE changes from -2 to 33 kJ/mol. For the PBE functional, the HF exchange dependence is slightly stronger, ca. 4 kJ/mol per 1% HF exchange as estimated from PBE0 and PBE.

Unfortunately, all the GGA functionals studied in this work, including many commonly used in computational chemistry and catalysis, display MAEs from 37 and up to 76 kJ/mol. Notably, the PBE functional over-binds massively, giving a very large MSE of 72 kJ/mol and a MAE of 76 kJ/mol. This fits well with results by Duanmu and Truhlar finding errors for oxygen chemisorption energies on four metal surfaces of 25-80 kJ/mol, with consistent tendency to over-binding^[99]. This confirms our previous findings that both total energies and errors of the diatomic M-O systems and the full pure surfaces are very strongly correlated for a large number of data across the 3d, 4d, and 5d periods ($R^2 \sim 0.89$ for PBE)^[30], and thus our analysis is very relevant to the large systems, and at much larger data coverage. Using the modified RPBE improves the MAE to 48 kJ/mol and MSE to 35 kJ/mol, which is however still far from accurate. Studies using PBE and RPBE for transition metal oxygen bonds are thus likely to substantially over-bind oxygen and overestimate the metal's ability to bind and activate oxygen. If these studies are insightful, it is only when they compare different metals without emphasizing the absolute bonding, since the relative BDEs are more accurate than the absolute BDEs, as illustrated later in this paper. The local density functional SVWN was included for completeness as a reference point, which is mainly of theoretical interest as a limit of DFT, but which is still used. As expected^[32,40] SVWN over-binds massively with an MAE and MSE of 178 kJ/mol.

Figure 1C shows the relation between the overall accuracy of the functional, as measured by the MAE, and its systematic error in terms of over- or under-binding, measured by the MSE. MAEs display a minimum at around 25 kJ/mol as discussed above. Mostly, the best functionals in terms of MAE also have the smallest systematic errors, as visualized by the third-order polynomial fitting line which, in contrast to a second-order polynomial, condenses the MAEs near the hard limit of ~25 kJ/mol determined mainly by the random experimental errors. Accordingly, we have good coverage of both under-binding and over-binding functionals. We can also identify functionals for which systematic errors do not follow the expected trend. Notable examples are M06 and B3LYP. We expect a “universal” functional to approach zero MAE and MSE uniformly. It is also interesting that two of the best-performing functionals in terms of MAE, B98 and B3P86, systematically under-bind with MSEs of -7.7 kJ/mol and -9.2 kJ/mol, respectively, whereas B97-1 (MSE = -0.4 kJ/mol) has almost no tendency to systematically under-bind or over-bind (unsigned MSEs smaller than 5 kJ/mol are not significant due to the general uncertainty of the experimental data).

Figure 1D shows the relation between the precision, measured as the standard deviation of the signed errors, and the accuracy measured by MAE. We can postulate that the universal functional will have maximal precision and accuracy. To support this postulate, we find a significant linear relationship ($R^2 = 0.46$, $p = 7.64 \cdot 10^{-5}$) between the precision and the accuracy of the density functionals, using these definitions. This relationship is important, because it shows that as functionals become more accurate, they mostly tend to become more precise in their predictions. However, the relation is far from perfect, and there are clear outliers in **Figure 1D** mainly for heavily or dispersion-parameterized functionals or meta functionals. For example, M06-2X is very inaccurate for this dataset (MAE ~60 kJ/mol) but has a high precision (STD = 37 kJ/mol), whereas MN15-L is fairly accurate (MAE = 37 kJ/mol) but very imprecise, with a large scatter of BDE values (STD = 50 kJ/mol). B3LYP* is another example of a functional that breaks the relationship, being less precise than its accuracy would imply. Whether these tendencies hold more generally beyond the data studied here needs to be explored.

Figure 2. A) The five largest absolute errors (AE) for the 30 functionals of **Table 1**. Tabulated values available in **Table S26**. B) Distribution of errors for all 30 studied functionals. C) Distribution of errors for the B98 functional.

System dependencies and distributions of errors. To identify whether any systems cause particular problems, we compiled the systems with the five largest AEs for each functional, as summarized in **Figure 2A**, ordered by MAE (full data in **Table S41**). The most problematic experimental data were identified and replaced by alternative data in cases where several data exist,^[30] and the errors should therefore mainly indicate the failures of specific functionals to specific electronic structures, although some of the error remains due to uncertainties in the experimentally determined BDE values.^[34] The AEs of **Figure 2A** range from 70 to 283 kJ/mol,

and the most important general observation is that the severity of the pathological cases grows monotonically with the overall performance of the functional. Ten systems account for 118 of the 150 pathological cases of **Figure 2A**: LaO^+ (19 occurrences), NiO^+ (14), PdO^+ (14), AuO^+ (13), TaO (13), LaO (12), OsO (12), MnO (9), MnO^+ (6) and TaO^+ (6). For LaO^+ , no functional displays an AE smaller than 52 kJ/mol (B97-D) indicating that none of the functionals describe this system well, assuming that the experimental value can be trusted. Since DFT does not have special problems with the valence-iso-electronic YO^+ and other neighboring systems, we however suspect that the experimental number could be uncertain by perhaps 30 kJ/mol or so. **Figure 2B** and **Figure 2C** show the distribution of the obtained errors for all functionals together and for the best-performing functional B98. Both histograms clearly indicate that DFT-errors for a wide suite of functionals are approximately normal-distributed, which is an important observation and relates to the statistical significance and precision discussed in other places in the paper. The outlier in the total plot to the right in **Figure 2B** is due to the strongly over-binding LDA functional.

In order to test whether our results depend on the nature of the data set, we calculated the MSE, MAE, and STD also for subsets of the total data where we left out LaO^+ specifically, any one of the 10 groups (groups 3-12) and any one period (3d, 4d, or 5d). The errors obtained for these various subsets of data are summarized in Supporting information, **Tables S28-S40**. Leaving out LaO^+ from the analysis (**Table S27**) does not change the ranking of the top-3 functionals, the ranking changes in some cases by 1-2 positions for very similarly performing methods, and thus the uncertainty in the value of LaO^+ is not affecting the overall conclusions of our work. Similar rankings within a few positions are generally obtained by disregarding any group (**Tables S28-S37**), with the top-3 unaffected in all cases except group 9 where B2PLYP marginally enters top-3 at the expense of B3P86. Exclusion of any period (**Tables S38-S40**) affects the accuracy of some functionals: Disregarding the 3d metals (**Table S38**) puts B2PLYP and PW6B95 into top-3 instead of B98 and B97-1. Disregarding the 4d metals (**Table S39**) puts B97-2 in top-3 replacing B3P86. Disregarding the 5d metals (**Table S40**) also places B97-2 in the top 3 instead of B3P86. Exclusion

of 5d metals lowers the MAE for most functionals by up to 10 kJ/mol. Thus, the accuracy for the 5d transition metals is generally lower than for the 3d and 4d metals, probably due to relativistic treatments. Similar period-wise errors are likely to exist in studies using less complete relativistic treatments, for example comparing Pt and Pd/Ni catalysts. Except for this effect, general tendencies in performance are very robust to reasonable variations in the data set.

Figure S1 and **Figure S2** show the MAE and MSE separately for the transition metal groups 3-12. The ranking of the functionals changes noticeably from group to group which is unsurprising for such small subsets of data, with generally six calculated errors (three neutral and three charged molecules), and only four and three errors for group 7 and 12 respectively (**Table S1**). However, most of the trends observed for the overall data set prevail for groups individually. Almost all groups are best described by hybrids with 10-20% HF-exchange (or the double hybrid B2PLYP), in contrast to what is seen for some other ligands.^[40] The most notable exception is group 12, for which the GGAs perform well. The best performing functional for group 6 is OPBE, but other GGAs still perform poorly and hybrids with 10-20 % HF exchange still perform very well for group 6. The group-9 metals also stand out with the best performing functional (B3P86) having an MAE of only 9 kJ/mol and generally very small MAEs for the best functionals. The experimental uncertainties are not smaller for group-9 metals than for the overall data set. The best functionals perform well across all transition metal groups, showing no bias towards any d^q configurations, despite the fact that the M-O BDEs change by many hundreds of kJ/mol from very oxophilic early transition metals to very weakly binding late transition metals. Correspondingly, the GGA functionals such as PBE and RPBE widely used in theoretical catalysis perform poorly across all groups.

Figure 3. Mean absolute error (MAE) and mean signed error (MSE) for the 3d, 4d, 5d systems separately, the neutral MO species, and cationic MO^+ species.

Figure 3 shows the MAE and MSE when dividing into 3d, 4d and 5d systems. MAEs tend to increase somewhat when going from the 3d to the 4d and 5d transition metals. As an example, the MAE for B97-1 for the 3d metals is 22 kJ/mol, for the 4d transition metals it is 26 kJ/mol and for the 5d transition metals it is 32 kJ/mol. This trend partly relates to the treatment of relativistic effects, which introduces an error on the between-period comparisons of approximately 5 kJ/mol, as shown previously using CCSD(T), because the spin orbit-coupling treatment of the all-electron scalar-relativist 3d systems and the effective core potential-based 4d and 5d systems are not fully consistent^[30]; specifically, we expect (and see) that the 4d and 5d frozen-core systems have their spin-orbit coupling energy underestimated relative to the 3d systems. The fact that the 5d systems tend to be best described by the best-performing functionals is thus potentially a cancellation of a systematic error of ~5 kJ/mol. Most studies in computational transition metal chemistry will tend to carry this between-period error with them, at best, if they treat relativistic corrections in this way as typically recommended. Most studies in theoretical catalysis consider the relativistic corrections at levels lower than this, in some cases ignoring spin-orbit coupling of some of the periods or scalar-

relativistic effects of the 3d systems, which will make errors substantially larger and of the order of 10-25 kJ/mol, adding to other errors in the study^[30].

Despite these uncertainties due to the relativistic treatment, hybrids with approximately 10-20% HF-exchange remain the most accurate for all three periods. Thus, the introduced errors arising from between-period comparisons, while affecting local rankings of functionals and thus making strong conclusions on overall performance unjustified, the general tendencies in the performance of types of functionals is very robust.

Figure 3 also shows the accuracy when the data is divided into the neutral MO species and the cationic MO⁺ species. The neutral MO systems display a significantly lower MAE than the cationic MO⁺ systems. As an example, B3LYP has a MAE of 24 kJ/mol for the MO species while the MAE for the MO⁺ species it is 36 kJ/mol. This trend is rather general for all functionals, where one functional APFD shows a very large variation in accuracy being the most accurate for the MO systems with an MAE of 23 kJ/mol while for the MO⁺ systems the MAE has risen to 40 kJ/mol, APFD now only the 16th most accurate. For both neutral and cationic systems the hybrid-GGAs with 20 % HF-exchange are still the most accurate.

DFT trend predictions for M-O bonds with different M. In addition to the errors analyzed above, which relate to overall accuracy and precision of the data groups, it is also important to evaluate the ability of DFT to describe relative values of BDEs as particularly relevant to computational studies where several metals are compared, e.g. when rationalizing the performance of different metals as catalysts for O-O bond activation. **Figure 4** shows the linear relationship between computed and experimental BDEs for the four most accurate functionals B98, B97-1, B3P86 and B2PLYP. The slope, intercept, and R² values are tabulated for all functionals in **Table S42** and linear correlation plots for all functionals can be seen in **Figures S3-S32**.

Generally, excellent correlation is observed for all functionals, showing R^2 values from 0.94 to 0.98 (**Table S42**). The four functionals of **Figure 4** have R^2 values of 0.97–0.98 and standard errors from the regression line of 33–37 kJ/mol. This implies that trend predictions are, on average, within ≈ 35 kJ/mol of the experimental value for the four functionals of **Figure 4**. The slopes vary in the interval 0.95–1.04, indicating good scalability of DFT across regimes of weak and strong binding. For the best-performing functionals, the intersection with the y-axis varies from -9.0 (B98) to 23.2 (B2PLYP) kJ/mol, i.e. the functionals interpolate well to the zero-bonding limit. There is a small, surprising tendency for errors to be larger for the weakly bound systems with small BDEs, which we suspect is due to errors in the experimental data, since we expect DFT errors to scale with the magnitude of the computed values. **Figure 4** illustrates the good practice of using DFT chemical energies only comparatively as error cancellations strengthen significance.^[32] The excellent behavior of DFT in terms of trend predictions is also shown along the 3d, 4d, and 5d groups in **Figure S33**, where CCSD(T) from previous work and experimental BDEs are compared to B98 as a representative example of an accurate functional reproducing excellently the trends and hump structure of the d-block M-O bonds. This tendency is interestingly true for all hybrids studied, but much less true for GGAs. Applications of DFT to chemical processes often involve regimes of both stronger and weaker binding modulated by surfaces or other ligands, and thus strong performance in both limits is essential for accurate theoretical catalysis.

Figure 4. Linear correlation between experimental (Table 2) and computed BDEs (Tables S18-S22) for the four functionals with the lowest MAE for all 60 MO and MO⁺ systems A) B98 B) B97-1 C) B3P86 D) B2PLYP.

Relation to previous work. This paper is as far we know the first to consider all diatomic transition metal oxides in their totality, giving a complete perspective on the performance of DFT for these systems, in particular by testing universality (in the definition “uniform accuracy”^[100]) vs. variations due to group and period. A comparison to previous work on MO and MO⁺ systems is however still of interest.

Furche and Perdew^[50] computed the BDEs for nine neutral 3d transition metal oxides Sc-Cu, with the functionals BP86, PBE, TPSS, B3LYP and TPSSh using a QZVP basis and ZPE corrections (summarized in **Table S43**). Results for ScO, CrO, MnO, FeO, CoO, and CuO are in fair agreement with the computations of this work, with AEs less than 20 kJ/mol, close to the experimental uncertainty. However, for TiO, VO, and NiO there is substantial disagreement between the computed values with AEs up to 60 kJ/mol. The most notable difference in methodology is the neglect of relativistic corrections by Furche and Perdew and the smaller basis set for very electronegative, electron-rich oxygen. A comparison of the MAE compared to the experimental data can be seen in **Table S44**. Overall, the conclusions on relative performance are similar for the subset of data. The GGAs values of Furche & Perdew tended to be more accurate than in our work, whereas B3LYP and TPSSh are equally accurate or slightly more accurate in our study.

Zhao & Truhlar^[46] computed the BDEs of TiO, MnO and CuO with a QZVP basis using the TPSS, B3LYP, TPSSh, BLYP and B97-2 functionals (**Table S45**). AEs between 13 and 289 kJ/mol are observed relative to our computations, and generally the agreement is poor. Especially CuO calculated by TPSSh deviates by 289 kJ/mol. The treatment of relativistic effects and basis set cannot explain these differences. Based on the experimental data used and curated in this work, it would seem that some computations of the previous work^[46] have been performed on an excited state for example for CuO, which was common before the protocol of spin annealing, which we used in this and our recent work^[30,39,40].

Jensen et al.^[20] computed the BDEs for the ten neutral MO systems of Sc-Zn with a TZVP basis set and the B3LYP, PBE0, BP86, PBE and BLYP functionals (**Table S46**), ZPE corrections, and scalar-relativistic effects. The agreement is generally quite good with AEs of 16-46 kJ/mol across all functionals. The main exception is TiO where the AE is 342-349 kJ/mol. As has been established previously^[30] a new BDE value is appropriate and thus the old tabulated BDE for TiO of 372 kJ/mol is much too low. Without this error, agreement is generally very good (**Table S46**).

Finally, Rinaldo et al^[47] (**Table S47**) studied 18 of the 60 systems of this work, i.e. the diatomic neutral molecules from ScO-CuO and the cationic diatomics of ScO⁺-CuO⁺ using B3LYP with a LACVP^[101] basis set on the metals and 6-31G* on oxygen. Good agreement is again seen with AEs only above 20 kJ/mol for NiO, MnO⁺, CoO⁺ and CuO⁺ (AEs of 31, 47, 22 and 24 kJ/mol respectively), largely due to differences in basis set and relativistic treatment. The agreement indicates (but cannot guarantee) that the same lowest-energy configurations were used for all atoms and molecules in the two studies, something that is otherwise the cause of most discrepancy and difficulty for these types of systems.

Conclusions

Transition metal oxygen bond energies vary by many hundreds of kJ/mol across the periods of the d-block, and theoretical catalysis and inorganic chemistry regularly uses DFT to study oxygen binding to transition metals across the groups and 3d, 4d, and 5d periods. Non-uniform accuracy across the d-block could substantially limit the predictions of theoretical catalysis comparing e.g. Pd and Pt (period-wise) or Fe and Ni (group-wise). To explore the universality (transferability) of DFT across all of the d-block, we benchmarked 30 diverse density functionals against the bond dissociation enthalpies (BDE) of the 30 MO and 30 MO⁺ diatomic systems of all the 3d, 4d, and 5d metals, correcting for vibrational and relativistic effects.

We find that seven functionals, B98, B97-1, B3P86, B2PLYP, TPSSh, B3LYP, and B97-2, display mean absolute errors (MAE) < 30 kJ/mol for the d-block as a whole, which is remarkably good considering the experimental uncertainty and performance of CCSD(T) for the same data set^[30]. However, we also find that many commonly used functionals such as PBE and RPBE overestimate M-O bonding by +30 kJ/mol and display MAEs from 48-76 kJ/mol. RPBE and OPBE reduce the over-binding of PBE but remain very inaccurate.

We show that there is a significant but modest linear relationship ($R^2 = 0.46$) between the *precision* and *accuracy* of DFT, i.e. inaccurate functionals such as PBE and RPBE tend to produce much larger random errors. We also show that there are interestingly substantial outliers from this tendency. Most notably, highly parameterized functionals commonly deviate from the relationship. We stress that both the accuracy and the precision, estimating the expected spread in computed outcome, is of major importance to accurate trend predictions as required in theoretical catalysis and inorganic chemistry. We show that there is a tendency for 5d systems to be differently described than 4d and 3d systems, with an error of 5-10 kJ/mol, relating partly to the relativistic treatment. We expect this error to prevail also in the many studies in theoretical catalysis that routinely compare 5d and 4d systems with relativistic corrections less elaborate than used here. The 4d and in particular the 5d frozen-core systems may have their spin-orbit coupling energy underestimated relative to the 3d systems.

The best-performing hybrids all tend to have 10-30% HF exchange, but we show that this requirement can be relaxed by double hybrids, with B2PLYP showing encouraging results. We note that uniform good accuracy across the d-block is one thing, the functional also needs to be accurate for diverse ligands binding to the metals. Considering previous results for metal-hydrogen bonds^[39], we can now conclude that chemical processes involving both M-O and M-H bond breaking or formation (e.g. transition metal catalyzed water oxidation, or oxygen reduction reactions) require advanced functionals such as double hybrids (B2PLYP), range-separated hybrids (CAMB3LYP), or meta hybrids (B98 or PW6B95), which uniquely show uniform accuracy and precision for both M-O and M-H bonds across the d-block.

Most functionals describe trends well, quantifying DFT's strength in relative predictions. Finally, we note that our benchmark study is relevant also to larger systems since, as shown previously^[30], the local M-O bonds dominate ($R^2 \sim 0.89$) the O₂ binding energies of full metal surfaces, as also expected from the fact that variations in cohesive energies (enthalpies of atomization of the metals) are up to an order of magnitude smaller than variations in M-O BDEs

and O₂ chemisorption energies, which puts an upper limit to the impact of metal-metal modulation effects on the local M-O bond at the metal surface.

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Supporting Information

The Supporting information file contains the experimental BDEs and the computed BDEs, including all converged electronic energies and other parameters needed to compute the BDEs from Equation 1. The supporting information file also contains the tabulated values for all figures in the text and the tabulated values of statistical assessments referred to in the text.

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We explored the ability of 30 density functionals to describe all bond enthalpies of the 30 MO and 30 MO⁺ 3d, 4d, and 5d systems. Some functionals (B98, B97-1, B2PLYP, and TPSSh) display errors below 30 kJ/mol, but performance varies greatly. We analyze the failure and success, accuracy and precision, as a first step towards accurate DFT for M-O bonds as required for theoretical catalysis.