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Final Technical Report: Controlling Molecular Structure and Spin with Multiconfigurational Quantum Chemistry

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Executive Summary

For many first-row transition metal complexes, structure-property relationships can be obtained from high-level molecular geometry optimizations and subsequent electronic structure studies. The project funded under this award utilized newly implemented fully internally contracted (FIC) nuclear gradients for extended multi-state (XMS) complete active space second-order multireference perturbation theory (CASPT2) to explore geometry changes in first-row transition metal coordination complexes. At the start of the project, only one full geometry optimization using FIC-CASPT2 analytical gradients had been reported (*J. Chem. Theory Comput.*, **2016**, 12 (8), 3781), and many open-questions regarding the performance and achievable accuracy in applying such computations to larger complexes persisted. Key deliverables in the report include the implementation of the numerical Hessian and subsequent vibrational analysis in the BAGEL program package. This includes both full Hessian vibrational analysis (FHVA) and a partial Hessian vibrational analysis (PHVA). The latter of which allows us to reduce the significant cost of computing the vibrational frequencies in a large molecule by focusing on the modes of highest interest. The gradient code also proved useful in the development of an approach to improve the Hubbard-U correction by removing bias in predicting spin-splitting in Fe(II) complexes via plane-wave density functional theory (DFT). Finally, we showed for three families of complexes (spin-crossover (SCO) complexes, metallocorroles complexes, and those with metal-metal bonds) that CASPT2 can result in good molecular geometries and established best practices in undertaking this work. We are now using this approach in collaborative projects with experimental groups, which would not have been possible at the start of this project. A common theme also arose through this work that static and dynamic correlation must be recovered in a balanced way to yield quantitative results. By systematically varying how both effects were included, we were able to make key chemical insights. This work supported the training of two postdoctoral scholars, one graduate student, and one undergraduate student in applying high-level wavefunction based methods to challenging systems.

Contents

1 Introduction and Research Objectives

This project made use of analytical gradients for multireference electron correlation methods (FIC-CASPT2) to explore geometry changes in first-row transition metal coordination complexes in which the importance of strong correlation varied. A special focus was placed on systems where either the molecular geometry or the ground-state electronic structure was not described well by traditional density functional theory (DFT). The families of coordination complexes selected for study undergo well characterized geometry changes, allowing for the performance of this method to be carefully assessed. Systematic studies that included comparisons among different levels of theory were performed for a series of transition metal complexes. Comparisons with experiment were made when possible, and the challenges of such indirect experiment-theory comparisions are noted in the resulting manuscripts.

The goal of this project was to demonstrate that geometry optimizations beyond DFT can be used to improve the description of complex electron correlation effects in first-row transition metal complexes providing insights important for the design of sensors, catalysts, and in molecular electronics. While there are notable examples of coordination complexes where the DFT-derived molecular geometries are in poor agreement with experiment, our hypothesis went a step further to explore how subtle but important relationships can also be identified in transition metal complexes due to the fact that the nature and the impact of the limitations of DFT are often not obvious *a priori*. Therefore, this project had three objectives: Improve Control Over Spin-Crossover Complexes (**Objective 1**), Provide Mechanistic Insights in Excited States and Catalysis (**Objective 2**), and Controlling Spin with External Stimuli (**Objective 3**). Overall, we sought to demonstrate that geometry optimizations beyond DFT can be used to improve the description of complex electron correlation effects in spin crossover complexes, metalated macrocycles, and metal-metal bonds to 1) develop a protocol for such computations, 2) demonstrate that these complexes can be performed on local resources, and 3) to ultimately provide chemical insights for the design of sensors, catalysts, and in molecular electronics. In other words, we argue that nowadays the molecular geometry can be obtained for the correct multiconfigurational electronic state in coordination chemistry.

1.1 Impact of Active Space and Basis Set Size on Fe(II) SCO Complexes

The investigation of molecular geometries in transition metal complexes is a crucial part of understanding their electronic structure and properties. In our first study, we employed fully internally contracted (FIC)-CASPT2 analytical gradients to perform geometry optimizations on a series of Fe(II) spin-crossover (SCO) complexes (see Finney PCCP in Section 2.1). This methodology was used for complexes with varying sizes, ranging from 13 to 61 atoms, shedding light on the role of active space and basis set choices in determining reliable molecular geometries. The complexes selected fall into two categories: A series of smaller Fe(II) SCO complexes (Figure 1a) and a series of larger complexes (Figure 1b). The smaller Fe(II) SCO systems were chosen since they have been used by us and others to compare the performance of computational methods for spin-state energetics in SCO complexes. On the other hand, the three larger complexes were chosen not only to be comparable with literature data, but also to represent the computational cost for molecules typically synthesized. Moreover, all of the complexes had been studied previously with DFT and resulted in reasonable geometries. This allowed us to test the method in a newly implemented code without the added layer of complexity that challenging electronic structure brings.

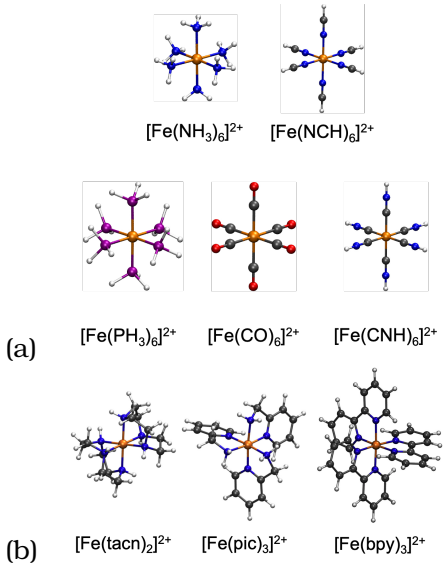

Figure 1: Set of Fe(II) octahedral complexes used in benchmarking tests. (a) Smaller and (b) larger complexes.

The strategy presented here showcases the utility of a wave function-based level of theory, demonstrating that it is possible to optimize the geometries of metal complexes efficiently while treating their molecular geometry and electronic structure at the same level of theory. The Fe(II) SCO complexes, particularly those of smaller size, reveal slightly larger differences between DFT and CASPT2 when strong field ligands in the low spin (LS) state are involved. Nevertheless, overall good agreement is observed between the two methods for all systems studied. These results also led to the recommendation to use a ($10e$,$12o$) active space in conjunction with the cc-pVTZ basis set (on the metal and first coordination sphere), as it more efficiently converges to minimum structures compared to truncated active spaces, despite the fact that even minimal ($6e$,$5o$) active spaces yield good Fe–ligand bond distances.

In the optimization of the larger complexes $[\mathrm{Fe(tacn)_2}]^{2+}$, $[\mathrm{Fe(bpy)_3}]^{2+}$, and $[\mathrm{Fe(pic)_3}]^{2+}$, the cc-pVTZ basis set was used on the metal, while the cc-pVDZ basis set can be employed on the remaining atoms without significantly compromising geometry quality. Then, the impact of active space choice was tested once more. Comparisons with crystal structures and various DFT functionals validate the reliability of CASPT2 geometries, particularly for larger complexes, where good agreement is observed both with DFT predictions and experimental data. This study focuses on Fe(II) complexes, known to exhibit reasonable geometries with DFT, but validated the choice of moderate-sized basis sets and active spaces in other complexes where multiconfigurational effects are more prominent. While the focus of this study was on the geometric parameters, we also computed the adiabatic energy differences, $\Delta \mathrm{E_{H\text{-}L}}$, between the high-spin (S = 2) and the low-spin (S = 0) states. CASPT2 energy differences were reported on the DFT and CASPT2 geometries showing at most differences on the order of 5 kcal/mol.

This work contributed to **Objective 1** and comprised the foundation for the following work by establishing the protocol for selecting a reasonably sized basis set size and changed the way in which we viewed selecting a minimal active space. The use of FIC-CASPT2 analytical gradients provided valuable insights into the molecular geometries of Fe(II) SCO complexes, paving the way for a broader understanding of transition metal complexes with diverse electronic structure. Future studies later explored the applicability of this approach to other systems (*vide infra*) where molecular geometry differences between DFT and CASPT2 are expected to be more pronounced.

1.2 Using FIC-CAPT2 Gradients to Improve the Choice of Hubbard U Value in Fe(II) SCO Complexes

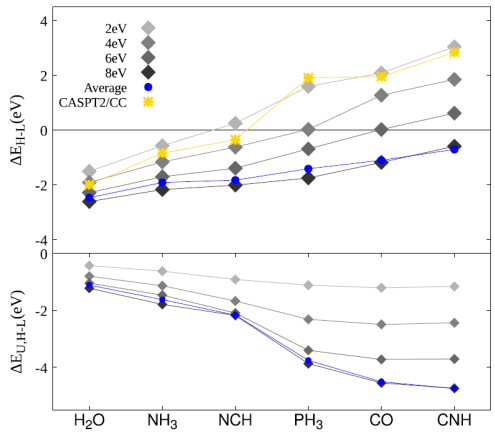

Figure 2: Adiabatic energy differences, $\Delta \mathrm{E_{H\text{-}L}}$, (upper panel) and energy difference of the Hubbard term, $\Delta \mathrm{E_{U,H\text{-}L}}$, computed at different values of U, with the PBE functional.

In collaboration with Dr. Roberta Poloni (CNRS Grenoble), we performed two related studies on Fe(II) SCO complexes. We showed in Section 1.1 that the CASPT2 and DFT geometries did not have a large impact on the energy splitting; however, we did not seek to address what was already well known, that the energy splitting is quite sensitive to functional choice and that DFT often predicts the energy gap poorly. Our collaborators were working on improving the DFT methods for predicting spin splittings and sought to use CASPT2 as a reference. In our first study (see Mariano JCTC 2020 in Section 2.1), we worked to understand how the Hubbard U parameter can be tuned to improve the reliability of DFT to describe spin splittings. Specifically, the spin-state energetics of six Fe(II) molecular complexes (the five in Figure 1a and $[\mathrm{Fe(H_2O)_6}]^{2+}$) were computed using the linear-response Hubbard U approach within DFT, denoted $\mathrm{DFT} + \mathrm{U_{sc}}$. As in the prior study, adiabatic energy differences between the high-spin (S = 2) and the low-spin (S = 0) states are computed, but this time the DFT+U results are compared

with coupled cluster-corrected CASPT2 results as the reference (CASPT2/CC). DFT+U fails in correctly capturing the ground state for strong-field ligands yielding energy differences that are almost constant throughout the molecular series (Figure 2). This bias toward high spin together with an analysis of the metal-ligand charge transfer upon U correction was quantified and explained via σ- and π-bonding interactions. With increasing ligand field strength, this bias also increases due to changes in the mixed metal-ligand contributions to the DFT orbitals, and in turn results in large deviations from the CASPT2/CC reference. We showed that smaller values of U can be used to reduce this effect and obtain the correct energetics (Figure 2).

While we had explained the performance of the DFT+U_{sc} approach in describing spin-state energetics, we wanted to understand the results in terms of the ligand field strength. For weak-field molecules, such as $[Fe(H_2O)_6]^{2+}$, the overstabilization of the LS state by standard functionals like PBE may cancel out with the bias introduced by the Hubbard correction thus giving good agreement with the reference values albiet for the wrong reasons. On the other hand, for stronger-ligand fields, the larger bias toward the HS state can lead to deviations from the reference CASPT2/CC values by as much as several eV. As a semiempirical approach, lower values of U, like the choice of U = 4 eV often employed in the literature, may perform better. We observed a density change when U is applied by examining the metal-ligand hybridization within the molecular orbital picture.

With this analysis in hand, we desired a general tool to interpret the U-induced charge redistribution (see Mariano JCTC 2021 in Section 2.1). Analytical gradients are not only useful to obtain molecular geometries, but also allow us to compute the CASPT2 relaxed density (Figure 3). In the aforementioned study, $\mathrm{DFT} + \mathrm{U_{sc}}$ yielded adiabatic energy differences that were biased toward high spin. Such a bias was removed by employing a density-corrected DFT approach where the PBE functional was evaluated on a Hubbard U-corrected density referred to as PBE[U]. While CASPT2/CC was used as a reference for the energy splitting in the initial study, the CASPT2 relaxed density computed using FIC-CASPT2 analytical gradients enabled the corrections herein. The adiabatic energy differences of six Fe(II) molecular complexes were computed using this PBE[U] approach which also involved a self-consistent approach for determining U. The PBE[U] results were in excellent agreement with the CASPT2/CC values for both weak and strong-field ligands with a mean absolute error (MAE) of 0.44 eV. This was smaller than for Hartree-Fock density corrected DFT (MAE = 1.22 eV) and any other tested functional, including the next top performer TPSSh (MAE = 0.49 eV). The computational efficiency of this approach was taken advantage of and allowed us to compute adiabatic energy differences of five molecular crystals at the PBE[U] level of theory employing periodic boundary conditions. The MAE was 0.07 eV with respect to experimentally extracted values. Other top performing functionals were M06-L (MAE = 0.08 eV) and TPSSh (MAE = 0.31 eV), although these results were obtained for molecular fragments.

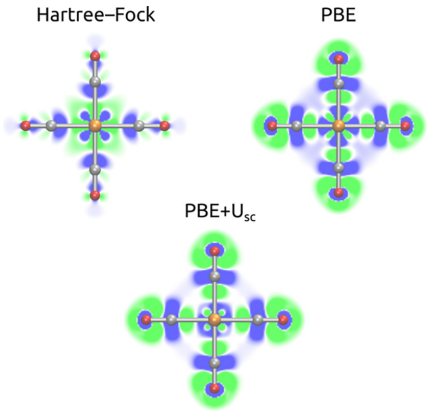

Figure 3: Density difference plot for $[Fe(CO)_6]^{2+}$ between Hartree-Fock (top left), PBE (top right), and $\mathrm{PBE} + \mathrm{U_{sc}}$ (bottom) with the relaxed CASPT2 density; green are positive values and blue are negatives values between 0.005 and 0.005 e/bohr^3.

1.3 The Role of Dispersion in Mn(III) SCO Complexes

Returning to XMS-CASPT2 molecular geometries, the Fe(II) SCO complexes discussed in Section 1.1 were selected despite being well-described by DFT. They allowed us to test a series of technical choices. Following this work, we turned to a pair of octahedral manganese(III) complexes and employ the best practices established (See Roy Chowdhury Inorg. Chem. in Section 2.1). Specifically, CASPT2 geometry optimizations are used to carefully assess why the $\mathrm{Mn - N_{amine}}$ bond distances in the high-spin geometry are significantly overestimated by DFT (Figure 4a). On the other hand, the geometry for the intermediate-spin is reasonably well-described. In addition to CASPT2, comparisons with several wavefunction-based methods demonstrate that the deviations

in bond distances were due to the limited ability of DFT to recover dispersion (Figure 4b).

Specifically, the DFT methods predicted the apical Mn−O and equatorial $\mathrm{Mn-N_{imine}}$ distances in excellent agreement with experiment and wavefunction theory for both spin states, but showed very poor agreement for the $\mathrm{Mn-N_{amine}}$ distances in the high-spin geometry with deviations as large as 0.2 Å in some cases (Figure 4a). The use of a hybrid functional and empirical dispersion correction improved the bond distances, but differences on the order of 0.1 Å remained. By conducting full geometry optimizations with wave function based second-order perturbation theory methods (MP2 and CASPT2), we discovered that it was the limited ability of the density functionals properly recover dispersion that resulted in such significant errors since both MP2 and CASPT2 provided a much better description of the $\mathrm{Mn-N_{amine}}$ bond distances in the high-spin state. However, MP2 performs slightly worse in describing the apical M − O bond distances, most notably in the intermediate-spin state of the complex with the methoxy functionalized ligand, $[\mathrm{Mn(OMe-sal_2323)}]^+$. This was attributed to the inability of restricted open-shell (RO)-MP2 to allow spin polarization along the Mn-ligand bonds as well as a small increase in the multireference character moving from the high- to the intermediate-spin states. Although computationally intensive, CASPT2 can balance the need to recover different types of electron correlation and best describes all bond distances. Specifically, it not only recovers weak interactions with similar accuracy to MP2, but allows sufficient flexibility in the reference wavefunction to properly describe the bond metrics in all spin states. A scan along $\mathrm{Mn-N_{amine}}$ distance of $[\mathrm{Mn(OMe-sal_2323)}]^+$ supported this result (Figure 4b), making it clear that the most important interaction was dispersion. Specifically, the DFT, MP2, and CASPT2 methods were compared with the domain-based local pair natural orbital (DLPNO) coupled cluster method, DLPNO-CCSD(T), and multiconfiguration pair density functional theory, MC-PDFT. DLPNO-CCSD(T) recovers more dynamic correlation than both MP2 or CASPT2 and predicted a bond distance in good agreement with experiment and CASPT2. On the other hand, MC-PDFT recovers strong correlation but treats dispersion at the DFT level. In turn, MC-PDFT performed similar to the DFT functionals herein. Despite the dramatic improvement, the CASPT2 $\mathrm{Mn-N_{amine}}$ distances for the high-spin state of $[\mathrm{Mn(OMe-sal_2323)}]^+$ still differ from experiment by $\sim$ 0.6 Å. Crystal packing or counter ion effects not considered in this study could contribute to these differences. Nevertheless, the use of CASPT2 analytical gradients to optimize geometries resulted in improved molecular geometries, offering a balance between treating dispersion correctly and including multiconfigurational effects. This project contributed to **Objectives 2 and 3**, while showing that such computations can be realized and employed in applied work to support chemical intuition and in turn synthetic design.

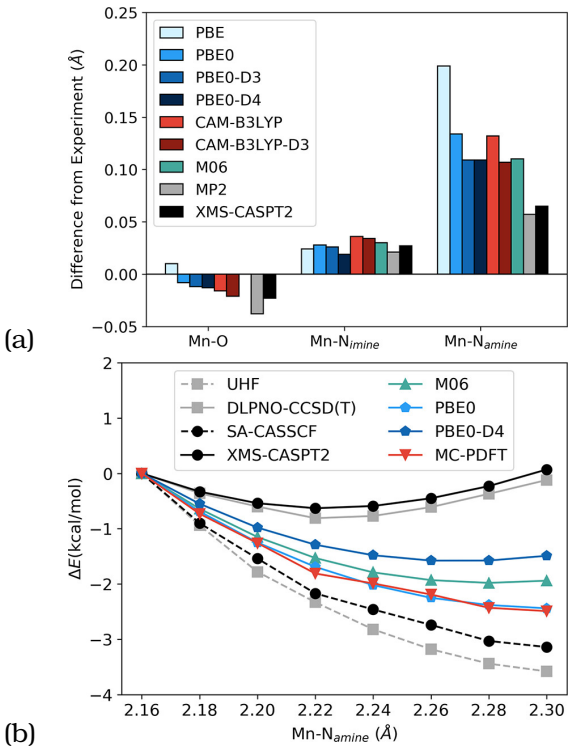

Figure 4: (a) Comparison of computed metal–ligand bond distances for the high-spin geometries of $[\mathrm{Mn(OMe-sal_2323)}]^+$ with respect to experiment. (b) Potential energy surface along the $\mathrm{Mn-N_{amine}}$ bond distance. The reference for the relative energy is the value computed for each method at the experimental distance of 2.16 Å.

1.4 Ground and Excited States of Cu Corrole Complexes

While the studies of Fe(II) and Mn(III) complexes predicted structures and spin-splittings, the geometry optimizations were performed for only the lowest energy state of each spin. **Objective 2** involves employing CASPT2 geometry optimizations to characterize excited states and catalysts. Therefore, copper corrole complexes were selected since they are used as both molecular sensors and catalysts. Furthermore, the ground state singlet is well-known to have a significant amount of multiconfigurational character thought to arise from orbital mixing between the conjugated π system of the corrole itself with a d-orbital of copper. This orbital mixing can only occur when the molecular geometry is not planar; however, the extent to which saddling occurs depends on the functional groups present on the ligand and the chosen computational method. While DFT provides reasonably good molecular geometries, the determination of the ground spin state and the associated energetics is heavily influenced by functional choice, particularly the percentage of the Hartree–Fock exchange. Moreover, DFT may obtain a geometry within the expected deviation from a solid-state experimental structure, but the optimization is not performed on the correct multiconfigurational ground state singlet. Some degree of difference in dihedral angles is generally accepted between experiment and theory making such a comparison indirect at best. Using XMS-CASPT2, the impact of functional choice on geometries, the nature of the electronic states, and energy differences can be assessed by making direct theory-to-theory comparisons. In the first study, the molecular geometries and electronic structures of both the unsubstituted and the *meso*-triphenyl copper corroles were investigated (See Bhowmick Inorg. Chem. in Section 2.1). On-going work supported by this project to study the impact of a series of electron donating and electron withdrawing groups in the *meso* position is expected to be published in the coming year. The first study contributes to **Objective 1**, while both studies contribute to **Objective 2**.

A minimal active space was employed for structural characterization, while larger active spaces are required to examine the electronic structure. The XMS-CASPT2 investigations conclusively identify the ground electronic state as a multiconfigurational singlet (S_0) with three dominant electronic configurations in its lowest energy (i.e., saddled) structure (Figure 5a, left hand side). In contrast, the planar geometry corresponds to the triplet state (T_0), which is approximately 5 kcal/mol higher in energy compared to the S_0 state for both the bare and substituted copper corroles. Notably, the planarity of the T_0 geometry is reduced in the substituted corrole compared with that in the unsubstituted one. By analyzing the potential energy surface (PES) between the S_0 and T_0 geometries of the unfunctionalized Cu corrole using XMS-CASPT2 (Figure 5a), the multiconfigurational electronic structure is shown to transition toward a single electron configuration as the saddling angle decreases and approaches a planar geometry. Despite the ability of the functionals to reproduce the minimum energy structures, only the TPSSh-D3 PES is reasonably close to the XMS-CASPT2 surface (Figure 5b). Note that there are significant deviations along the PES are observed with other functionals. The planarity of the resulting structures was assessed both by reporting a series of dihedral angles and also by report-

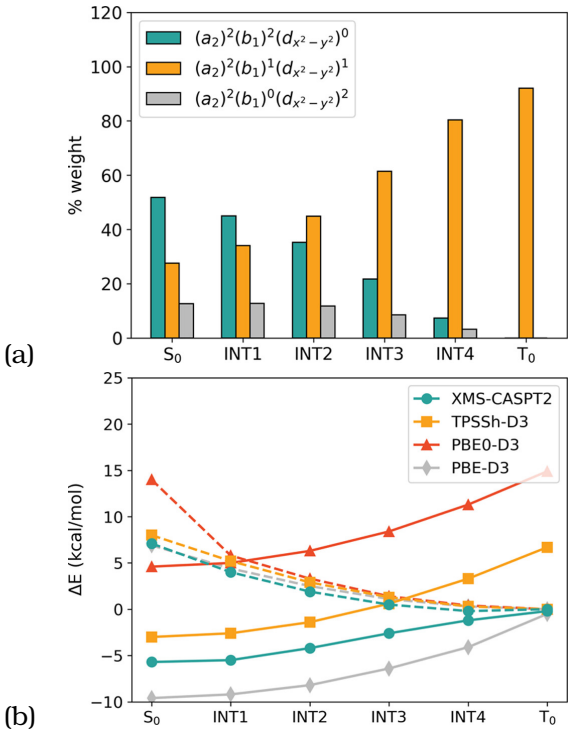

Figure 5: Linear interpolation of internal coordinates between saddled and planar molecular geometries. (a) Changes in the CASSCF wavefunction (b) Energy difference as a function of method choice. Ground state singlet with solid line and excited state singlet with dashed line.

ing the degree of deviation from planarity (D_{oop}). Both the selected dihedral angles and the D_{oop} were consistent with larger saddling in the XMS-CASPT2 geometries in both structures compared to DFT. Calculations with a larger restricted active space were performed on the XMS-CASPT2 geometries to include the full π system and metal orbitals in the electronic structure analysis.

In the forthcoming study of functionalized copper corroles, the impact of electron-withdrawing and donating groups (R = NO_2, CF_3, CN, F, OH, CH_3, and OCH_3) in the *meso*-position of the corrole are examined. With DFT, the saddling angle decreases when moving from the most electron donating to most electron withdrawing groups. All complexes retain the saddling in the S_0 state and are near planar in S_1 and T_0 states. A subsequent electronic structure study with a restricted active space is being performed to understand how the charge transfer between the corrole and metal d-orbibtals is impacted by ligand modification.

1.5 Vibrational Spectroscopy in Chromium-Chromium Bonds

Following a geometry optimization, vibrational analysis is employed to confirm strutures as minima or to determine spectroscopic properties. We performed an accurate computational vibrational analysis of the Cr–Cr bond in dichromium complexes using second-order multireference complete active space methods (CASPT2), allowing direct comparison with experimental spectroscopic data both to facilitate interpreting the low-energy region of the spectra and to provide insights into the nature of the bonds themselves. The prior implemenations of the FIC-CASPT2 gradients made this calculation possible for the first time. Moreover, accurate simulation of the vibrational structure of these compounds has been hampered by their notorious multiconfigurational electronic structure that yields bond distances that do not correlate with bond strength. This work also included code implementation in the BAGEL program package. Specifically, the CASPT2 second-order energy derivatives were computed by the finite difference of the first-order derivatives calculated using the analytical nuclear gradients. The use of the analytical gradient program is essential in realizing the CASPT2 vibrational analysis because it reduced the computational cost by two- to three-orders of magnitude for the molecules in this study. An embarrassingly parallel algorithm has been included that allows the user to select the number of MPI processes required for each gradient calculation and distribute the 6N displacements among different tasks. The Hessian is symmetrized, mass weighted, and the translational and rotational degrees of freedom are set to zero using the usual projection. The normal modes are obtained by diagonalizing the projected mass-weighted Hessian yielding the normal modes (eigenvectors), and the corresponding harmonic vibrational frequencies can be calculated from the eigenvalues. The infrared intensity is also computed from the transition dipole moments. Raman intensities are not yet implemented. We then implemented Partial Harmonic Vibrational Analysis (PHVA) as described first by Head and coworkers and later by Li and Jensen to reduce the computational cost of such an analysis. In PHVA, a subblock of the Hessian matrix is diagonalized to obtained vibrational frequencies within that portion of the molecule. This scheme was particularly useful in this study because the Cr–Cr stretching mode is localized, allowing us to avoid computing a large number of displacements require for constructing the numerical Hessian, especially those associated with bulky ligands, that do not couple directly or indirectly with the Cr–Cr stretching mode.

Table 1: M06, CASPT2, and experimental Cr-Cr bond distances in Å.

Complex	M06	CASPT2	Exp.
$[Cr_2(O_2CCH_3)_4](H_2O)_2$	1.721	2.419	2.362
$Cr_2(mhp)_4$	1.704	1.989	1.889(1)
$Cr_2(dmp)_4$	1.698	1.922	1.849(2)

Two complexes were of particular chemical interest. In $Cr_2(mhp)_4$ and $Cr_2(dmp)_4$, one measured Cr–Cr vibrational stretching modes, $\nu(Cr_2)$, suggested weaker bonding, even for these so-called ultrashort Cr–Cr bonds, while another is in line with the bond distance. We optimized the geometries of a series of well-characterized Cr–Cr complexes (Table 1) and computed $\nu(Cr_2)$ with CASPT2. We obtained Cr–Cr bond distances and $\nu(Cr_2)$ in excellent agreement with experiment and use these values to assign which of the observed experimental stretching modes is the fundamental

Cr-Cr stretch. Consistent with prior literature on diatomic molecules, we found via normal mode sampling that the addition of the IPEA shift leads to improved bond distances. A quartic fit was used to assess the importance of anharmonic effects but had a smaller impact than improving the treatment of electron correlation. This project contributed to **Objectives 1 and 2**.

2 Products from the Funded Work

2.1 Published Manuscripts

- R. Bhowmick, S. Roy Chowdhury, and B. Vlaisavljevich "Molecular Geometry and Electronic Structure of Copper Corroles" Inorg. Chem. 2023, 62, 34, 13877-13901.
- S. Roy Chowdhury, N. Nguyen, and B. Vlaisavljevich "Importance of Dispersion in the Molecular Geometries of Mn(III) Spin Crossover Complexes" J. Chem. Phys. A 2023, 127, 14, 3072-3081. (Published as part of a virtual special issue Early-Career and Emerging Researchers in Physical Chemistry Volume 2.)
- B. A. Finney, S. Roy Chowdhury, C. Kirkvold, and B. Vlaisavljevich "CASPT2 Geometry Optimizations of Fe(II) Spin-Crossover Complexes" Phys. Chem. Chem. Phys. 2022, 24, 1390-1398.
- T. Shiozaki and B. Vlaisavljevich "Computational Spectroscopy of the Cr–Cr Bond in Coordination Complexes" Inorg. Chem 2021, 60, 24, 19219-1922.
- L. A. Mariano, B. Vlaisavljevich, and R. Poloni "Improved Spin-State Energy Differences of Fe(II) Molecular and Crystalline Complexes via the Hubbard U-corrected Density" J. Chem. Theory Comput. 2021, 17, 5, 2807-2816.
- L. Mariano, B. Vlaisavljevich, and R. Poloni "Biased Spin-State Energetics of Fe(II) Molecular Complexes within Density Functional Theory and the Linear-Response Hubbard-U Correction" J. Chem. Theory Comput. 2020, 16 (11), 6755-6762.
- S. C. Coste, T. J. Pearson, A. B. Altman, R. A. Klein, B. A. Finney, M. Y. Hu, E. E. Alp, B. Vlaisavljevich, and D. E. Freedman "Orbital Energy Mismatch Engenders High-Spin Ground States in Heterobimetallic Complexes" Chem. Sci. 2020, 11, 9971-9977.
- J. W. Park, R. Al-Saadon, M. K. MacLeod, T. Shiozaki, and B. Vlaisavljevich "Multireference Electron Correlation Methods: Journeys Along Potential Energy Surfaces" Chem. Rev. 2020, 120 (13), 5878-5909.

2.2 Invited and Contributed Seminars

- B. Vlaisavljevich. Computational Insights for Energy Solutions. Pacific Northwest National Laboratory. Richland, WA (June 27, 2023), Invited.
- B. Vlaisavljevich. CASPT2 Geometry Optimizations of Transition Metal Complexes. Molecular Magnetism Virtual Seminar Series Organized by Prof. Alessandro Lunghi (June 15, 2023), Invited.
- B. Vlaisavljevich. Understanding Spin-Crossover Complexes with Multireference Methods. Presented at the American Chemical Society National Meeting, Indianapolis, IN, (March 29, 2023), Contributed.
- B. Vlaisavljevich. Computational Insights for Energy Solutions. Presented in the University of Missouri Chemistry Department Seminar Series. Columbia, MO, (February 7, 2023), Invited.
- B. Vlaisavljevich. CASPT2 Molecular Geometries in Transition Metal Chemistry. Presented at the Midwest Regional American Chemical Society National Meeting, Iowa City, IA (October 21, 2022), Contributed.
- B. Vlaisavljevich. Insights from Multireference Methods in Transition Metal Chemistry. Presented at the Chemistry Department's Seminar Series, Baltimore, MD. (September 23, 2022), Invited.
- B. Vlaisavljevich. CASPT2 Molecular Geometries in Transition Metal Chemistry. Presented at the American Chemical Society National Meeting, San Diego, CA (March 21, 2022), Invited.
- B. Vlaisavljevich. CASPT2 Molecular Geometries in Transition Metal Chemistry. Presented in the University of Texas El Paso Chemistry Department Seminar Series (February 25, 2022), Virtual, Invited.
- B. Vlaisavljevich. Insights from Multireference Electron Correlation Methods in Transition Metal Chemistry. Presented in the Johns Hopkins Chemistry Department Seminar Series (September 7, 2021), Invited.
- B. Vlaisavljevich. Computational Spectroscopy of Cr-Cr Bonds. Presented at the Department of Energy's Computational and Theoretical Chemistry (CTC) Virtual PI Meeting, (August 2, 2021), Invited.

- B. Vlaisavljevich. CASPT2 Molecular Geometries of Dichromium Complexes. Presented at the Great Lakes Regional Meeting (GLRM) of the American Chemical Society, (June 7, 2021). Contributed
- B. Vlaisavljevich. Insights from Multireference Electron Correlation Methods in Transition Metal Chemistry. Presented in the South Dakota State University Department Seminar Series (April 16, 2021), Invited.
- B. Vlaisavljevich. CASPT2 Molecular Geometries of Transition Metal Complexes. Presented at the ACS Sioux Valley Local Section's Fall Research Symposium, Virtual, (September 21, 2020), Contributed.
- B. Vlaisavljevich. CASPT2 Molecular Geometries of Transition Metal Complexes. Presented at the University of South Dakota, Chemistry Department Seminar Series, (September 21, 2020), Invited.
- CASPT2 Molecular Geometries and Electronic Structures of Transition Metal Complexes. Presented at the Department of Energy's Computational and Theoretical Chemistry (CTC) Virtual PI Meeting, (July 16, 2020), Invited.
- CASPT2 Molecular Geometries of Late Transition Metal Complexes. Presented at the Virtual 260th American Chemical Society National Meeting. Oral Presentation On-Demand (August 17–20, 2020), Contributed.
- CASPT2 Molecular Geometries and Electronic Structures of Transition Metal Complexes. Presented at the 258th American Chemical Society National Meeting, San Diego, CA. (August 27, 2019), Invited.

2.3 Student Training and Professional Development

This project provided essential training and professional development opportunities for one chemistry graduate student and one undergraduate student. Both students were female and the PhD student was a person of color (Dr. Rina Bhowmick). The graduate student is currently pursuing postdoctoral research under the supervision of Dr. Pere Miro at the University of South Dakota. The undergraduate student, Clara Kirkvold, also demonstrated remarkable success. She was awarded a Goldwater Scholarship and an NSF Graduate Student Research Fellowship (GRFP), mentored by the PI. She is currently a graduate student at the University of Minnesota under the supervision of Prof. Jason Goodpaster. Despite pandemic related interruptions with respect to in person presentations, the graduate and undergraduate student supported on this project successfully presented at regional, national, and international conferences, with acknowledged DOE support (see list in Section 2.5). Additionally, the undergraduate student was awarded a third place prize for her poster presentation at the American Chemical Society's Midwest Regional Meeting in 2019 and had planned to give an oral presentation at the Spring ACS meeting in 2020 (cancelled for COVID-19). Collectively, these outcomes demonstrate how the project provided important student training and workforce development in molecular modeling. It also demonstrates how the project supported students from underrepresented backgrounds. Finally, Dr. Bhowmick and the PI are also parents of small children and were impacted by a lack of childcare during the COVID-19 pandemic (which occured in the middle of this project).

2.4 List of Students and Postdoctoral Scholars Supported

- **Postdoctoral Scholars (2 total):** Dr. Brian Finney and Dr. Sabyasachi Roy Chowdhury
- **Graduate Students (1 total):** Rina R. Bhowmick (PhD Awarded at USD in 2023)
- **Undergraduate Researchers (1 total):** Clark Kirkvold (BS Awarded at USD in 2020)

2.5 Presentations by Students and Postdoctoral Scholars

- R. Bhowmick, S. R. Chowdhury, and B. Vlaisavljevich. Molecular Geometry and Electronic Structure of Copper Corroles. Presented at the American Chemical Society National Meeting (Spring ACS), Indianapolis, IN, USA (March 2023) (Oral).
- S. Roy Chowdhury, N. Nguyen, and B. Vlaisavljevich Role of Dispersion in the Molecular Geometries of Mn(III) Complexes. Presented at the American Physical Society National Meeting (March Meeting APS), Las Vegas, NV, USA (March 2023). (Oral)

- S. Roy Chowdhury and B. Vlaisavljevich. Molecular Geometries of Transition Metal Complexes by Multireference Methods. Presented at the Indian Institute of Science Education and Research Kolkata, Kolkata, West Bengal, India (January 2023). (Oral)
- S. Roy Chowdhury and B. Vlaisavljevich. Molecular Geometries of Mn(III) Complexes by Multireference Methods. Presented at the American Chemical Society Midwest Regional Meeting (ACS MWRM), Iowa City, IA, USA (October 2022). (Oral)
- R. Bhowmick, S. R. Chowdhury, and B. Vlaisavljevich. Molecular Geometry and Electronic Structure of Copper Corroles. Presented at the American Chemical Society National Meeting (Fall ACS), San Diego, CA, USA (March 2022) (Oral).
- S. Roy Chowdhury and B. Vlaisavljevich. CASPT2 Molecular Geometries of Transition Metal Complexes. Presented at the Indian Association for the Cultivation of Science, Kolkata, West Bengal, India (June 2022). (Oral)
- S. Roy Chowdhury and B. Vlaisavljevich. Exploring Molecular Geometries of Transition Metal Complexes by Multireference Methods. Presented at the S. N. Bose National Center for Basic Science, Kolkata, West Bengal, India (June 2022). (Oral)
- S. Roy Chowdhury and B. Vlaisavljevich. Exploring Molecular Geometries of Transition Metal Complexes by Multireference Methods. Presented at the Indian Institute of Technology Kharagpur, Kharagpur, West Bengal, India (June 2022). (Oral)
- S. Roy Chowdhury and B. Vlaisavljevich. Exploring the Role of Charge Transfer States on the Spin Crossover of the Fe(II) Complexes. Presented at IdeaFest at the University of South Dakota, Vermillion, SD, USA (April 2022). (Oral)
- S. Roy Chowdhury and B. Vlaisavljevich. Investigating Geometries of Mn(III) Spin Crossover Complexes by Multireference Methods. Presented at the American Chemical Society National Meeting (Spring ACS A), San Diego, CA, USA (March 2022). (Oral)
- S. Roy Chowdhury and B. Vlaisavljevich. Investigating Spin Crossover of Fe(II) Complexes by CASPT2 Method. Presented at IdeaFest at the University of South Dakota, Vermillion, SD, USA (April 2021). (Virtual, Poster)
- R. Bhowmick. Electronic Structure of Copper Corrole Complexes presented in the three minute thesis competition (3MT) at the University of South Dakota, Vermillion, SD, USA (February 2021) (Oral)
- R. Bhowmick and B. Vlaisavljevich, The Impact of Molecular Geometry on the Electronic Structure of Metallocorrole Complexes presented in Sioux Valley Local Section of the American Chemical Society's Annual Research Symposium, Sioux Falls, SD, USA (November 2020) (Virtual, Oral).
- C. Kirkvold, B. Finney, and B. Vlaisavljevich, CASPT2 Geometries and Energies of Spin-Crossover Complexes, Presented at the ACS Midwest Regional Meeting, Wichita, KS, USA (October 2019) (Poster)
- C. Kirkvold, B. Finney, and B. Vlaisavljevich, CASPT2 Geometries and Energies of Spin-Crossover Complexes, Presented at the Sioux Valley Local Section of the American Chemical Societies Fall Research Symposium, Sioux Falls, SD, USA (September 2019) (Poster)
- C. Kirkvold, B. Finney, and B. Vlaisavljevich, CASPT2 Geometries and Energies of Spin-Crossover Complexes, Presented at the South Dakota EPSCoR Undergraduate Research Symposium, Sioux Falls, SD, USA (August 2019) (Poster)
- B. Finney and B. Vlaisavljevich, CASPT2 Geometries and Energies of Spin-Crossover Complexes, Presented at the American Chemical Society National Meeting (Fall ACS), San Diego, CA, USA (August 2019) (Oral)
- B. Finney and B. Vlaisavljevich, Molecular Geometries of Fe(II) Spin-Crossover Complexes, Presented at the American Physical Society National Meeting (March Meeting APS), Boston, MA, USA (March 2019) (Oral)

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