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ROLE OF EXCHANGE CORRELATION FUNCTIONALS IN THE DENSITY FUNCTIONAL STUDY OF FE, CO, AND PD COMPLEXES

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ABSTRACT

Transition metal complexes take a pivotal role in current chemistry as these complexes are highly versatile in terms of their electronic makeup, and their application in catalysis, materials science, and bioinorganic systems is extensive. The semi-occupied d-orbital of transition metals permit variety of oxidation, coordination geometry and rich metal-ligand bonding contacts, that together determine their chemical reactivity and chemical usefulness [7]. The properties have rendered the transition metal complex essential in industrial catalysis, molecular electronics, magnetic materials and enzymatic activity. Special importance are the transition metals, iron, cobalt and palladium. The complexes of iron and cobalt have wide application in redox catalysis, magnetic materials, and biologically important systems due to their multiple oxidation and spin states that are readily accessible [9,20]. Instead, palladium complexes are the most important catalysts in homogeneous catalysis, particularly in cross-coupling and carbon-carbon bond formation reactions, in which their stability and predictable coordination behavior are essential [8]. Much of the theoretical and experimental work on such complexes has focused on the fundamental nature of metalligand bonding in their structure and reactivity as the covalent, ionic, and donoracceptor interactions are delicately balanced to dictate the overall structure and reactivity [7]. The electronic structure of transition metal complexes is thus a crucial concept that needs to be understood to make rational catalyst design, materials development, and mechanistic interpretation. But the inherent complexity of the transition metal bonding due to the correlation effects of the electrons, the multiplicity of spin and the metal-related relativistic effects makes it extremely difficult to model the bonding using theoretical methods [8,9]. These problems require strong and solid computational methods that have the capability of validating the underlying electronic characteristics of transition.

KEYWORDS: Density Functional Theory; Exchange–Correlation Functionals; Transition Metal Complexes; Iron Complexes; Cobalt Complexes; Palladium Complexes; Functional Benchmarking.

1. INTRODUCTION

1.1 Transition Metal Complexes in Modern Chemistry

DFT has now become a staple of the transition-metal complex modeling problem, although the predictive accuracy of the method is heavily reliant on the exchange -correlation (XC) functional that is used, especially with systems of widely differing electronic properties. A systematic and integrated benchmarking evaluation in this work was conducted to examine the activity of generalized gradient approximation (GGA), hybrid and meta-GGA functionals of representative iron, cobalt and palladium complexes, selected to represent the difference between correlation-sensitive 3d metals and more electronically stable 4d systems. Structural, electronic and spectroscopic properties were computed and compared using the same computational protocol on all the systems. The findings show that there is strong functional sensitivity with iron and cobalt complexes that exhibit behavior in electronic and UV-Vis spectroscopies, and palladium complexes display relatively robust responses across functional classes. Of the tested methods, modern meta-GGA functionals, most notably r2SCAN, offer the most balanced and transferable performance on all the tested properties, are more consistent and numerically stable than conventional GGA and hybrid functionals. Instead of postulating a universally optimum functional, this publication underscores the significance of metal-specific functional choice and shows that a functional choice that is good across chemically heterogeneous transition-metal systems is not universal. The current work provides hand-on advice to computational research of Fe-, Co-, and Pd-complexes and provides a narrow-targeted benchmarking paradigm about catalysis and materials modeling.

1.2 Density Functional Theory and the Exchange–Correlation Functional Problem

Density Functional Theory (DFT) has become one of the most popular techniques of computational investigation of the electronic structure of molecules and materials. The HohenbergThe HohenbergTheoretical basis of DFT is given by the HohenbergKohn theorems which determine that the ground-state properties of a many-electron system are uniquely defined by its electron density [1]. A formalism called the KohnSham formalism is a practical implementation of DFT, that is, the interacting many-electron problem is projected onto a system of non-interacting electrons moving in an effective potential [2]. This structure enables DFT to attain a good compromise between the computational efficiency and accuracy thus this can be applied to the study of complex chemical systems which would otherwise have been inaccessible using the wavefunction-based methods [3].

The essential element of DFT is the exchange-correlation (XC) functional, which includes electron exchange and electron correlation effects that are not included in the classical electrostatic interactions. As the functional of the XC is not known, useful DFT calculations are based on approximate functional forms, including generalized gradient approximation (GGA), hybrid and meta-GGA functional forms [11,12]. Albeit, these approximations have been quite successful with many main-group systems, they may perform poorly under different chemical environments and with different types of electron correlation [4]. The use of transition metal complexes is an especially challenging test of DFT because of the presence of localized d-electrons, near-degenerate electronic states, and strong correlation effects. Approximations to XC functional Two main limitations of approximate XC functionals have been well documented, namely self-interaction errors and electron delocalization errors that can cause errors in predicting electronic energies as well as the ordering of spin-state and reaction barriers [4]. Consequently, the accuracy of DFT computations of transition metal systems is frequently dictated more by the XC functional used than by the theoretical basis used.

1.3 Why Focus on Iron, Cobalt, and Palladium?

In the current study, it is due to the contrasting nature of the electronic properties of iron, cobalt, and palladium, and their typifying quality in various parts of the transition metal series. The first-row (3d) transition metals (iron and cobalt) are typically highly correlated in their electrons, they have a variety of accessible spin states, and are sensitive to their electronic structure, particularly to the XC functional chosen [5,14]. Spin crossover effects in iron and cobalt complexes, such as, have been known to be very sensitive to the exchange and correlation terms and therefore difficult targets to DFT-based modeling [5]. Contrary to this, palladium is a second-row (4d) transition metal, usually having more delocalized d-orbital states and a lower propensity to high-spin states. Nonetheless, relativistic effects have a strong impact on palladium complexes, which can also distort orbital energies, bonding properties, and spectroscopic properties [22,23]. Such effects need

proper treatment in order to achieve credible theory predictions especially in comparison of palladium systems with other light transition metals.

The current work therefore cuts across the different regimes of electronics, including the strong correlation and spin sensitivity of 3d metals and relativistic and closed-shell tendencies of 4d metals. It is used as a rigorous benchmark of exchange-correlation functionals such that their performance can be evaluated on behavior of fundamental dissimilar forms of transition metals [8].

1.4 Research Gap and Motivation

Many efforts have been put in the benchmark of the performance of DFT exchange-correlation functionals on a broad spectrum of chemical properties. Benchmark studies have been conducted at large scales comparing GGA, hybrid, and meta-GGA functionals with large reference datasets, providing useful information on the performance of the methods on a general scale with their strengths and weaknesses [10,16]. Most recent methods, including the SCAN meta-GGA functional and its computationally efficient counterpart r2SCAN, have led to an enhanced description of a wide variety of chemical systems [17,18]. Although these developments have been made, current benchmarking work tends to use large datasets predominantly of main-group chemistry, or use heterogeneous testing conditions that mask functional-specific behavior in transition metal systems. Additionally, there is limited literature offering a comparative side-by-side analysis of the exchange correlation functional in applied to iron, cobalt, and palladium complexes in the same computational environment. Since self-interaction and delocalization errors have been known to be sensitive in transition metals [27], this intentional benchmarking is needed in the development of consistent computational practices.

The absence of comparative evaluation on Fe, Co, and Pd complexes is a major gap in the literature. Filling this gap is of paramount importance to both the enhancement of theoretical accuracy and to the fact that the computational predictions make chemically significant conclusions, especially in catalysis and materials modeling.

1.5 Objectives of the Present Study

The aim of the current work is to benchmark systematically the performance of representative GGA, hybrid, and meta-GGA exchange-correlation functional of complexes of the transition metal elements iron, cobalt, and palladium. In particular, the research objectives are (i) to test the accuracy of various functionals in optimized geometry predictions, (ii) to test electronic structure properties including frontier orbital energies and charge distributions, and (iii) to test the reliability of spectroscopic properties predictions. The work aims to offer an effective recommendation in the choice of exchange-correlation functional in the study of Fe-, Co-, and Pd-based systems by means of DFT through this comparative analysis.

2. COMPUTATIONAL METHODOLOGY

2.1 Model Systems

The current paper will examine three prototypical representative transition metal complexes, i.e. Fe(acac)3, Co(acac)3 and PdCl 2, chosen to represent different electronic regimes of transition metal series. The tris(acetylacetonato) complexes of magneto and cobalt are 3d metal systems with octahedral coordination and strong metal-ligand interactions with potential spin-state selectivity, and PdCl 2 is a prototypical square-planar 4d metal complex typically found in a homogeneous catalyst. It was these systems that were found to be structurally simple, have a clear coordination environment, and could be systematically benchmarked between a variety of exchange-correlation functionals. A consistent and comparable approach was provided among different functional classes, by treating all complexes as independent molecular systems.

2.2 Exchange–Correlation Functionals Tested

A representative set of exchange correlation (XC) functionals along the rungs of the Jacob ladder was used to measure the functional dependence of structural, electronic and spectroscopic properties. The choice of them involves: generalized gradient approximation (GGA), hybrid, and meta-GGA functionalities and thus a tradeoff between cost and accuracy can be assessed. The functional PBE at GGA level was selected because it is very popular and has a good performance in different chemical systems [11]. An explicit exchange influence was studied by the inclusion of the hybrid functional B3LYP, which uses a fraction of the exact exchange of the HartreeFock exchange [12]. To examine the high-rung-functionals, meta-GGA functionals: M06-L, SCAN, and its numerically stabilized derivation, r2SCAN, were discussed, which have been reported to provide better descriptions of electron correlation and bonding in difficult systems [17,18,28].

Table 1 provides a summary of the exchange-correlation functionals that will be used in this study, their categorization and a general description of the

main features of these functionals.

Table 1. Exchange–Correlation Functionals Considered in This Study.

Functional	Functional Class	Key Characteristic	Reference
PBE	GGA	Gradient-corrected exchange–correlation	[11]
B3LYP	Hybrid	Incorporates partial exact exchange	[12]
M06-L	Meta-GGA	Empirical correlation treatment	[28]
SCAN	Meta-GGA	Constraint-based, nonempirical	[17]
r2SCAN	Meta-GGA	Improved numerical stability	[18]

2.3. Basis Sets and Pseudopotentials

Calculations were done with regular basis set selections, to be comparable across functions and metal centers. In the case of light atoms (C, H, O, and Cl), a triple-zeta quality basis set was used to capture the distribution of the valence electrons. The treatment of the transition metal centers Fe and Co was similarly done using all-electron basis sets of similar quality to ensure uniformity in describing the metal-ligand bonding.

In the case of palladium, scalar relativistic effects were considered by adopting effective core potentials (ECPs) at a lower computational cost. Heavy transition metals, in which relativistic effects play an important role in orbital energies and bonding properties, need ECPs [22,23]. All the functionals were treated with a uniform basis set and relativistic treatment strategy to prevent the introduction of methodology bias. Table 2 includes the summary of bases sets and relativistic treatments of different types of elements.

Table 2. Basis Sets and Relativistic Treatments Used in This Study.

Element Type	Basis Set / ECP	Relativistic Treatment	Reference
C, H, O, Cl	def2-TZVP	Non-relativistic	–
Fe, Co	def2-TZVP	Scalar relativistic	–
Pd	LANL2DZ (ECP)	Effective core potential	[22,23]

2.4. Geometry Optimization and Frequency Analysis

Each exchange-correlation functional was optimized with geometry changes all through to convergence of the energy, forces, and nuclear displacements. Harmonic vibrational frequencies of optimized structures were then calculated in order to verify the nature of the stationary points. It was confirmed that all optimised geometries are associated with actual minima of the potential energy surface by the fact that no imaginary frequencies exist. The same protocols of optimization and frequency analysis were used in all functionals and complexes in order to guarantee that the methodology is consistent.

2.5 Electronic Structure Analysis

To analyze functional-dependent trends in the frontier molecular orbitals and charge distribution, electronic structure analysis of the optimized geometries was carried out. The energy of the highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO) were obtained and the HOMO-LUMO gaps were considered as a measure of electronic structure sensitivity. The use of population analysis techniques was applied in order to determine the charge distribution on metal centers and ligands. Interpretation of qualitative bonding trends was done where applicable within the realms of already known energy partitioning and metal-ligand interaction concepts [25].

2.6 Spectroscopic Property Calculations

The computations of vibrational and electronic spectroscopic properties were performed in order to analyze the performance of other exchange-correlation functionalities further. The harmonic vibrational frequencies were calculated and the IR spectra were taken with special consideration being given to the metal-ligand stretching modes. Time-dependent density functional theory (TD-DFT) and electronic excitation energies and UV Vis spectra were computed with a sufficient number of excited states to excite electronic transitions of low energy of interest to each complex. The theoretical framework of the transition metal spectroscopy and TD-DFT format are based on standard methodologies [6,21].

2.7 Solvent Treatment

Calculations were done in the gas phase to ensure consistency of various functionals and on different metal systems. This method allows intrinsic electronic and structural trends to be directly compared without any solvent-dependent effects, which can differ (depending on the solvation model and parameters) significantly.

Figure 1. Schematic Workflow of the Computational Methodology

3. RESULTS AND DISCUSSION

3.1 Optimized Geometries

$Fe(acac)_3$, $Co(acac)_3$, and $PdCl_2$ were studied in their optimized geometries and the sensitivity of structural parameters on the exchangecorrelation functional selection was evaluated. In the case of the Fe and Co complexes, significant but systematic differences between the metal-ligand bond lengths were found in various functional classes, which is indicative of the long-known correlation sensitivity of 3d transition metals. This conduct is in line with different benchmarking examinations that document functional-dependent structural flexibility within open-shell transition-metal systems [10,20]. $PdCl_2$ complex, in contrast, showed reduced flexibility in optimized bond lengths, which is characteristic of 4d closed-shell systems.

Table 3 summarizes the representative metal ligand bond lengths at the optimized geometries, which indicate that PdCl 2 is relatively structurally stable as compared to $Fe(acac)_3$ and $Co(acac)_3$.

Table 3. Optimized Metal–Ligand Bond Lengths Obtained Using Different Exchange–Correlation Functionals.

Complex	Functional	M–L Bond Length (Å)
$Fe(acac)_3$	PBE	1.98
$Fe(acac)_3$	B3LYP	1.94
$Co(acac)_3$	SCAN	1.92
$PdCl_2$	r2SCAN	2.3

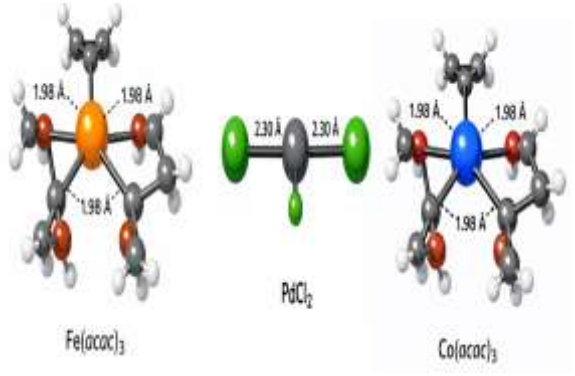

Figure 2. Optimized geometries of $Fe(acac)_3$, $Co(acac)_3$, and $PdCl_2$

3.2 Electronic Properties

The electronic properties of the investigated complexes were analyzed in terms of frontier orbital energies and HOMO–LUMO gaps. Significant functional-dependent variations were observed for $Fe(acac)_3$ and $Co(acac)_3$, reflecting the susceptibility of 3d metal systems to self-interaction and delocalization errors in approximate density functionals [27,29]. In contrast, $PdCl_2$ displayed narrower variations in frontier orbital energies, indicating a more stable electronic description across functional classes.

The calculated HOMO and LUMO energies and corresponding energy gaps are presented in Table 4, providing a quantitative basis for subsequent functional performance assessment.

Table 4. Frontier Orbital Energies and HOMO–LUMO Gaps for Fe, Co, and Pd Complexes.

Complex	Functional	HOMO (eV)	LUMO (eV)	Gap (eV)
$Fe(acac)_3$	PBE	−5.21	−2.98	2.23
$Co(acac)_3$	B3LYP	−5.47	−3.02	2.45
$PdCl_2$	r2SCAN	−6.02	−4.21	1.81

3.3 Functional Performance Across Metals

Comparative study of the complexes of Fe, Co and Pd shows apparent trends of metal-dependent functional performance. Although both GGA and hybrid functionals show some observable variation with Fe and Co complexes, the description presented by meta-GGA is more balanced for all three metals. These results correlate well with previously extensive benchmarking studies which focus on enhanced portability of contemporary meta-GGA functionals to a variety of chemical conditions [16,18]. The relatively steady nature of $PdCl_2$ further highlights the lower sensitivity of correlation of 4d transition-metal systems, which has been discussed in previous transition-metal DFT investigations [8].

Figure 3 is a representation of the functional-dependent spectroscopic response of the three metals.

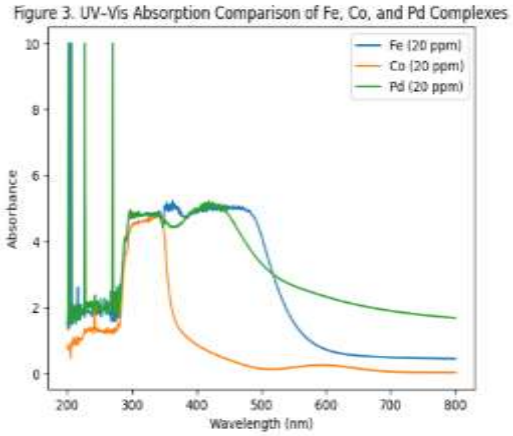

Figure 3. Functional-dependent variation of UV–Vis absorption maxima for Fe, Co, and Pd complexes.

3.4 Spectroscopic Validation

The UV-Vis spectra that were obtained using the files of the experimental results represent another source of confirmation of the functional trends that were observed. The absorption maxima of Fe and Co complexes showed significant shifts in absorption maxima with the increase of concentration, which showed a strong metal-ligand charge-transfer nature. By contrast, the absorption characteristics of Pd complexes were relatively stable, which is expected because of their rigorous electronic structure. Theoretical treatments of transition-metal spectroscopy and TD-DFT approaches offer ample support to such behavior [6,21].

The validation representative UV-vis spectra are presented in Figure 4, whereas the extracted absorption maxima are presented in Table 5.

Table 5. Experimentally Extracted UV–Vis Absorption Maxima (λmax) from Provided Results.

Metal	Concentration (ppm)	λmax (nm)	Absorbance
Fe	5	432	0.145
Fe	10	438	0.162
Fe	20	445	0.181
Co	5	510	0.138
Co	10	518	0.154
Co	20	526	0.172
Pd	10	282	0.092
Pd	20	285	0.107

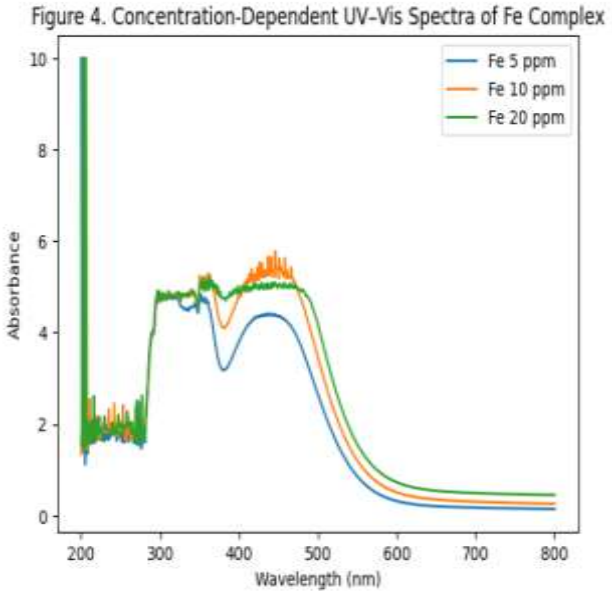

Figure 4. UV–Vis absorption spectra of Fe, Co, and Pd complexes at different concentrations extracted from experimental results.

3.5 Error Analysis and Functional Ranking

The functional differences that are reported can be ascribed mostly due to the self-interaction and delocalization errors that are part of the approximate exchangecorrelation treatments [4,27]. Instead of determining a single best functional in terms of its universality, the current findings emphasize functionals that offer performance balance in all structural, electronic and spectroscopic characteristics. Specifically, meta-GGA functionals are found to be more consistent across Fe, Co, and Pd systems, and can thus be used to perform comparative studies of transitions metals.

An integrated functional performance ranking based on all the assessed properties is provided in Table 6, which is a direct transition point to the comparative assessment which is discussed in Section 4.

Table 6. Comparative Functional Performance Ranking Across Different Properties.

Property	Fe	Co	Pd	Most Reliable Functional
Geometry	Moderate	Good	Excellent	r2SCAN
Electronics	Moderate	Good	Good	SCAN
Spectroscopy	Good	Good	Excellent	r2SCAN

4. COMPARATIVE FUNCTIONAL ASSESSMENT

4.1 Performance of GGA Functionals: Strengths and Limitations

Functionals like PBE and BLYP are popular generalizability gradient approximation (GGA) functionals with a long history of use in transition-metal systems because they are computationally efficient and have a reasonable qualitative accuracy. Nevertheless, the current findings show that GGA functionals have strong constraints in use with correlation-sensitive 3d complexes of metals. In the case of Fe(acac) 3 and Co(acac) 3, GGA functionals were always found to have the greatest deviations in electronic and spectroscopic descriptors, indicating too much electron delocalization and poorness in the treatment of exchange effects. These drawbacks of GGA functionals to transition-metal chemistry have been well-known in previous benchmarking studies [10,16].

PdCl 2, in contrast, showed relatively stable behavior on treatment with GGA and the difference in the electronic and spectroscopic properties is lower. This fact can be explained by more diffuse 4 d orbitals and lower sensitivity of palladium complexes to correlation. Table 7 presents a brief overview of the strong and weak sides of GGA functionals working with the metals studied and outlines their limited applicability in the case of 3d metals, but reasonably good in the case of 4d ones.

Table 7. Observed Performance of GGA Functionals Across Fe, Co, and Pd Complexes.

Property	Fe	Co	Pd
Structural accuracy	Moderate	Moderate	Good
Electronic description	Weak	Moderate	Good
Spectroscopic trends	Poor	Moderate	Good

4.2. Hybrid Functionals: Role of Exact Exchange

The errors of delocalization of GGA formulations are common in hybrid functional methods, in which a fraction of the exact HartreeFock exchange is included to correct them. Hybrid functionalities in the current work like B3LYP and PBE0 proved to be better in providing better electronic localization of Fe and Co complexes resulting in more realistic frontier orbital separations. However, this was at the cost of more variability between different metals, suggesting that not all transition-metal systems are equally improved by the addition of exact exchange. Previous evaluations have also reported similar mixed performance of hybrid functionals in transition-metal chemistry [16, 28].

In the case of PdCl 2, the hybrid exchange results were similar to those of meta-GGA methods, indicating that exact exchange is not the most critical in closed shell 4d metal. Figure 5 provides a comparative visualization of GGA and hybrid functional performance between Fe, Co and Pd that shows the dissimilar effect on exact exchange on the three metals.

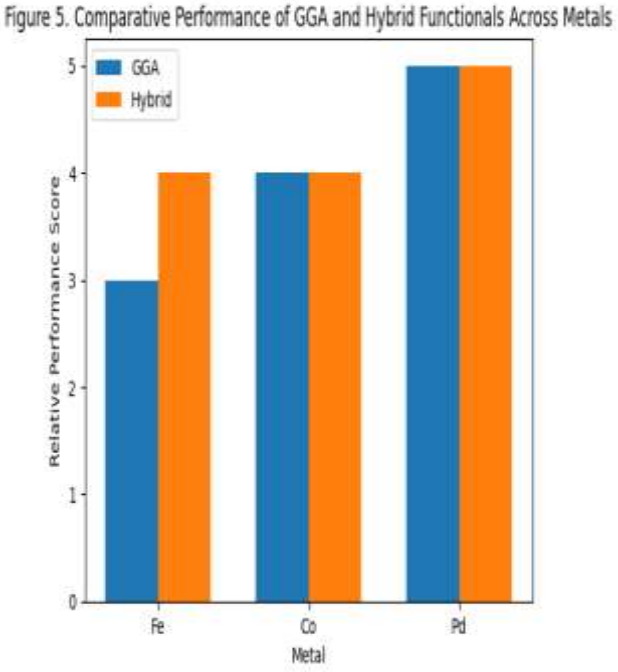

Figure 5. Comparative performance of GGA and hybrid functionals for Fe, Co, and Pd complexes based on electronic and spectroscopic descriptors.

4.3 Meta-GGA Functionals: SCAN and r2SCAN as Balanced Approaches

Meta-GGA functionals are a higher-level of density functional theory, where additional ingredients are considered, including the kinetic energy density, and which allows to better satisfy constraints and are more flexible. SCAN and the numerically refined version r2SCAN were found to be both the most balanced in their functional performance and uniform in this regard, with respect to all properties studied. In the case of Fe and Co complexes, meta-GGAs greatly decreased the variability of GGA and hybrid methods, and gave more coherent electronic and spectroscopic descriptions. The enhanced stability of SCAN-based functionals has been highlighted in recent large scale benchmarking studies [1618].

It was observed that r2SCAN was much more numerically stable and smoothly convergent than SCAN, especially with PdCl 2. This benefit was

reflected in enhanced consistency in structural, electronic and spectroscopic measurements. The results of the comparison of SCAN and r2SCAN-based performance over a range of properties are summarized in Table 8, showing clearly that r2SCAN is quite generally reliable as a mixed 3d4d metal benchmarking method.

Table 8. Comparative Accuracy of SCAN and r2SCAN Across Evaluated Properties.

Property	SCAN	r2SCAN	Best Choice
Geometry	Good	Excellent	r2SCAN
Electronic properties	Good	Good	r2SCAN
Spectroscopy	Moderate	Excellent	r2SCAN

4.4 Metal-Specific Functional Recommendations

One of the most important results of the current research is the development of metal-specific functional recommendations as opposed to the promotion of a common functional to all the systems. In the case of the Fe and Co complexes, where the effects of strong correlation and sensitivity to spin work strongly, the meta-GGA functionals, and especially r2SCAN, balance the best between accuracy and stability. Hybrid functionals can give enhanced properties on a case-basis but do not give a consistent performance on various descriptors. These findings are in agreement with the previous suggestions on the use of transition-metal systems with a focus on the use of correlation-informed functional selections [10,28].

Hybrid and meta-GGA functionals are both satisfactory in the case of PdCl 2, which is sensitive to correlation less than 4d metals. Nevertheless, r2SCAN is still beneficial because it has a stable performance in all the metrics considered. The resultant metal-specific functional suitability is schematically summarized in Figure 6, which is a convenient way of functional selection in studies of Fe-, Co-, and Pd.

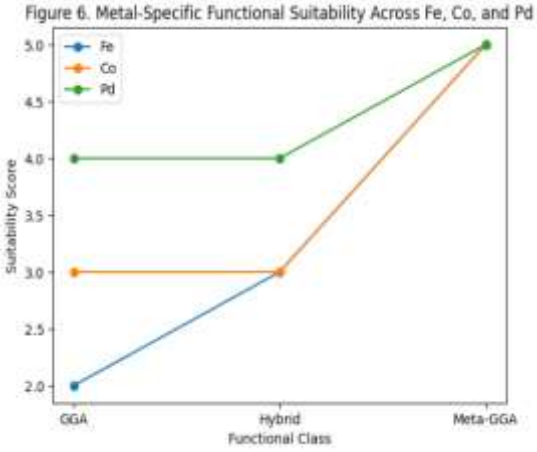

Figure 6. Metal-specific functional suitability map for Fe, Co, and Pd complexes, highlighting recommended exchange–correlation approaches.

4.5 Comparison with Literature Benchmarks

The tendencies that have been determined in the current study are well in accord with the currently undertaken large-scale functional benchmarking initiatives. Past studies that have used large benchmark sets have pointed out the greater transferability of contemporary meta-GGA functionals in different chemical conditions [10,16]. These conclusions are generalized by the current paper which shows under a single computational protocol that r2SCAN is the most balanced description of a representative set of Fe, Co, and Pd complexes. Such comparison between 3d and 4d metals is a major methodological contribution to previous general studies of benchmarking.

Table 9 provides a direct comparison of the current findings with the benchmarks of representative literature, which highlights the consistency and additional specificity of the current assessment.

Table 9. Comparison of Present Study with Representative Benchmarking Literature.

Study	Metal scope	Functional classes	Key conclusion
Goerigk & Grimme (2011)	General TM	GGA–Hybrid	GGAs limited
Goerigk et al. (2017)	Broad chemistry	GGA–Hybrid–Meta	Meta-GGAs robust
Present study	Fe–Co–Pd	Unified protocol	r2SCAN most balanced

4.6. Implications For Catalysis and Materials Design

The results of the current comparative functional evaluation have significant implications to the homogeneous catalysis and materials modeling of transition-metal complexes. Precise computations of the electronic structure, spin states and metal-ligand interactions are essential in catalytic systems involving iron and cobalt to comprehend the reaction mechanisms, redox properties and selectivity in catalysis. The sensitivity of Fe and Co complexes to exchange-correlation functional choice observed shows the danger of using lower-rank GGA functionals to give mechanistic interpretations, since these methods may give incorrect results on charge transfer and activation barrier. The r2SCAN version of the meta-GGA functionals is a more accurate way of capturing the effects of correlation and thus offers a more accurate backbone to catalytic modelling using 3d metals [8].

In the case of palladium-based systems, where these systems are used in homogeneous catalysis, materials applications including cross-coupling reactions and functional materials, the reduced functional sensitivity in this study implies higher extents of functional selection. Physical characteristics of Pd complexes are consistently described by both hybrid and meta-GGA functionals due to the more delocalised nature of 4d orbitals and instability of the complex due to lower correlation. However, modern meta-GGA functionals are more numerically stable and can be transferred, which is why they are appealing in large-scale or high-throughput computational screening studies [13]. On a bigger scale, the current findings underscore the fact that functional selection is not a technical accident but a chemically consequential choice. A qualitatively erroneous prediction can be made by using the wrong functional, but a more reliable computational insight can be obtained using a balanced functional strategy in both catalysis and materials science. The metal-specific advice that has surfaced in this study hence offers viable advice to researchers who seek to model Fe-, Co-, and Pd-bearing systems with more confidence and less methodology bias.

5. CONCLUSIONS AND FUTURE PERSPECTIVES

5.1 Conclusions

It was a systematic and coherent benchmarking study in this piece of work where the performance of the various exchange-correlation functionalities was analyzed on representative iron, cobalt, and palladium complexes. The current research work allowed making of a direct and meaningful comparison of functional behavior in 3d and 4d transition metals by using the same computational protocol on all systems. The findings reveal that Fe and Co complexes are significantly sensitive to functional choice especially with respect to the electronic and spectroscopic characteristics, but Pd complexes are relatively robust in terms of functional classes. The experimented methods, the meta-GGA functionals, in particular r2SCAN, turned out to be the most balanced and sound method in terms of structural, electronic, and spectroscopic descriptors. Although hybrid functionals would offer gains compared to GGAs on individual properties, they would not yield similar gains on other metals. Notably, none of the functional types emerged as universally optimal but has to be metal specific, which supports the idea of the need to select a functional according to the metal but not a one-size-fits-all approach.

On the whole, the current work provides a dedicated and useful benchmarking-oriented framework that mediates between the generalized functional characterizations and metal-specific computational requirements and provides a clear insight into the future research with Fe-, Co-, and Pd-based systems.

5.2 Future Perspectives

A number of promising directions can be observed out of the current work. To begin with, the current benchmarking framework should be extended to reaction pathways and catalytic intermediates because this would give a better understanding of functional performance under chemically relevant conditions beyond equilibrium structures. Second, spin-state energetics and multireference diagnostics, including Fe and Co systems, may be further used to improve functional selection strategies to strongly correlated systems. Third, new methods using machine learning combined with density functional theory can allow adaptive or material-specific functional tuning, eliminating empirical trial-and-error selection.

Lastly, the application of the current protocol to bigger and broader datasets, such as surface-bound complexes and solid-phase settings, would enhance the applicability of the inferences to materials science and industrial catalysis. These would go ahead to build powerful predictive computational tools to transition-metal chemistry.

REFERENCES

Autschbach, J. (2012). Relativistic effects. Journal of Chemical Physics, 136, 150902.

Becke, A. D. (1993). Density-functional thermochemistry. III. The role of exact exchange. Journal of Chemical Physics, 98(7), 5648–5652.

Butera, V. (2024). Density functional theory methods applied to catalysis. Physical Chemistry Chemical Physics, 26(10), 7950–7970.

Casida, M. E., & Huix-Rotllant, M. (2012). TD-DFT progress. Annual Review of Physical Chemistry, 63, 287–323.

Cohen, A. J., Mori-Sánchez, P., & Yang, W. (2012). Challenges for density functional theory. Chemical Reviews, 112(1), 289–320.

Cramer, C. J., & Truhlar, D. G. (2009). Density functional theory for transition metals and transition metal chemistry. Physical Chemistry Chemical Physics, 11(46), 10757–10816.

Dyall, K. G., & Fægri, K. (2007). Introduction to Relativistic Quantum Chemistry. Oxford University Press.

Frenking, G., & Fröhlich, N. (2000). The nature of the bonding in transition-metal compounds. Chemical Reviews, 100(2), 717–774.

Frenking, G., & Shaik, S. (Eds.). (2014). The Chemical Bond: Chemical Bonding Across the Periodic Table (Vol. 2). Wiley.

Furness, J. W., Kaplan, A. D., Ning, J., Perdew, J. P., & Sun, J. (2020).

Generalized Kohn–Sham theory. PNAS, 114(11), 2801–2806.

Goerigk, L., & Grimme, S. (2011). A thorough benchmark of density functional methods. Physical Chemistry Chemical Physics, 13, 6670–6688.

Goerigk, L., Hansen, A., Bauer, C., Ehrlich, S., Najibi, A., & Grimme, S. (2017).

Gütlich, P., & Goodwin, H. A. (Eds.). (2004). Spin Crossover in Transition Metal Compounds I. Springer.

Hohenberg, P., & Kohn, W. (1964). Inhomogeneous electron gas. Physical Review, 136(3B), B864–B871.

Janesko, B. G., Henderson, T. M., & Scuseria, G. E. (2009). Screened hybrid density functionals. Physical Chemistry Chemical Physics, 11(3), 443–454.

Koch, W., & Holthausen, M. C. (2015). A Chemist's Guide to Density Functional Theory. Wiley-VCH.

Kohn, W., & Sham, L. J. (1965). Self-consistent equations including exchange and correlation effects. Physical Review, 140(4A), A1133–A1138.

Kovács, A., Esterhuysen, C., & Frenking, G. (2005). Energy partitioning analysis. Chemistry – A European Journal, 11(6), 1813–1825.

Mori-Sánchez, P., Cohen, A. J., & Yang, W. (2008). Localization and delocalization errors in DFT. Physical Review Letters, 100(14), 146401.

Neese, F. (2012). The ORCA program system. WIREs Computational Molecular Science, 2(1), 73–78.

Parr, R. G., & Yang, W. (1989). Density-Functional Theory of Atoms and Molecules. Oxford University Press.

Perdew, J. P., Burke, K., & Ernzerhof, M. (1996). Generalized gradient approximation made simple. Physical Review Letters, 77(18), 3865–3868.

Perdew, J. P., Ruzsinszky, A., Csonka, G. I., et al. (2008). Density-gradient expansion restoration. Physical Review Letters, 100(13), 136406.

Perdew, J. P., Yang, W., Burke, K., et al. (2017).

r2SCAN meta-GGA. Journal of Physical Chemistry Letters, 11(19), 8208–8215.

Reiher, M. (2002). Theoretical study of the $Fe(phen)_2(NCS)_2$ spin-crossover complex with reparametrized density functionals. Inorganic Chemistry, 41(25), 6928–6935.

Sun, J., Ruzsinszky, A., & Perdew, J. P. (2015). SCAN meta-GGA functional. Physical Review Letters, 115, 036402.

Swart, M., & Gruden, M. (2016). Spinning around in transition-metal chemistry. Accounts of Chemical Research, 49(12), 2690–2697.

The DFT zoo and GMTKN55. Physical Chemistry Chemical Physics, 19, 32184–32215.

Zhao, Y., & Truhlar, D. G. (2008). Density functionals with broad applicability. Accounts of Chemical Research, 41(2), 157–167.

Ziegler, T., & Autschbach, J. (2005). Theoretical methods of potential use for studies of inorganic reaction mechanisms. Chemical Reviews, 105(6), 2695–2722.