# DISSERTATION

# "YOU ARE YOUNG AND CAN AFFORD TO DO SOMETHING STUPID.": FOSTERING AN UNDERSTANDING OF ELECTRONIC SPIN IN CHEMISTRY

Submitted by

Justin P. Joyce

Department of Chemistry

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Fort Collins, CO

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Doctoral Committee:

Advisor: Matthew P. Shores Co-advisor: Anthony K Rappé

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#### ABSTRACT

# "YOU ARE YOUNG AND CAN AFFORD TO DO SOMETHING STUPID.": FOSTERING AN UNDERSTANDING OF ELECTRONIC SPIN IN CHEMISTRY

In this dissertation I develop tools with electronic structure methods to resolve electronic spin as the inciting property of diverse chemical phenomena. The content is organized as follows:

Chapter 1 provides the historical context of the events leading to the conception of electronic spin. I align the application of this intrinsic quantum mechanical property with advancing the impact of chemistry. The Chapters dedicated to my research are separated by their focus of closed- or open-shell electronic systems. The sections are predicated with a theoretical method that provides quantitative and visual insight into the electron-electron interactions. The methods developed with model systems are then extended to new results garnered from close collaboration with experimental researchers.

In Chapter 2 we characterize the impact of the Pauli Exclusion principle on the relative stability of the structural isomers of octane ( $C_8H_{18}$ ). We develop that the asymmetry of the electronic wavefunction exerts a complementary relationship with respect to the strain and stability of chemical systems. This is demonstrated with respect to both the magnification of medium-range electron correlation and the reduction of vibrational enthalpy *via* exchange repulsion. We refer to the dynamic interplay between these forces as a *Gestalt interaction*. Most of the text and graphics have been previously published, its reference provided as follows: J.P. Joyce, M.P. Shores, Rappé, A.K. *Phys. Chem. Chem. Phys.* 2020, **22**, 16998-17006.

In Chapter 3 we extend the principle of complementarity developed in Chapter 2 to the relative stability of the labile spin states of octahedral  $Fe^{2+}$  coordination complexes. This establishes the analogous impact of geminal and *cis*-contacts on the electronic energy of structural and spin isomers, respectively. In the tradition of Pauling, we develop an empirical structural parameter based on the principle of s-p hybridization that is benchmarked with experimental crystallographic structures from the Cambridge Structural Database (CSD). Our parameter assigns whether an  $[Fe^{2+}N(sp^2)_6]$  structure can display spin crossover with a probability of approximately 95%, our method being generalizable to systems irrespective of transition metal identity or coordination geometry. This chapter has been submitted, in part, as a manuscript to *Inorganic Chemistry*: Joyce, J.P.; Shores, M.P.; Rappé, A.K. *Submitted*.

Chapter 4 is a close collaboration with an experimental group that develops electronic structure as a promising materials design principle. We ultimately find strong parallels with established organometallic mechanisms and the nanoparticle synthesis of the recently reported material, Cu<sub>3</sub>PSe<sub>4</sub>. We further establish the noncovalent interaction of chalcogen bonding facilitates the covalent bond formation between phosphorus and selenium. We propose that established properties of organometallic chemistry and chalcogen bonding interactions could generally apply to the synthesis of extended materials.

In Chapter 5 we perform a detailed theoretical characterization of the ground and excited state properties of the isoelectronic (d<sup>3</sup>)  $Cr^{3+}$  and  $V^{2+}$  polypyridyls. This is in collaboration with experimental efforts that provide the first crystallographic structures of  $V^{2+}$  polypyridyls, allowing us to align geometric and electronic structure properties. Herein, we develop several methods to visualize the fluctuation in spin density associated with the excited states of open-shell systems. We find that the attractive photophysical properties of  $Cr^{3+}$  polypyridyls evades their  $V^{2+}$  analogues because of greater metal-ligand  $\pi$ -covalency that is foundational to our interpretation of the following Chapters. Most of the text and graphics have been previously published, its reference provided as follows: Joyce, J.P.<sup>+</sup>; Portillo, R.I.<sup>+</sup>; Nite, C.M.; Nite, J.M.; Nguyen, M.P.; Rappé, A.K.; Shores, M.P. *Inorg. Chem.* **2021**, *60*, 12823.

In Chapter 6 we develop a model that provides quantitative and visual insight to the discrete electron-electron interactions in open-shell systems that we refer to as the Heisenberg-Dirac-van Vleck-Strongly Orthogonal (HDvV-SO) model. This provides the first example of a graphical representation of coulombic and exchange integrals that we establish with respect to the allotropes of oxygen. We provide the theoretical context for ferromagnetic and antiferromagnetic interactions and develop how our visual tools can aide in the qualitative assignment of the sign of the magnetic interaction between unpaired electrons.

In Chapter 7 we find that the foundational electronic principles of hybridization and resonance facilitates an inversion between the quartet ground and doublet excited state of a  $V^{2+}$  tripodal complex. This unique electronic structure is engendered by the redox-noninnocence of the iminopyridine ligand and hypervalency with the tren-scaffold. We further extend our HDvV-SO model to three-electron systems to characterize the weakened exchange interactions of the quartet state and the strong antiferromagnetic couple of the doublet state.

In Chapter 8 we extend the fascinating electronic structure of Chapter 7 to the carbon monoxide hydrogenation mechanism of the vanadium nitrogenase cofactor. We frame the tripodal complexes described in the preceding chapter as biomimetic systems that provides insight to both the substrate binding and reduction of nitrogenase. This is principally developed through the reinterpretation of previous reports on these enzymatic systems that is supplemented with theoretical characterization of

a model complex. We are excited that our proposal is tenable to nitrogenase reactivity that could provide resolution to two long-standing mysteries in bioinorganic chemistry.

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#### **Chapter 1 An Introduction to Electronic Spin**

The following text is intended as a Viewpoint. It presents the historical context to the conception of electronic spin and the scientific innovations that followed. The details were collected from the following book by Theodore Arabatzis that I strongly recommend to those interested in electronic structure theory: (Representing Elections: A Biographical Approach to Theoretical Entities).

Pieter Zeeman incinerated asbestos and table salt under an applied magnetic field in 1896. The well-defined doublet, or D-lines, of the sodium atomic spectrum split into multiplets. There was no precedent in physics, neither classical nor quantum, to explain the relationship between magnetism and optics. Because his result evaded comprehension, the finding was known as the "anomalous Zeeman effect." Landé and Heisenberg independently developed models in 1921 to assign the origin of this spectral curiosity. They both expanded the basis of quantum numbers that assigned a nonvanishing angular momentum to the atomic core, where the alignment with that of the valence electron would yield nondegenerate states in the presence of a magnetic field.

Questions remained. For instance, what force separated the valence electrons from the atomic core? The problem of why elements progressed past the lowest-energy state of atomic hydrogen plagued Pauli, who accosted a colleague with the question, "How can one be happy when he is thinking about the anomalous Zeeman effect?" His publication of the Pauli Exclusion principle in 1925 resolved this conundrum, but only as a formality of quantum bookkeeping. While Pauli made the explicit connection between the Zeeman effect and the valence electron, he assigned no physical meaning to the variable of  $\pm 1/2$ . Unable to define the "two-valuedness of the electron," Pauli's publication adopted the vernacular of the Old Testament: "*There can never be two or more equivalent electrons in an atom.*"

Projecting character flaws to the subatomic level, Pauli would affectionately refer to the electron as an "antisocial" particle. Concerned with atomic spectra, physicists were content having built-up the periodic table on unshakable grounds that one was the largest dividend. However, this contradicted an earlier model of chemical bonding that portrayed electrons as monogamous. Developed by G.N. Lewis in 1916 and popularized by Langmuir in 1920, the strength of nonpolar bonds was attributed to covalency where each atom effectively shares an electron to obtain a total of eight valence electrons. Coulombic forces untenable as they were, Lewis proposed the stability of covalent bonds derived from the magnetic moment of the electron. But the theoretical limitations of the time hobbled Lewis' proposal, forcing him to admit in 1917 that "we do not at present understand" the magnetism of a chemical bond.

The advent of spin reconciled what seemed like incompatible electronic models in Physics and Chemistry. Gouldsmit and Uhlenbeck presented the new quantum numbers associated with Pauli's publication as an electron's fourth degree of freedom that would become electronic spin. Their seminal submission in 1925 was beyond reproach save for one concern: They were certain it was wrong. Upon consulting with Lorentz, they determined that an electron would need a radius of 10<sup>-12</sup> cm, rotating around its axis an order of magnitude greater than the speed of light, to derive the electron's magnetic moment. Desperate to withdraw their submission, the graduate students contacted their advisor, Ehrenfest, to no avail: *"Both of you are young,"* he responded, *"and can afford to do something stupid."* 

The conception of spin seems inseparable from inner turmoil. Ehrenfest was lauded for a preternatural understanding of quantum mechanics, a translator between the feuding vanguards of Physics. Ehrenfest would die by suicide in 1933 after shooting his fifteen-year-old son, who had Down syndrome. Lewis is considered to have conceived the hidden nature of the electron through sheer intuition, where we still refer to the lines that we draw between elements as 'Lewis dot diagrams'. Lewis would die from cyanide poising in 1941 in an apparent suicide. With rare exception is the

adjective 'arrogant' omitted from descriptions of Pauli. Common enough of an occurrence, Sommerfield would coin the 'inverse Pauli effect' to describe injuries Pauli would sustain in drunken bouts. Occurring in tandem, Pauli suffered from depression that would manifest itself in a failed marriage, vivid night terrors, and an extended correspondence with the psychologist Carl Jung to validate extrasensory perception

The darkness that murres the advent of spin is counterbalanced by the level of insight provided to the sciences. In calculations that would result in the development of Valence Bond (VB) theory, Heitler and London derived the first quantum mechanical treatment of the chemical bond in 1927. Provided the context of quantum mechanics, Pauli's Exclusion principle required that an electron's wavefunction be antisymmetric. This attributed the covalent bond of  $H_2$  with the anti-alignment of their electronic spins, the asymmetric singlet  $(M_s = 0)$  spin eigenfunction. Alternatively, the interaction between two electrons of parallel spin, the symmetric triplet  $(M_s = 1)$  spin eigenfunction, was principally a repulsive interaction. Both kismet and a Guggenheim fellowship would place Linus Pauling in the orbit of Heitler and London during their extension of quantum mechanics to diatomic hydrogen. Pauling was uniquely qualified to integrate electronic spin into the covalent bonding model as the German translator of Gouldsmit's doctoral thesis that resulted in the publication of the seminal "The Nature of the Chemical Bond" in 1931. Although the author was both a husband and a father to four children, G.N. Lewis would receive the sole dedication to Pauling's resulting textbook in 1939. Robert Mulliken characterized Pauling as a "master salesman and showman" in rationalizing the initial underwhelming response to his molecular orbital (MO) theory. However, we argue that Pauling's success and the dedicated accolades that embraced VB theory is a direct result of his groundings in crystallography. Geometric structure provides chemists the tangible impact of the unobservable properties of quantum mechanics. The extension of VB theory, both hybridization and resonance, to the full range of organic and inorganic systems rested on providing chemists something that they could see, a general insight that illuded the spectroscopic groundings of MO theory. Pauling's approach to

electronic spin maintains such concepts as hybridization and resonance as a first-line-of-defense in characterizing the chemical properties of a new system.

It is in this tradition that I cast my graduate research and my culminating dissertation. While seemingly disparate, the following chapters are each dedicated to establishing the basis of a chemical property with electronic spin. This interpretation ranges from obvious, with respect to magnetic coupling in multi-electron systems, to obscure, with the thermodynamics of saturated hydrocarbons. Advancing beyond experimental structures, I employ a diverse set of electronic structure techniques to both quantify and visualize the impact of electronic spin, with respect to noncovalent interactions and covalent bonding. I demonstrate the utility of these graphical methods in close collaboration with experimental chemists, or previously published experimental results, to provide insight to properties that might otherwise be considered "anomalous."

# Chapter 2 Protobranching as Repulsion-Induced Attraction: A Prototype for Geminal Stabilization<sup>1</sup>

## 2.1 Outline

Noncovalent interactions are traditionally defined within the context of their attractive components, such as electrostatics and dispersion. Sources of molecular strain are derived through the destabilization of coulombic and exchange repulsion. Due to this binary designation, the underlying origin of geminal stability with respect to alkanes (referred to as protobranching) has been an active subject for debate between these competing perspectives. We recast this stabilization as a complementary (*Gestalt*) interaction between dispersion and exchange repulsion, each impacting the other that is illustrated in the graphic in Figure 2.1. We use triplet hydrogen and argon dimer as foundational van der Waals adducts to develop a procedure for the visualization and quantification of both exchange repulsion,  $\Delta \rho_{SCF}$ , and medium-range correlation,  $\Delta \Delta \rho$ , as perturbations in electron density. We use the framework of the DFT-D3 correction to reproduce the shape of the dispersion potential at medium range and successfully model the trend in stability for the eighteen isomers of octane with a diverse series of functionals: BLYP, B3LYP, BP86, PBE, and PBE0. Collectively, our findings show that protobranching is a manifestation of steric repulsion-reduction in vibrational enthalpy *and* medium-range electron correlation.

#### 2.2 Division of Labor

All the work in this Chapter was completed by Justin P. Joyce

#### 2.3 Introduction

Geminal (1,3) interactions are a fertile but under-explored source of energetic differentiation: They occur in all molecules larger than nuclear diatomic, their number

<sup>&</sup>lt;sup>1</sup> J.P. Joyce, M.P. Shores, Rappé, A.K. *Phys. Chem. Chem. Phys.* 2020, **22**, 16998-17006. Reproduced in party by permission of the Royal Society of Chemistry.

increasing with chemical complexity. While these contacts are traditionally treated as afterthoughts to orbital hybridization at the central atom and electron pair repulsion,<sup>1</sup> geminal relationships are important in understanding the preferential stabilization of branched alkanes compared to their straight-chain isomers, a phenomenon known as protobranching (Figure 2.2).<sup>2</sup> These interactions are pivotal for comparing the thermodynamics of reaction pathways for the pyrolysis of hydrocarbons,<sup>3,4</sup> where low temperature, controlled pyrolysis is essential to improved isomeric product distribution in petroleum refinement and the viability of the emerging chemical recycling of olefin-based polymers.<sup>5–7</sup>



**Figure 2.1** The complementarity of overlap-induced exchange repulsion and electron correlative dispersion suggests that each is important to a complete understanding of branched hydrocarbon stability.

The physical origin of protobranching has been a source of passionate contention extending over sixty years. Conflicting reports by Pitzer and Catalano<sup>8</sup> and Bartell<sup>9</sup> initially assigned the 2 kcal mol<sup>-1</sup> stability of *iso*-butane to attractive dispersion and nonbonded repulsion, respectively. These seemingly trivial systems have humbled traditional computational approaches. The speed and efficiency of DFT methods were challenged in the early part of the 21st century by their inability to treat hydrocarbons of greater complexity than butane, with errors approximately proportional to system size.<sup>10–13</sup> Previously attributed to reduced steric repulsion<sup>14–18</sup> and enhanced hyperconjugation<sup>19–22</sup>, more recent reports propose that protobranching arises from medium-range correlation.<sup>23–26</sup> The decisive contribution of medium-range correlation for hydrocarbons was originally identified by Grimme and suggested as a critical benchmark system for functional development.<sup>27</sup>



**Figure 2.2.** The  $\Delta_f H^\circ$  of *n*-pentane (*left*) and isopentane (*right*) where the blue arrows denote an alkylalkyl geminal contact, or protobranch.

Pairwise medium-range electron correlation interactions occur at intermediate distances between a covalent bond distance and a nonbond contact. While dispersion is the omnipresent source of attraction, it is often associated with its long-range properties, which are defined by London's attractive dipole-dipole model. Exchange repulsion is a prerequisite for stability and the counterbalance to attractive electrostatics and dispersion. With few exceptions, researchers have overlooked its ability to facilitate noncovalent interactions.<sup>28–31</sup> Recent reports have highlighted exchange repulsion and dispersion as an "either-or" relationship where the two are in competition for molecular stability.<sup>32–34</sup> We note that exchange and Pauli repulsion are synonymous, and that it is always a constituent of steric repulsion, while electrostatics are system-dependent.

Here, we build upon these interpretations and present these seemingly opposing interactions as complementary: We argue their *interplay* is the source of protobranching. We frame this as a *Gestalt* interaction, about the psychological school of thought, to illustrate their

complementary nature despite their contrasting properties. We begin by examining computed potential curves for a series of diatomic complexes. The medium-range properties of  ${}^{3}\text{H}_{2}$  establish dispersion as a direct consequence of exchange repulsion. The attractive impact persists at separations on the order of a covalent bond. The canonical noble gas dimer, Ar<sub>2</sub>, is used to develop a procedure for visualizing and quantifying the observation that exchange repulsion and dispersion are complementary perturbations of electron density. This contributes to recently developed methods to plot dispersion.<sup>35–37</sup> Next, we reparametrize the DFT-D3 dispersion correction, based on argon dimer, to reproduce medium-range dispersion.<sup>38</sup> We present our D3( ${}^{3}\text{Ar}_{2}$ ) and D3(Ar<sub>2</sub>) corrections as a treatment for medium-range correlation, as it reproduces protobranching within the eighteen isomers of octane when paired with a diverse set of popular DFT functionals. Collectively, our findings highlight the decisive contribution of dispersion as a natural consequence of exchange repulsion.

#### 2.4 Results and Discussion

### 2.4.1 Dispersion Within the Repulsive Wall of Diatomic Species

The conception of dispersion forces was developed by London in 1930 to rationalize the observation of anomalous attractive interactions between inert gases. The charge neutrality and spherical symmetry of noble gas atoms preclude alignment of disparate charges or permanent multipole moments as the source of interatomic attraction. Instead, London's foundational work attributes the attractive interactions to the polarization of an atom in response to the electrostatic potential of its nearest neighbor, resulting in an induced dipole moment. These symmetry interactions are displayed in Figure 2.3 with respect to the prototypical Argon dimer system  $Ar_l/Ar_r$ . As  $Ar_l$  is polarized by  $Ar_r$ ,  $Ar_r$  is equivalently adept to polarize  $Ar_l$ , resulting in a simultaneous exhibition of attractive dipole moments. This phenomenon can be further expanded to higher-order multipole moments to include the stabilization associated with dipole-induced quadrupole moments.



**Figure 2.3**. The London simultaneously-induced multipole modes between Ar atoms, where the blue and red colors depict positive and negative dipole moments, respectively. The  $C_6$  and  $C_8$  terms describe the long- and medium-range effects of dispersion, respectively.

This interpretation results in the following relationship in Eq. 2.1 where  $C_6$  and  $C_8$  detail the attractive dipole-induced dipole and dipole-induced quadrupole moments, respectively. They are both constants based on the ionization potential and polarizabilities of the chemical identity of the pairwise interaction.

(Eq. 2.1) 
$$E_{disp} \propto -\frac{C_6}{R^6} - \frac{C_8}{R^8}$$

The London model accurately describes the long-range attraction of dispersion, but its character in the repulsive wall is ambiguous.<sup>36,39</sup> These conditions are produced in scattering experiments of noble gases, where persistent stabilization at contracted separations has been observed.<sup>40</sup> Electron correlation at close contacts is inseparable from repulsion because overlapping electron densities violate the Pauli principle, a caveat London originally addressed.<sup>41,42</sup> We note that electron correlation predominantly consists of parallel and antiparallel double excitations, which we refer to as triplet and singlet correlation, respectively. Dispersion has been largely attributed to triplet correlation.<sup>43,44</sup>

Triplet hydrogen, <sup>3</sup>H<sub>2</sub>, was selected as a model system as its electronic structure prohibits covalent bonding and allows for close approach.<sup>45</sup> A Full-CI calculation was performed on <sup>3</sup>H<sub>2</sub>

with an extended basis set and report an equilibrium separation of 4.15 Å that is stabilized by 0.013 kcal mol<sup>-1</sup>, as presented in Figure 2.4.<sup>46</sup> The correlation energy (parallel excitations) was plotted alongside the London approximation,  $C_6 \text{ R}^{-6}$ . While the dipole-dipole model accounts for dispersion at extended separations, it deviates upon contraction due to its asymptotic decay. Dispersion persists as an attractive force far inside the van der Waals minimum, since triplet correlation displays a minimum at 0.70 Å, the approximate bond length of ground state H<sub>2</sub>. is noted that its maximal attraction of -3.6 kcal mol<sup>-1</sup> is modest in comparison to the strength of the ground state H<sub>2</sub> covalent bond.



**Figure 2.4.** The Full-CI energy of  ${}^{3}\text{H}_{2}$  (dashed black line) as a function of distance. The solid red line is the associated correlation energy while the dotted blue line presents the atom-pairwise dipole-dipole term ( $C_{6} = -89.0$  kcal mol<sup>-1</sup> Å<sup>-6</sup>). The equilibrium separation is highlighted in the inset.

When the H-H distance is shortened and their orbitals overlap, exchange repulsion destabilizes the ground state while the more diffuse excited state orbitals are stabilized due to interatomic potential attraction. Cumulatively, this lowers the excitation energy of the complex and increases the magnitude of electron correlation. Far from vanishing within the repulsive wall, exchange repulsion magnifies the contribution of dispersion. This interplay is depicted in Figure 2.5, which illustrates how the double excitations polarize their adjacent orbitals to yield the anticipated dipole-dipole attractions. Pitzer presented a similar interpretation of  ${}^{3}\text{H}_{2}$  as a natural precursor to protobranching, although he was selfadmittingly hindered by the computational capability of the period.<sup>47</sup>



**Figure 2.5.** The perturbation of the ground and excited state of  ${}^{3}\text{H}_{2}$  upon orbital overlap, where the black dots denote an electron. The parallel excitations of  $\sigma$ -symmetry are overlaid with their equivalent dipole-dipole attractions, where red and blue denote an excess and depletion of electron density, respectively.

We further characterized the interplay between exchange repulsion and electron correlation with respect to the noble gas dimer  $Ar_2$ , which has served as the basis for numerous dispersion corrections.<sup>48–50</sup> and detail the computed difference between the SCF electron density of  $Ar_2$  and the isolated atoms. Bader and Ponder previously applied this formalism to exchange repulsion, which they analyzed in terms of an electrostatic interaction, while Ruedenberg presented this as a quantum mechanical expression of kinetic energy.<sup>29,51,52</sup>

The DLPNO-CCSD(T) based Local Energy Decomposition (LED) method was used to calculate exchange repulsion as a function of distance, their separation (R  $\Sigma v dW^{-1}$ ) scaled with respect to the sum of their van der Waals radii. This quantity is denoted as electronic preparation energy,  $\Delta E_{HF}^{el-prep}$ , in its original notation.<sup>53</sup> The *depleted*(-) electron density was summed within the area of overlap ( $\Delta \rho_{SCF}^{-}$ ) and a strong exponential relationship with its corresponding value for exchange repulsion was found. Its units are percent of the density of a single electron and highlight that its magnitude never exceeds more than a fraction of an electron.



**Figure 2.6** (*top*) The variation of distance (black) and exchange repulsion (red) with respect to its  $\Delta \rho_{SCF}^{-}$  value for Ar<sub>2</sub>. The green diamond and blue square denote the  $\Delta \rho$  plots presented in the middle (1.00 R  $\Sigma vdW^{-1}$ : 3.75 Å) and bottom panel (0.75 R  $\Sigma vdW^{-1}$ : 2.80 Å), respectively. The contour of the  $\Delta \rho_{SCF}$  plots are layered with isovalues of 4.00, 3.00, and 2.00 E<sup>-5</sup> a.u., where the colors blue and green denote an increase and decrease in electron density, respectively.

DLPNO-CCSD explicitly treats the double excitations that define dispersion. The impact of electron correlation was isolated by referencing its relative electron density to the associated SCF value as detailed in Eq. 2.3. The  $\Delta\Delta\rho$  plots in show a build-up of electron density in the area that is vacated through exchange repulsion. Electron correlation decreases exchange repulsion by permitting electron density to flow back into the overlap region. Rather than stabilization rooted in attractive polarization, the plots suggest that medium-range dispersion operates through a reduction in exchange repulsion. The summation of this electronic density build-up ( $\Delta\Delta\rho^+$ ) follows an exponential relationship with respect to the LED assignment of dispersion. Further decomposition of the dispersion term denotes a nearly constant 3:1 contribution of parallel and anti-parallel excitations, respectively.





**Figure 2.7** (*top*) The variation of distance (black) and exchange repulsion (red) with respect to its  $\Delta\Delta\rho^+$  value for Ar<sub>2</sub>. The green diamond and blue square denote the  $\Delta\Delta\rho$  plots presented in the middle (1.00 R  $\Sigma$ vdW<sup>-1</sup>: 3.75 Å) and bottom panels (0.75 R  $\Sigma$ vdW<sup>-1</sup>: 2.80 Å), respectively. The contour of the  $\Delta\Delta\rho$  plots are layered with isovalues of 4.00, 3.00, and 2.00 E<sup>-5</sup> where the colors blue and green denote an increase and decrease in electron density, respectively.

Fluctuations in electron density can be modulated with the existing framework of Spin-Component Scaled MP2 (SCS-MP2), that adjust the contributions of singlet and triplet correlation.<sup>54</sup> We varied these scaling factors for Ar<sub>2</sub> at a fixed distance and found that these terms display an identical impact on  $\Delta\Delta\rho^+$ . Unmodified MP2 exagerates the perturbation of correlated electron density. This agrees with its tendency to overestabilize van der Waals adducts.<sup>55,56</sup> When the correlation energy is analyzed, its overestimation is due solely to intermolecular parallel excitations. The scaling factors previously published by Grimme (Singlet =  $\frac{5}{4}$  and Triplet =  $\frac{1}{3}$ ) largely correct for this and provide quantitative agreement with DLPNO-CCSD. This procedure could similarily be applied to double-hybrid DFT functionals.

## 2.4.2 Application to Protobranching.

The stabilization of geminal contacts reiterates the importance of dispersion within the repulsive wall, as we have detailed in the context of Ar<sub>2</sub>. While we have shown that medium-range correlation can be modulated with SCS-MP2, this procedure quickly becomes cost-prohibitive with increasing size of the system. It is due to this expense that dispersion is routinely treated with the DFT-D3 correction, its formulation presented in Eq. 2.4.<sup>38</sup> Here, medium-range correlation is modelled with the expansion of the usual dipole-dipole ( $C_6$ ) term to include its dipole-quadrupole ( $C_8$ ) interactions. Due to the R<sup>-8</sup> distance dependence of the dipole-quadrupole term it has a more pronounced contribution at close contacts. The DFT-D3 model corrects for the short-range, asymptotic, behaviour of the London approximation with a damping functional.<sup>44,57,58</sup> While the a<sub>1</sub> and a<sub>2</sub> terms define the threshold distances within which dispersion is treated as a constant, the s<sub>6</sub> and s<sub>8</sub> parameters scale the contributions of dipole-dipole dipole dipole dipole-dipole interactions, respectively.

(Eq. 2.4) 
$$E_{disp}^{DFT-D3} = -\frac{1}{2} \sum_{A \neq B} \sum_{n=6,8} \frac{s_n C_n^{AB}}{R^n + \left(a_1 \sqrt{\frac{C_8^{AB}}{C_6^{AB}} + a_2}\right)^n}$$

The inability of DFT to treat dispersion is traditionally associated with its long-range behaviour operating outside of the bounds of the local density approximation.<sup>59,60</sup> Dispersion corrections are often addressed with a pragmatic approach in order to avoid 'double counting' due to the ambiguous assignment of electron correlation by the exchange-correlation functional of DFT methods.<sup>61</sup> It has been reported that the D3 correction compounds error upon contraction from equilibrium separation.<sup>62–64</sup> This limitation was addressed with a reparameterization, DFT-D3M, through expansion of the benchmark set to more adequately weigh structures that have short-range non-bonded contacts.<sup>65</sup>

The stabilization of 2,2,3,3-tetramethyl-butane with respect to *n*-octane has been employed as a benchmark for functional development due to the challenges associated with its treatment: The structures possess six to twelve protobranches, zero to six *gauche*-conformations and their stabilization  $(\Delta\Delta_t H^\circ)$  ranges across 4 kcal mol<sup>-1</sup>.<sup>66–69</sup> Geminal-alkyl, alkyl and *gauche*-contacts are separated by approximately 0.75 (2.55 Å) and 0.90 R  $\Sigma v dW^{-1}$  (3.06 Å), respectively. We expand upon this and consider the relative stability of the eighteen isomers of octane, as shown in Figure 2.8.



**Figure 2.8** The eighteen structural isomers of octane. Their number of protobranches are included alongside their gauche-torsional modes, in parenthesis. Their experimental  $\Delta\Delta_f H^\circ$ , with respect to *n*-octane, are included below.

The experimental values for  $\Delta\Delta_{\rm f}H^{\circ}$  do not account for variations in the zero-point energy and the temperature dependence of the enthalpy ( $\Delta\Delta_{\rm trv}H^{\circ}$ ) and the thermal population of higher-energy torsional modes ( $\Delta\Delta_{\rm config}H^{\circ}$ ) to the absolute energy difference ( $\Delta E$ ), as detailed below. Gronert previously attributed hydrocarbon stability to the reduced steric interactions of alkane branching.<sup>14</sup> We find that approximately 15-30% of protobranch attraction derives from  $\Delta\Delta_{\rm trv}H^{\circ}$ . Figure 2.9 shows its inverse relationship to number of geminal contacts, where a negative value indicates weaker bond

strength. We found a similar trend for gauche torsional modes, vicinal (1,4) contacts, that similarly increase with alkane branching. This suggests that geminal and vicinal contacts are a source of strain in paraffins that paradoxically contributes to protobranching stability.



(Eq. 2.5)  $\Delta\Delta_{\rm f}H^{\circ} = \Delta E + \Delta\Delta_{\rm trv}H^{\circ} + \Delta\Delta_{\rm config.}H^{\circ}$ 

**Figure 2.9** The relative enthalpy  $(\Delta \Delta_{trv} H^\circ)$  with respect to the trans-conformation of *n*-octane. The open-brown squares denote the twenty-two gauche-conformations of n-octane. The open-navy circles present the number of protobranches for the eighteen isomers of octane, corrected for their number of gauche-conformations. The inset depicts the  $\Delta \Delta_{trv} H^\circ$  of 2,2,3,3-tetramethyl-butane (red) with respect to *n*-octane (blue).

We initially performed LED analysis on the six intramolecular contacts of neopentane to isolate the stabilizing component of protobranching, our procedure detailed in the experimental. This reported that a single alkyl, alkyl-interaction contributes -1.78 kcal mol<sup>-1</sup> from dispersion, resulting in a total stabilization of -10.67 kcal mol<sup>-1</sup> with respect to neopentane. It is encouraging that its experimental isodesmic value is -13.51 kcal mol<sup>-1</sup>, that suggests dispersion is a significant contribution to the medium-range correlation of hydrocarbon systems. The collective interactions are presented in Figure 2.10 in terms of its Dispersion Interaction Density (DID) map<sup>36</sup> and our detailed  $\Delta\Delta\rho$  surfaces.



**Figure 2.10** (*left*) Dispersion Interaction Density (DID) map of the six protobranch neopentane. (*right*)  $\Delta\Delta\rho$  plot of the six protobranch contacts of neopentane in which blue and green indicate an accumulation and depletion of electron density, respectively.

We further considered hyperconjugation<sup>21</sup> as the origin of alkane stability, whose charge transfer states were investigated through the recent redevelopment of Natural Resonance Theory (NRT).<sup>70,71</sup> Hyperconjugation within paraffins possess four distinct modes,  $\sigma_{CH} \rightarrow \sigma_{CH}^*$ ,  $\sigma_{CH} \rightarrow \sigma_{CC}^*$ ,  $\sigma_{CC} \rightarrow \sigma_{CH}^*$ , and  $\sigma_{CC} \rightarrow \sigma_{CC}^*$ , as presented below in Figure 2.11.



**Figure 2.11** The four possible hyperconjugation states of a paraffin, illustrated with respect to 2methyl-butane. The charge transfer states are labeled with respect to the electron-donating  $\sigma$ -bonding and electron-accepting  $\sigma^*$ -antibonding orbital. The product of each charge transfer state is shown with respect to the oxidized (blue) and reduced (red) species and the resulting double bond.

The electron delocalization associated with the increased number of  $\sigma_{CC} \rightarrow \sigma_{CC}^*$  in branched isomers has been reported to result in their preferential stabilization. We found an inverse relationship between the total number of protobranches for the pentane isomers and the resonance contribution of its charge transfer states. This strong linear relationship was similarly reproduced with respect to the eighteen isomers of octane, as presented in . With respect to hyperconjugation this suggests that the charge transfer states do not equally contribute, and that straight-chain alkanes should possess the largest resonance stabilization energy, contradictory to their experimental  $\Delta\Delta_f H^\circ$ .

Based on our characterization of repulsive diatomic species, the components of strain detailed above should concertedly enhance electron correlation. shows DLPNO-CCSD(T) calculates a -0.80

and -1.15 kcal mol<sup>-1</sup> stabilization of the cumulative singlet and triplet correlation ( $\Delta E^{C-CCSD}$ ) for the *gauche*-torsional modes and geminal-alkyl, alkyl contacts of the octane series, respectively. The isodesmic reaction for the formation of propane from ethane and methane estimates its relative stability as -2.8 kcal mol<sup>-1</sup> suggesting that approximately half of the protobranching phenomenon is due to medium-range correlation. In relation, MP2 overestimates their attractive nature and assigns a relative correlation stabilization,  $\Delta E^{C-MP2}$ , of -1.09 and -1.70 kcal mol<sup>-1</sup> for vicinal and geminal contacts, respectively. The SCS-MP2 procedure largely corrects the MP2 error and reports  $\Delta E^{C-MP2}$  of -0.81 and -1.40 kcal mol<sup>-1</sup> for *gauche*-modes and protobranching, respectively. This agrees with our  $\Delta \Delta \rho^+$  analysis of Ar<sub>2</sub> that suggests that SCS-MP2 reproduces the impact of medium-range correlation.



**Figure 2.12** The hyperconjugation contribution (%), with respect to Natural Resonance Theory (NRT), as a function of the total number of protobranches to the isomers of pentane (red) and octane (black). The black and red dashed lines indicate the linear fit of their respective alkane series.

We used agreement between theoretical and experimental  $\Delta\Delta_f H^\circ$  for the eighteen isomers of octane as a measure of performance for a diverse series of functionals that have been previously parameterized for the DFT-D3 and D3M corrections: BLYP, B3LYP, BP86, PBE, and PBE0. In agreement with prior results, the unmodified functionals fail to model the  $\Delta\Delta_f H^\circ$  of extended alkanes.<sup>[29]</sup> While no linear trends are displayed, ( $R^2 \approx 0$ ), the chosen functionals treat alkane branching as net repulsive. The functionals display a strong linear relationship between the error in the DFT functional with respect to experiment, ( $\delta\Delta\Delta_f H^\circ$ ), and  $\Delta E^{C-CCSD}$  as shown in . This relationship suggests these functionals do not address the stabilization associated with medium-range correlation. The challenges associated with obtaining a proper long-range exchange term have been discussed extensively in the literature.<sup>72–76</sup>



**Figure 2.13** The relative parallel and anti-parallel correlation energy ( $\Delta E^{C-CCSD}$ ) with respect to the trans-conformation of *n*-octane. The open-brown squares denote the twenty-two gauche-conformations of *n*-octane. The open-navy circles present the number of protobranches for the eighteen isomers of octane, corrected for their number of *gauche*-conformations. Their linear fit is shown by the associated dashed line. The inset depicts the  $\Delta\Delta\rho$  plots the gauche-conformation of *n*-butane (*left*) and the protobranch of propane (*right*), its procedure detailed in the Experimental.

We build upon our findings to develop functional-independent dispersion corrections. We fit the  $s_8$ ,  $a_1$ , and  $a_2$  parameters of Eq. 2.4. to the LED assignment of dispersion for  $Ar_2$  to separations of up to 0.80 R  $\Sigma v dW^{-1}$ . We refer to this dispersion correction as D3(Ar<sub>2</sub>). However, the exchange-hole dipole model of Becke and Johnson treats dispersion as the natural extension of exchange repulsion. Of similar interest, the LYP correlation functional is derived from electron correlation in the ground state of the helium atom and thus precludes triplet correlation. To address this, we further decomposed the LED dispersion term into its constituent triplet correlation to generate the data for the fit for a D3(<sup>3</sup>Ar<sub>2</sub>) correction. Both are shown in Figure 2.15 alongside parameter values of the B3LYP-D3 and B3LYP-D3M corrections. For Ar<sub>2</sub>, triplet and singlet correlation possess an approximate 3:1 ratio that decays with decreased separation. We anticipate that DFT functionals whose slope of

 $\delta\Delta\Delta_{\rm f}H(\Delta E^{\rm C-CCSD})$  are roughly 1.0 and 0.75 will be most compatible with the D3(Ar<sub>2</sub>) and D3(<sup>3</sup>Ar<sub>2</sub>) correction, respectively. Both methods can be implemented within the current versions of the Gaussian and ORCA electronic structure software packages.



**Figure 2.14.** The relationship between the error of the detailed DFT functional, with respect to the experimental  $\Delta\Delta H^{\circ}$  ( $\delta\Delta\Delta_{\rm f}H^{\circ}$ ), and  $\Delta E^{\rm C-CCSD}$ . BLYP (red squares), B3LYP (blue circles), BP86 (brown diamonds), PBE (green pentagon), and PBE0 (purple stars) are reported alongside their slope.



**Figure 2.15.** The potential of the specified empirical dispersion correction for  $Ar_2$  ( $C_6 = -890.8$  kcal mol<sup>-1</sup> Å<sup>6</sup>,  $C_8 = -8890.4$  kcal mol<sup>-1</sup> Å<sup>6</sup>)

We first consider the D3, D3M, D3(<sup>3</sup>Ar<sub>2</sub>), and D3(Ar<sub>2</sub>) dispersion corrections for the popular B3LYP and PBE0 hybrid-DFT functionals, shown in Figure 2.16. The D3 correction dramatically improves both functionals for the isomeric energies of octane, although it consistently underestimates

geminal stabilization and is weakly correlated with experiment. Performance is modestly improved with use of the D3M correction which also addresses medium-range correlation, albeit through a different parameterization procedure than ours. The strongest performance is obtained with the  $D3(^{3}Ar_{2})$  and  $D3(Ar_{2})$  corrections for PBE0 and B3LYP, respectively.



**Figure 2.16** The relationship between  $\Delta\Delta_f H^\circ$  calculated with the PBE0 (left) and B3LYP (right) DFT functionals with respect to experiment. Each functional is used with their DFT-D3 (blue circles) and D3M (red diamonds) corrections and our D3(<sup>3</sup>Ar<sub>2</sub>) (green pentagon) and D3(Ar<sub>2</sub>) (purple stars) parameters.

The performance of the selected functionals in tandem with their D3 and D3M corrections, as well as the current D3(<sup>3</sup>Ar<sub>2</sub>) and D3(Ar<sub>2</sub>) corrections, are collected in . and shown. While BLYP and B3LYP are best paired with D3(Ar<sub>2</sub>), the BP86, PBE, and PBE0 functionals are closer aligned with D3(<sup>3</sup>Ar<sub>2</sub>). These results are consistent with their  $\delta\Delta\Delta_f H(\Delta E^{C-CCSD})$  dependence. In no instance do the DFT-D3 or D3M corrections outperform the current Ar<sub>2</sub> based scheme. We emphasize that the parameters of the current corrections are not optimized for any discrete functionals. A wavefunction-based conceptualization of electron correlation is compatible with DFT, whose functionals require a dispersion correction. Lastly, we detail the performance of a series of modern functionals: APF-D,  $\omega$ B97X-D,  $\omega$ B97X-D3, M06-2X, MN15, and DSD-BLYP-D3. APF-D and  $\omega$ B97X-D significantly underestimate the stability of alkane branching while  $\omega$ B97X-D3 and MN15 exaggerate its impact. Medium-range correlation remains a challenge for modern DFT functionals. M06-2X reproduces the relative enthalpies of the octane series, noting that alkane isomerization energetics was included in its parameterization.<sup>68</sup> The double-hybrid DSD-BLYP-D3 functional accurately assigns the stability of the octane series, in agreement with previous benchmark studies.<sup>77</sup> It is particularly noteworthy that the APF functional, a 41.1, 58.9% combination of B3PW91 and PBE0, parameters selected to minimize spurious interactions in the Ne dimer displays quantitative accuracy (Slope = 1.00,  $R^2$  = 0.955) when paired with the current D3(<sup>3</sup>Ar<sub>2</sub>) correction.

**Table 2.1** The slope (and  $R^2$ ) of the linear best-fit between  $\Delta \Delta_f H^\circ$ , calculated with the specified DFT functional and dispersion correction, and their experimental values. The dispersion correction that resulted in the closest agreement to experiment bolded.

	DFT	-D3	-D3M	$-D3(^{3}Ar_{2})$	-D3(Ar <sub>2</sub> )
BLYP	0.255	0.549	0.690	0.764	0.823
	(0.018)	(0.500)	(0.772)	0.802)	(0.872)
B3LYP	-0.334	0.543	0.648	0.753	0.990
	(0.041)	(0.483)	(0.688)	(0.821)	(0.955)
BP86	0.029	0.680	0.688	0.937	1.133
	(0.000)	(0.811)	(0.833)	(0.927)	(0.893)
PBE	0.154	0.559	0.645	1.036	1.264
	(0.016)	(0.508)	(0.689)	(0.937)	(0.837)
PBE0	0.154	0.575	0.677	1.113	1.343
	(0.016)	(0.536)	(0.729)	(0.911)	(0.799)

#### 2.5 Conclusion

Foundational van der Waals adducts were used to observe the persistence of dispersion at separations on the order of a covalent bond. This is a consequence of exchange repulsion. A quantitative procedure is developed that permits visualization of exchange repulsion ( $\Delta \rho_{SCF}$ ) and medium-range correlation ( $\Delta \Delta \rho$ ) as complementary perturbations in electron density. Classified as a *Gestalt* interaction, the interplay between medium-range correlation and steric

repulsion resolves conflicting reports in the literature of the origin of the protobranching. The framework of the DFT-D3 correction is used to reproduce the medium-range dispersion of Ar<sub>2</sub> and its constituent triplet correlation that yields the reported D3(Ar<sub>2</sub>) and D3(<sup>3</sup>Ar<sub>2</sub>) corrections, respectively. With the application of either of the corrections to a diverse series of popular DFT functionals the  $\Delta\Delta H^{\circ}_{\rm f}$  for the octane series are accurately reproduced. Depending on perspective, one could see protobranching as the result of either attraction or repulsion. But to fully characterize the scope of the interaction, one must acknowledge the interplay between the seemingly paradoxical pairing.

#### 2.6 Experimental

The following calculations were performed with the Gaussian09 electronic structure software package.<sup>78</sup> The <sup>3</sup>H<sub>2</sub> potential energy curve used a CISD wavefunction<sup>79</sup>, its basis set and polarization functionals developed from the references provided.<sup>46,80</sup> The <sup>9</sup>C<sub>2</sub> surface was generated with a  $CCSD(T)^{81,82}$  wavefunction using an aug-cc-pvtz<sup>83–86</sup> basis augmented by d (0.86, 0.436, 0.219, 0.11), f(0.86, 0.308, 0.12), g(0.36, 0.14), and h(0.17) polarization functions. The analogous <sup>2</sup>HHe and <sup>1</sup>He<sub>2</sub> calculations were performed with Gaussian16<sup>87</sup> at the CCSD(T) level of theory with an aug-cc-pV5Z basis set. The basis set superposition error (BSSE) was addressed with a counterpoise correction.<sup>88</sup>

Computations for Ar<sub>2</sub> were performed with the ORCA 4.1 electronic structure software package<sup>89</sup> with the aug-cc-pVQZ basis set and its associated auxiliary basis set, within RIJK approach<sup>90,91</sup>. The reported geometries were calculated at the restricted Hartree-Fock and DLPNO-CCSD level of theory. The DLPNO-CCSD(T)<sup>92,93</sup> based Local Energy Decomposition (LED)<sup>94</sup> module was conducted with TightSCF and TightPNO<sup>95,96</sup> criteria. MP2<sup>97</sup> and SCS-MP2<sup>54</sup> were performed with an unrestricted wavefunction and the RI-approximation with the basis set previously described. The contribution of Singlet (E<sub>S</sub>) and Triplet (E<sub>T</sub>) correlation were calculated with the following equations:<sup>43</sup>

(Eq. 2.6) 
$$E_{T} = \frac{3}{2} (E_{\alpha\alpha} + E_{\beta\beta})$$
  
(Eq. 2.7)  $E_{S} = E_{\alpha\beta} - \frac{1}{3} E_{T}$ 

The  $\Delta\rho_{SCF}$  and  $\Delta\Delta\rho$  plots were generated through subtraction of the specified electron density in the context of Gaussian cubes. The DLPNO-CCSD and MP2 electron densities applied were unrelaxed and relaxed, respectively. The  $\Delta\rho_{SCF}^-$  and  $\Delta\Delta\rho^+$  values were calculated through separately integrating the positive and negative electron densities for the area of overlap. As previously detailed, the  $\Delta\Delta\rho$  plots of the geminal and vicinal contact of propane and *n*-butane in Figure 8,, respectively, were generated by replacing their methyl groups with BH<sub>3</sub>.<sup>98</sup>

The DFT-D3( $^{3}$ Ar<sub>2</sub>) correction has the following parameters:

 $s_6 = 1.0000, s_8 = 0.35050, a_1 = 0.06010, a_2 = 4.63455$ 

The DFT-D3(Ar<sub>2</sub>) correction has the following parameters:

 $s_6 = 1.0000, s_8 = 0.99838, a_1 = 0.11019, a_2 = 4.64540$ 

For the octane series, vibrational frequencies and zero point correction were calculated using the APF hybrid density functional<sup>99</sup> with our D3( ${}^{3}$ Ar<sub>2</sub>) dispersion correction and a def2-TZVP basis set.<sup>100</sup> The  $\Delta\Delta_{config}H^{\circ}$  was taken as a Boltzmann distribution of the individual conformations as an ideal gas at 298 K enthalpies and referenced against *n*-octane. Both variables were applied as constants for the specified functionals. The eighteen isomers of octane were optimized at the detailed level-of-theory with the specified dispersion correction and a def2-TZVP basis set. The BLYP<sup>101</sup>, B3LYP<sup>102</sup>, BP86<sup>103,104</sup>, PBE<sup>105</sup>, PBE0<sup>106</sup>, APF<sup>99</sup>,  $\omega$ B97X-D<sup>107</sup>, M06-2X<sup>108</sup>, and MN15<sup>109</sup> functionals were calculated using Gaussian16. An analogous procedure was used in ORCA 4.1 for the optimization of the  $\omega$ B97X-D3<sup>110</sup>, MP2<sup>97</sup>, SCS-MP2<sup>54</sup>, and DSD-BLYP-D3<sup>38,111</sup> functionals. The RI-approximation was used for the MP2 methods. DLPNO-CCSD(T) was calculated with an aug-cc-pVTZ, and its associated auxiliary,

basis set and TightPNO settings with the SCS-MP2 optimized geometries. Functional performance was determined by experimental values from the National Institute of Standards and Technology (NIST).<sup>112</sup>

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# Chapter 3 Developing a Correlation Between Ligand-Ligand Structure and Spin State for the Labile Electronic Structure of Fe(II)N6 Complexes<sup>2</sup>

## 3.1 Outline

We develop an empirical structural parameter ( $\beta$ ) that assigns the spin state of Fe<sup>2+</sup> in an octahedral coordination environment of N(sp<sup>2</sup>) donor atoms with an approximately 95% certainty. Our parameter is benchmarked against the Cambridge Structural Database (CSD), which provides the largest catalogue of spin labile complexes, with approximately 3,000 unique structures. We strictly consider the discrete noncovalent interactions between coordinated ligands in the primary coordination sphere that fluctuate with spin state geometry changes. To model this, we combine the ionization potential of the lone pairs based on the hybridization of the nitrogen-donor atoms and their separation between *cis*-contacts. Both features are characteristic of the exchange repulsion in the primary coordination sphere that, in turn, initiates a concurrent stabilization from both medium-range electron correlation (dispersion) and vibrational enthalpy (zero-point energy).

## **3.2 Division of Labor**

All work in this Chapter was performed by Justin P. Joyce.

#### **3.3 Introduction**

Spin crossover is traditionally conceptualized as a delicate balance between ligand field stabilization and exchange interactions of the low- and high-spin states, respectively.<sup>1–4</sup> While researchers have taken a variety of approaches toward developing tools for spin-state prediction, there remains a need for a comprehensive model that assigns spin state probability to an arbitrary structure to reduce the 'trial-and-error' associated with inorganic synthesis.

<sup>&</sup>lt;sup>2</sup> This chapter has been submitted, in part, as a manuscript to *Inorganic Chemistry*: Joyce, J.P; Shores, M.P.; Rappé, A.K. *Submitted*.

Electronic considerations for spin crossover are often diagnostic rather than predictive, due to the dynamic interplay of  $\sigma$ - and  $\pi$ -effects on ligand field strength.<sup>5–7</sup> The ambiguous characterization of diimines as  $\pi$ -donors or  $\pi^*$ -acceptors further complicates the use of ligand field strength as a spin crossover design principle.<sup>8,9</sup> Alternatively, structural models have detailed the bite angle that diimines form upon chelation as descriptive of metal-ligand bond strength. Alvarez developed a minimal distortion pathway between spin states, reminiscent of a Bailar twist, in the context of the continuous shape measure (CShM) that is correlated with  $T_{1/2}$ .<sup>10–12</sup> Shatruk more recently considered the local geometry of uncoordinated diimines, separation between N-donor atoms, as an indicator of its ability to distort between spin states.<sup>13,14</sup> However, the quantitative insight of both models detailed above are specific to the spin state properties of a tris-bidentate coordination environment. Generalization of such models to resolve the root-causes of spin state switching is highly desirable for molecular and materials development.<sup>15–19</sup>

Due to variable population of their antibonding  $(e_g^*)$  orbitals, each spin state in Fe<sup>2+</sup> complexes displays distinct structural properties that modulate the ligand-ligand noncovalent interactions of the twelve *cis*-contacts in an octahedral coordination environment.<sup>20,21</sup> Species in the high-spin state show both lengthened and weakened metal-ligand bonds with respect to the low spin state, resulting in an entropically driven population of the high spin state with increasing temperatures.<sup>22,23</sup>

Less-explored for incitement of spin crossover are ligand-ligand interactions. Originating with crystal field theory and developed by the ligand close-packing model, *ligand-ligand* interactions have been treated as a source of strain, the sum of electrostatic and exchange (Pauli) repulsion between bound ligands.<sup>24–27</sup> Recent reports have challenged this outlook by rebranding sterically congested ligand sets as dispersion energy donors, stabilizing organic and

organometallic complexes through London dispersion interactions.<sup>28–31</sup> In this report, we suggest that such rebranding may also be useful to spin state prediction.

Our proposed model is inspired by efforts to elucidate the phenomenon of protobranching, where paraffin structural isomers with a greater number of geminal (1,3) alkyl, alkyl contacts are preferentially stabilized with respect to their straight-chain analogues.<sup>32,33</sup> The enthalpy of formation  $(\Delta_f H^\circ)$  is stabilized by 5.0 kcal mol<sup>-1</sup> for neopentane with respect to *n*-pentane, illustrated in Figure 3.1 as a representative example. Counterintuitively, hydrocarbons achieve greater stability when their bonding environment exhibits greater strain due to steric congestion. We recently conceived the complementarity between strain and dispersion as the basis of protobranching, which we label a *Gestalt* interaction.<sup>34</sup> Our  $\Delta\Delta\rho$  plots, detailed below, illustrate the stabilization provided from proximal nonbond contacts, where blue shows an attractive accumulation of correlated electron density.



**Figure 3.1.** (*top*) The enthalpy of formation of isopentane with respect to its structural isomer, *n*-pentane. The blue arrows denote a geminal (1,3)-alkyl,alkyl interaction. (*bottom*) The enthalpy of the low spin state of an octahedral transition metal complex with respect to its high spin state. The dashed blue lines indicate a *cis*-contact between the ligand donor atoms. The  $\Delta\Delta\rho$  plots, as detailed in the main text, that display the attractive electron correlation between geminal-CH<sub>3</sub>,CH<sub>3</sub> groups in propane and the cis-coordinated NH<sub>3</sub> ligands (blue shading).

The energy governing protobranching stabilization is of the same magnitude as the spin state energetics of spin crossover complexes ( $\Delta H_{\text{HS/LS}}$ ) where the low-spin state is stabilized by approximately 0.5-6.5 kcal mol<sup>-1</sup>.<sup>35</sup> In terms of structural similarities of their 1,3-separation, noncovalent interactions involving *cis*-contacts between donor atoms in octahedral transition metal complexes are analogous to geminal interactions in hydrocarbons. Thus, we propose that the noncovalent interactions between *cis*-contacts of octahedral transition metal complexes will similarly impact spin labile systems to preferentially stabilize their low-spin state. Here, our particular focus is Fe<sup>2+</sup> in an octahedral coordination environment, due to the large number of structures known and the relative importance of the d<sup>6</sup> ion in photovoltaic and catalytic systems.<sup>36–41</sup>

Herein, we develop an empirical structural parameter to assign Fe<sup>2+</sup> spin state *based solely on ligand-ligand interactions* in the primary coordination sphere with respect to the accrued strain and stability. We report the quantitative assignment of the magnetic properties for the full crystallographic catalogue of Fe<sup>2+</sup> complexes with an octahedral coordination environment of nitrogen-(sp<sup>2</sup>) donor atoms, comprising nearly 3,000 unique Fe<sup>2+</sup> metal centres.<sup>18,42-45</sup> We find that spin crossover properties can be related to ligand-ligand (Gestalt) interactions with an approximate 95% probability, regardless of the connectivity between the nitrogen-donor atoms.

#### **3.4** Results and Discussion

## 3.4.1 Ligand-Ligand Contacts as Gestalt Interactions

As an illustrative example, we consider the energy constituents of the noncovalent interactions between two *cis*-oriented molecules of bipyridine (bpy) at a geometry associated with the octahedral low-spin Fe<sup>2+</sup> complex, [Fe(bpy)<sub>3</sub>]<sup>2+</sup>. The ligand-ligand separations of the Fe<sup>2+</sup> octahedral coordination geometries vary as widely as a factor of 0.85-1.05 between its spin states, as scaled to the sum of their van der Waals radii (R  $\Sigma$ vdW<sup>-1</sup>).<sup>46</sup> Exchange repulsion is the strain that results from the proximity of electrons of parallel spin, the energetic penalty undergirding the Pauli exclusion principle.<sup>47,48</sup> Hartree-Fock theory addresses electron anti-symmetry with the Slater determinant. We reference the HartreeFock electron density of the bpy adduct with respect to its isolated fragments. Figure 3.2 shows the resulting  $\Delta \rho_{SCF}$  plot of Eq. 3.1 that illustrates the depletion of electron density (green) from the area of overlap between the nitrogen lone pairs that results from the orthogonalization of their occupied orbitals.

(Eq. 3.1)  $\Delta \rho_{SCF} = \rho_{(bpy)_2} - \rho_{(bpy)_1} - \rho_{(bpy)_r}$ 



**Figure 3.2** The  $\Delta \rho_{SCF}$  (*left*) and  $\Delta \Delta \rho$  (*right*) plots depicting the noncovalent interaction between two bipyridine molecules shown with respect to their low-spin geometry in  $[Fe(bpy)_3]^{2+}$ ; two different orientations are shown (*top*) and (*bottom*). Green and blue denotes a decrease and increase in electron density, respectively, of the complex,  $(bpy)_2$ , with respect to the isolated molecules. The plots are overlaid with the structure of  $[Fe^{2+} (bpy)_3]$  to aid visualization; however, the metal-centre was omitted from the calculation.

At the long-range separation associated with the high-spin geometry, approximately 3.0 Å, the ligand-ligand non-bond contacts include a component of electron correlation that the London dipole-induced dipole model treats accurately. Another word for this attraction is dispersion.<sup>31</sup> In quantum mechanics, dispersion is the symmetric configuration interactions that result from the excitation of a pair of electrons with parallel spin on separate centres. The system's electron correlation polarizes the occupied excited state orbitals to separate the electrons of parallel spin and thus lowers interelectronic repulsion of the system.<sup>49</sup> This stabilizes the  $\pi^*$ -orbitals of our current system, as illustrated in Figure 3.3 Concurrently, exchange repulsion destabilizes the electronic ground state that raises the energy of the  $\sigma$ -orbitals and magnifies the contribution of electron correlation.



**Figure 3.3** (*left*) The positive orbital overlap (orange) between the nitrogen lone pairs of *cis*coordinated pyridine groups in a perpendicular conformation. (*right*) The symmetric dipoleinduced dipole interactions between the pyridine groups that result from double excitations, triplet correlation. Red and blue denote increase and decrease of electron density, respectively, in the presence of a dipole moment. (*bottom*) The impact of excitations on orbital energies is provided.

Using the procedure detailed for computing  $\Delta \rho_{SCF}$ , we calculate the relative density of the bipyridine adducts at the DLPNO-CCSD level-of-theory, generating a  $\Delta \rho_{DLPNO-CCSD}$  plot. The DLPNO-CCSD approach accounts for the double excitations, illustrated in Figure 3.3, that allow us to isolate the impact of medium-range correlation on the system.<sup>50–52</sup> The resulting  $\Delta \Delta \rho$  plot is detailed in Eq.

3.2 and shown in Figure 3.2. Through polarization of the  $\pi^*$ -orbitals, electron density is reallocated to the area of overlap (blue) between adjacent nitrogen groups.

(Eq. 3.2) 
$$\Delta\Delta\rho = \Delta\rho_{\text{DLPNO-CCSD}} - \Delta\rho_{\text{SCF}}$$

With respect to perturbations in electron density, medium-range correlation and exchange repulsion are complementary interactions. We note that correlation is most pronounced between pyridine groups in a perpendicular conformation that we refer as an 'L-shape' that is depicted in Figure 3.3.<sup>53</sup> The conformational dependence illustrates that the stability provided by electron correlation is also dependent on ligand topology and the electronic character of the secondary coordination sphere.<sup>54,55</sup>

We characterize the impact of the ligand-ligand interactions on the metal-centre properties with respect to the *mer*- and *fac*-structural isomers of the model complex,  $[Fe(NH_3)_3(py)_3]^{2+}$ . Our model system is inspired by meticulous reports from Piguet and co-workers that *fac*-coordination environments display higher transition temperatures than their *mer*-analogues.<sup>55,56</sup> Their analysis aligned the spin-switching property with the *trans*-effect, the *fac*-coordination environment providing for stronger metal-ligand bonds. The *fac*- and *mer*- structures possess three and two nonbond *cis*-contacts between their N-donor pyridyl ligands, respectively. The ligand-ligand electron correlation consists of  $\pi$ - $\pi$  and C-H/ $\pi$  noncovalent interactions, and the *fac*-structure displays more of these. We note that the pyridyl ligands of the *fac*-stereoisomers intertwine the pyridyl ligands with correlated electron density, as shown in Figure 3.4. We do not observe this entanglement for the *mer*-structure. While these are noncovalent interactions, we address the accumulation of correlated electron density between the N-donor atoms as a bonding-type interaction that should inhibit the structural deformation associated with adopting a high-spin state.

Our DLPNO-CCSD(T) calculations on the ligand sphere support this claim, demonstrating that the *fac*-ligand sphere possesses 0.69 kcal mol<sup>-1</sup> greater electron correlation than its *mer*-analogue. We note

that this greater electron correlation is accompanied by an additional 1.60 kcal mol<sup>-1</sup> of ligand strain in the *fac*-complex, suggesting that its stereochemistry is net repulsive. Nevertheless, when considering the influence of *ligand-ligand* contacts on the energetics of the *metal-ligand* bonds, we find that the *fac*-stereoisomer is enthalpically stabilized relative to the *mer*- form. We perform a frequency calculation on both structural isomers with the hybrid-DFT functional, TPSSh, which has been reported to accurately assign spin state energetics.<sup>57,58</sup> Fascinatingly, the difference in the zero-point energy and the thermal vibrational correction to enthalpy preferentially stabilizes the *fac*-stereoisomer by 0.97 kcal mol<sup>-1</sup>. We refer to this term as  $\Delta\Delta_{trv}H^{\circ}$  and attribute it to the repulsion-induced reduction in vibrational enthalpy (Figure 3.5). The TPSSh treatment ultimately assigns the *fac*-isomer as the molecule's ground state, whose enthalpy is stabilized by 1.57 kcal mol<sup>-1</sup> with respect to the *mer*-structure. While the magnitude of this energy difference is seemingly inconsequential, this perturbation in spin state energetics will shift the *T*<sub>1/2</sub> of the complex by approximately 110-140 K, with the range depending on the entropy of the spin state change.<sup>57</sup>



**Figure 3.4** (*top*) The *fac*- and *mer*-stereoisomers of the model complex  $[Fe(py)_3(NH_3)_3]^{2+}$  that possess three and two *cis*-contacts between their pyridyl ligands, respectively, illustrated by the purple shading. (*bottom*) The corresponding  $\Delta\Delta\rho$  plot of the noncovalent interactions between the three pyridine groups.

## 3.4.1 Quantifying Impacts of Ligand-Ligand Interactions on Local Spin

Drawing from the electronic structure insights discussed above, the low-spin state should be preferred, depending on the magnitude of its ligand-ligand noncovalent interactions. Coordination environments with short separations between their 1,3-donor atoms will exhibit a pronounced influence on these noncovalent interactions. The stability provided from these pairwise terms will depend on the ionizability and polarizability of the ligand identity as illustrated in Figure 3.2



**Figure 3.5** The enthalpy with respect to the Fe-N bond distance for the *fac*-(red) and *mer*-(blue) stereoisomers of  $[Fe(py)_3(NH_3)_3]^{2+}$  where their *cis*- and *trans*-contacts between the pyridyl ligands are highlighted in shades of purple. The zero-point energies are shown with the corresponding stabilization of the *mer*- with respect to the *fac* isomer  $(\Delta \Delta_{trv} H^\circ)$ 

We present an empirical structural parameter that assigns the spin state of octahedral [Fe<sup>2+</sup>N<sub>6</sub>] coordination complexes, where N is formally sp<sup>2</sup> hybridized. Each pairwise contact between *cis*-donor atoms is characterized by their separation and the hybridizations of their lone pairs. The hybridization of orbitals is not restricted to integer values, where sp<sup>n</sup> orbitals are traditionally assigned values of one, two, or three based on the valency of the atom center.<sup>59,60</sup> Eq. 3.3 describes the fractional amount of p-character, sp<sup>n</sup>, of a divalent pnictogen lone pair, where  $\theta$  is the ∠C-N-C angle of the coordinated ligand set. A lone pair of a smaller ionization potential will have lesser exchange repulsion associated with

its redistribution of electron density. As illustrated in Figure 3.6, greater bond angles of divalent molecules are associated with greater p-character of their lone pairs. Significant deviations from the ideal bond angle of  $120^{\circ}$  for a sp<sup>2</sup>-hybridized nitrogen result from ring strain that is illustrated in Figure 3.6. This model is consistent with experimental observations that 6-membered heterocycles stabilize the low-spin state of Fe<sup>2+</sup> complexes while 5-membered heterocycles can support spin crossover.<sup>13</sup>



**Figure 3.6** The hybridization of a nitrogen (imine) lone pair as a function of its bond angle where X can refer to C-H, N-H, or N groups. The ideal sp and sp<sup>3</sup> hybridized orbitals are provided on the left and right, respectively.

Combining ligand-ligand distance and N-donor hybridization considerations, we propose the

Gestalt parameter (B) a spin state parameter, provided in Eq. 3.4 and depicted in the figure below.

(Eq. 3.4) 
$$\beta = \frac{1}{N} \sum_{A \neq B} \frac{4}{9 \sum v dW} \left( \frac{d_{A,B}}{s p_A^n s p_B^n} \right)$$

**Figure 3.7.** The primary coordination sphere of an octahedral  $[Fe^{2+}N_6]$  complex whose N donor atoms are formally sp<sup>2</sup>-hybridized. The separation between the N-donor atoms is highlighted in orange (d<sub>A,B</sub>). The bond angle of the divalent N-donor ligands is highlighted in green ( $\theta_A$  and  $\theta_B$ ) that impact the hybridization of their lone pairs.

Based on our findings detailed above, a description of exchange repulsion should similarly address the stabilization provided by medium-range electron correlation and the vibrational enthalpy stabilization of the metal-ligand bonds by virtue of their complementary relationship. Furthermore, the p-orbital composition of the lone-pair of the  $\sigma$ -donor ligands is scaled relative to a pure sp<sup>2</sup>-hybridized orbital.

While our focus is on variations in nonbond contacts, our method is consistent with traditional considerations of metal-ligand bond strength for spin state stability. For example, Kulik has previously developed an artificial neural network that assigns the spin state of Fe<sup>2+</sup> and Fe<sup>3+</sup> complexes based on experimental and simulated metal-ligand bond lengths,<sup>61–63</sup> where shorter *cis*-contacts will result from shorter metal-ligand bond length. Also, the  $\sigma$ -donor strength of a ligand increases with the p-orbital composition of its lone-pair that stabilizes a low-spin state. Rather than assign cause-and-effect to either structural property, we maintain the following interpretation: ligand-ligand interactions concurrently stabilize metal-ligand bonding.

To test and validate  $\beta$ , we refer to a dataset that constitutes the largest catalogue of spin crossover complexes structurally analysed, a product of the Cambridge Structural Database (CSD) that reports approximately 3,000 unique Fe<sup>2+</sup> centers.<sup>64</sup> The CSD structures are assigned as low- or high-spin or spin crossover based on their accompanied publications. For our current analysis, we do not distinguish between changes of spin state based on counter-anion or co-crystalized solvent identity or substituent groups that strictly impact the ligand electronics.<sup>65,66</sup> As such, we are designating whether a structure *can* exhibit spin crossover under reasonable experimental conditions, rather than *will* exhibit spin crossover. We note that our assignments are not processed by machine learning but are allocated by 'manual' learning. For this data set,  $\beta$  ranges from approximately 0.75 – 3.00, where complexes with lesser values of  $\beta$  are associated with shorter contacts and lone pairs of greater p-character. These properties should concurrently decrease exchange repulsion and increase electron correlation and the vibrational stabilization to enthalpy that would favour a low-spin configuration.

Figure 3.8 (*top*) shows the distribution of Fe<sup>2+</sup> spin state as a function of  $\beta$ . The 1,616 low-spin structures are centred at 1.00 with a narrow distribution of  $\sigma_{LS} = 0.09$ ,  $R^2 = 0.999$ , that is detailed in Eq. 3.5. We assign 1,621 structures as able to undergo spin crossover that conform to a Gaussian distribution centred at 1.72 with its range spanning from approximately 1.1-2.3 ( $\sigma_{SCO} = 0.30$ ) with an  $R^2 = 0.973$  that is detailed in Eq. 3.6. While the current ligand set only supports 90 high-spin structures, their distribution does not conform to a Gaussian function. This distribution more generally shows that our current ligand set does not readily support a Fe<sup>2+</sup> high-spin state. The data suggest that the primary coordination sphere of octahedral Fe<sup>2+</sup> low-spin complexes is well-defined while spin crossover and high-spin structures are flexible. We attribute this small deviation to the interplay of steric and electron correlation between the N-donor ligands that are magnified at the short *cis* contacts associated with the low-spin geometry.

For comparison, we also include the spin state distribution of the detailed data set with respect to the average Fe-N bond distance (Figure 3.8, *bottom*). The spin crossover complexes are separated into two distributions of metal-ligand bond lengths that correspond to whether their structure was collected in the low or high-spin state. There is no distinction between the bond length of low-spin state and spin crossover complexes whose structures were collected in their low-spin state. We note that there is no connection between the average metal-ligand bond distance and our assigned Gestalt parameter that is included in Figure 3.9. Our Gestalt parameter exhibits fine resolution between the low-spin and spin crossover complexes, and thus illustrates how consideration of ligand-ligand interactions offers unique insights for elucidating the electronic structures of coordination complexes.

(Eq. 3.5) 
$$y_{LS} = 950.6e^{-\frac{(1.000-x)^2}{2(0.083)^2}}$$
  
(Eq. 3.6)  $y_{SCO} = 370.3e^{-\frac{(1.724-x)^2}{2(0.297)^2}}$   
(Eq. 3.7)  $P_{SCO} = \frac{y_{SCO}}{y_{LS} + y_{SCO}}$ 



**Figure 3.8** (*top*) The histogram of the assigned low-spin (blue), spin crossover (purple), and high-spin (red) structures, with respect to  $\beta$ , of the detailed CSD data set for Fe<sup>2+</sup> complexes with N<sub>6</sub> first coordination sphere. The dashed lines represent the Gaussian fits, whose color corresponds to the distribution of the low-spin and spin crossover complexes. No fit was provided for the distribution of high-spin complexes. (*bottom*) The histogram of the dataset detailed above with respect to the average Fe-N bond distance of each complex.

Eq. 3.5 and 3.6 provide the best fits of the Gaussian distributions of the low-spin and spin crossover complexes. Based on the data analyzed here, we propose that a structure can exhibit spin crossover with a  $\beta$ -value greater than  $+3\sigma_{LS}$  of the average low-spin  $\beta$ -value that is detailed in Eq. 3.7. The instances of high-spin structures are a small constituency of the data set, approximately 3%, and are not addressed in our current model. The normal distributions of the low-spin and spin crossover structures are well-separated, with only 5.56% of the spin crossover structures overlapping in this range. Based on this finding, our  $\beta$ -parameter should assign a structures ability to exhibit spin crossover with an approximate certainty of 95%. We note that a significant portion of the seventy structures

whose spin states were unassigned in their accompanied publication are promising candidates to exhibit spin state lability.



**Figure 3.9.** Our calculated Gestalt Parameter ( $\beta$ ) as a function of the average Fe<sup>2+</sup> - N bond distance of the octahedral complex.

Lastly, we detail complexes that do not conform to our current analysis. Inspecting individual outliers (<  $+3\sigma_{LS}$ ), we find that the complexes that show spin crossover but are assigned as low-spinonly have substituents that inhibit metal-ligand bonding. This category largely consists of pyridyl ligands that have a substituent located *ortho-* to the coordinated nitrogen.<sup>67</sup> We also find instances where low-spin complexes are incorrectly assigned as to exhibit spin crossover. These instances primarily consist of tripodal complexes whose pendant group is a sp<sup>3</sup>-hybridized carbon, suggesting that the ligand architecture cannot distort toward a high-spin geometry.<sup>68,69</sup> Both anomalies were addressed by Shatruk and coworkers<sup>13</sup>, the corresponding structures being omitted from their data set. Similarly, complexes that display significant noncovalent interactions in their ligand topology exhibit larger  $\beta$ -values than their low-spin state would predict. We interpret this finding to mean that nonbond contacts in the secondary, as well as primary, coordination spheres can impact the local electronic structure of their metal centres, and such structural features should be considered in the design of spin labile complexes.<sup>57,70</sup>

## **3.5 Conclusions**

Analysis of the current data set of nearly 3000 Fe(II)N<sub>6</sub> complexes strongly supports the conjecture that noncovalent interactions between coordinated ligand sets can impact the spin state of the metal centre. This is rooted in the complementary relationship between exchange repulsion and dispersion. Similarly, molecular strain can impact the metal-ligand bonds to stabilize the complex by a reduction in vibrational enthalpy. This interaction is magnified in low-spin structures due to the proximity between ligands and the stronger  $\sigma$ -donor strength that provides a well-defined coordination sphere illustrated by our structural parameter detailed herein. Our Gestalt ( $\beta$ ) parameter can assign the probability that a complex can display spin crossover from both experimental and computed structures. This current data set also highlights direct impacts of peripheral ligand characteristics on metal-centred properties. These results should naturally extend to other transition metal systems and coordination environments where currently accessible structural data could allude to promising candidates with labile spin states. Our analysis also illustrates the decisive impact of nonbond contacts in the secondary coordination sphere that should inform future iterations of spin state-structural relationships.

We also suggest that the β-value obtained from DFT geometry optimizations of a low-spin state should provide a valuable tool to discern whether a complex can display spin crossover.<sup>71</sup> We anticipate this will provide a facile method to screen spin crossover complexes prior to synthetic efforts. This tool is valuable given the challenge in the direct calculation of spin state energetics *via* DFT functionals.<sup>72–74</sup> Our proposed protocol would only require a single calculation of a diamagnetic structure whose electronic structure is single-determinantal in nature, which is easily accessible to any electronic structure software suite. The notation provided is general enough that it can be applied to systems irrespective of metal or coordination geometry. We selected our current focus on 6-coordinate ferrous complexes with imine-type ligands to employ the largest available data set to maximally validate our model. Extension of our current method to other spin and conformationally labile species are in progress for our groups.

## **3.6 Experimental Methods**

## *3.6.1 Theoretical Methods.*

The following calculations were performed with the ORCA 4.1 electronic structure software package.<sup>75</sup> The *fac*-[Fe(NH<sub>3</sub>)<sub>3</sub>(py)<sub>3</sub>]<sup>2+</sup> and *mer*-[Fe(NH<sub>3</sub>)<sub>3</sub>(py)<sub>3</sub>]<sup>2+</sup> low-spin geometries were optimized with the TPSSh hybrid-DFT functional.<sup>76</sup> A def2-TZVP basis set was used with its corresponding auxiliary basis set with the RIJK approximation.<sup>77,78</sup> The parameterized DFT-D3 empirical dispersion correction was used.<sup>79</sup> Solvation effects were addressed with the polarizable continuum model (CPCM) for acetonitrile.<sup>80</sup> Analytic frequency calculations were performed at room temperature at the detailed level-of-theory that verified them as energetic minima.

The geometry of the low-spin (singlet) state of  $[Fe(NH_3)_6]^{2+}$  and  $[Fe(bpy)_3]^{2+}$  was optimized where the six metal-ligand bond lengths were constrained to 1.90 Å. The  $\Delta\Delta\rho$  plot of propane in Figure 3.1 was generated by replacing its methyl groups with BH<sub>3</sub>. The metal centre was omitted in the generation of the  $\Delta\rho_{SCF}$  and  $\Delta\Delta\rho$  plots of the ligand-ligand interactions of the transition metal complexes.

The following calculations were performed on the ligand sphere of the Fe<sup>2+</sup> complexes detailed above in the absence of their metal center. The Hartree-Fock, DLPNO-CCSD, and DLPNO-CCSD(T) calculations were performed with a restricted wavefunction and a cc-pVTZ basis set, and their corresponding axillary basis set with the RIJK approximation.<sup>81,82</sup> The electron densities used to generate the  $\Delta\Delta\rho$  plots from the DLPNO-CCSD wavefunction were unrelaxed. The interaction energies were corrected for their basis set superposition error (BSSE) with a counterpoise correction.<sup>83</sup>

For the decomposition analysis we define strain as the Hartree-Fock interaction energy. With respect to the Local Energy Decomposition (LED) analysis this is the sum of the electronic preparation, electrostatic, and exchange energies.<sup>84</sup> We define electron correlation as the interaction energy of the strong pair, doubles excitations, correlation energy. With respect to LED analysis this is the sum of dispersion, charge transfer, and the correlation preparation energy.

The following Gaussian surfaces were generated using in-house FORTRAN codes: Relative electron densities, Orbital overlap, Dipole-induced Dipole, and s-p hybridized orbital.

## 3.6.2 Data Sampling.

The CSD submissions of  $[Fe^{2+}N(sp^2)_6]$  complexes were accessed on May 13th, 2021.<sup>11</sup> The submissions were restricted to those whose chemical identity specified a +2 oxidation state of the iron center. The structural parameters were obtained for the twelve *cis*-contacts where an angle between the two N-donor atoms was constrained from 60°-120°. The N-donor atoms were required to be covalently bonded to two groups so that its hybridization was nominally sp<sup>2</sup>. No restriction was placed on the total charge of the complex. We did not filter complexes whose chemical identity has multiple submissions. This is particularly relevant for the homoleptic tris(bidentate) complexes of bipyridine and phenanthroline. No restriction was placed on the data collection temperature for crystal structures: that is relevant for variable temperature crystallography that is sometimes performed on spin labile complexes.

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## Chapter 4 Chalcogen Bonding as a Materials Design Principle for the Colloidal Nanoparticle Synthesis of Cu<sub>3</sub>PSe<sub>4</sub>

## 4.1 Outline

We previously reported the solution-phase synthesis of  $Cu_3PSe_4$ . Here, we direct our focus to the Se precursor to monomer transformation, specifically Se powder in 1-octadecene, and the role its molecular transformation has on the assembly of Se-P bonds and on the synthesis of Cu<sub>3</sub>PSe<sub>4</sub>. The combination of Se powder and octadecene as a solvent is common in the synthesis of binary and ternary selenide nanoparticles, so an understanding of the complexity of the selenium activation to selenide is broadly applicable to a wide range of reactions. In the context of the reaction described herein, the formation of Se-P, rather than Se-Cu, bonds are anomalous in the context of HSAB principles. Through judicious selection of selenide monomers, we probe the molecular-level impact of a Lewis basic  $(H_2Se)$ and Lewis acidic ( $R_2Se$ ) source on bond formation. We show that the Se monomer  $R_2Se$ , which is Lewis acidic along its Se-R bond axis, contributes largely to the formation of phase-pure Cu<sub>3</sub>PSe<sub>4</sub> due to its ability to chalcogen bond and subsequently undergo reductive elimination with Cu<sub>3</sub>P precursor to form P-Se bonds and an extended and unsaturated hydrocarbon. The application of chalcogen bonding in supramolecular assembly and organic transformations of the precursor, due to the interaction of non-innocent solvent, alludes to a fertile method for materials development where bonds can be formed between seemingly antagonistic groups to enable the controlled synthesis of a compositionally complex material.

### 4.2 Division of Labor

The following Chapter was a collaborative effort between theoretical and experimental techniques. The computational work was done by Justin P. Joyce under the guidance of Dr. Anthony K. Rappé and Dr. Matthew P. Shores. The experimental was largely developed and performed by Jennifer M. Lee with the guidance of Dr. Amy L. Prieto. Nathan Neissius performed the solution-based GC-MS and provided insight on its limitations. Devon Leimkuhl performed part of the synthesis of the starting materials and performed some of the control experiments. This chapter was prepared for submission to *Chemical Science* by the forementioned parties.

## 4.3 Introduction

As the demand for materials with coveted physical properties for diverse applications<sup>1-4</sup> such as energy conversion<sup>5–7</sup> and storage<sup>7,8</sup> increases, a concomitant diversity in the chemical composition of candidate materials is required. Colloidal nanoparticle (NP) synthesis provides a method to expand the accessible compositional phase space of semiconductor materials by virtue of its solution-based regime.<sup>9-16</sup> However, increasing the complexity of nanoparticle composition inherently introduces synthetic challenges. Contrary to the classical nucleation theory in which nanoparticles nucleate and grow by monomer additions, nanoparticles can also be formed through dynamic chemical processes in which molecular rearrangements occur at very short time scales.<sup>17,18</sup> These reactions are often convoluted because they involve molecular species dissolved in fairly complex solvents to yield a diversity of species as well as the nucleation and growth of extended solids with high surface area.<sup>19–22</sup> Refinement of this toolkit is currently limited by the difficulty in assigning mechanistic detail to the molecular level transformations that yield extended materials, which hinders the development of new reactions. Thus, it is imperative to investigate these molecular level transformations to gain a global understanding of the reaction.<sup>23-28</sup> Such mechanistic understanding would lead to a general design strategy for controllably making materials of diverse composition, structure, and morphology.

Ternary copper-based chalcogenide nanoparticles have been an area of intense focus due to their application as photovoltaic absorbers and their non-toxic and earth-abundant composition.<sup>29–32</sup> We previously reported the solution-phase synthesis of copper

selenophosphate, Cu<sub>3</sub>PSe<sub>4</sub>, an earth abundant alternative to other PV-related materials.<sup>33</sup> Successful synthesis of Cu<sub>3</sub>PSe<sub>4</sub> NPs involved the selenization of phase-pure Cu<sub>3</sub>P NPs with Se powder in 1-octadecene (1-ODE) precursor. Our focus was to target specific bond formations through planned reaction pathways which enabled controlled synthesis of the ternary material. We found that product formation was acutely sensitive to the Se precursor and solvents used. The reactivity of the Se with the solvent used was complex, and a deeper understanding of that chemistry would be widely applicable for the synthesis of selenide-based semiconducting nanoparticles. Here, our scope focuses on the selenium precursor to monomer transformation, specifically Se powder in 1-octadecene (1-ODE) solvent, and the role its molecular transformation has on the assembly of Se-P bonds toward the material's synthesis.

The formation of Se-P, rather than Se-Cu, bonds is anomalous in the context of Hard-Soft Acid-Base (HSAB) principles.<sup>19,31,34,35</sup> While hardness is a global parameter, selenides are classified as ambiphilic, possessing directionally dependent Lewis acidic (LA) and Lewis basic (LB) properties due to a non-uniform electronic distribution.<sup>36</sup> With respect to chalcogen bonding, selenides display short and directional non-bond contacts with nucleophiles.<sup>37,38</sup> Here we specifically investigate noncovalent interactions between nucleophilic Cu<sub>3</sub>P and Se sources of contrasting electronic properties and their impact on Cu<sub>3</sub>PSe<sub>4</sub> formation pathway(s).

We have identified two species of interest based on their opposing hydrogen and chalcogen bonding properties: hydrogen selenide, H<sub>2</sub>Se, which is Lewis basic along the Se-H bond axis; and selenide, R<sub>2</sub>Se, which is Lewis acidic along the Se-R bond axis. The resonance structures of the Lewis acid-base interaction of hydrogen and chalcogen bonding are presented below (Figure 4.1), that highlights reduction and oxidation of the Se- and P-containing groups, respectively.<sup>39–42</sup> Since chalcogen bonding occurs at medium-range separations, we hypothesize that it can serve as a templating agent for the redox and bond formation processes ultimately observed in the formation of  $Cu_3PSe_4$ .

#### Hydrogen Bond (Selenium Lewis Basic)



Chalcogen Bond (Selenium Lewis Acidic)



**Figure 4.1** Directional Lewis acidic and basic properties in  $H_2Se$  and  $R_2Se$  in comparison to a molecular unit of nucleophilic Cu<sub>3</sub>P. Highlighted in blue are Lewis acidic (LA) orbitals and in red are Lewis basic (LB) orbitals. Se-H bonds are Lewis acidic based on resonance, where the LB proton orbital interacts with the LA Cu<sub>3</sub>P to give an overall LA bond. Se-R bonds are Lewis basic and can directly interact with LA Cu<sub>3</sub>P.

We present a combined experiment-theory study to probe the formation of Se-P bonds in Cu<sub>3</sub>PSe<sub>4</sub>. The application of chalcogen bonding in supramolecular assembly and organic transformations alludes to a materials development strategy in which bonds are formed between seemingly antagonistic groups, expanding HSAB principles in relation to the reactivity of the precursor, or more aptly monomer, due to the interaction of non-innocent solvent.<sup>37,43–46</sup> We demonstrate that specific bond formations can be planned and executed for extended materials of complex chemical composition.

## 4.4 **Results and Discussion**

## 4.4.1 Impact of Selenium Precursor

Our total reaction is the following:  $Cu_3P$  nanoparticles with Se powder and 1-octadecene (1-ODE) are ramped to 300 °C and held for 20 mins to yield  $Cu_3PSe_4$ .<sup>33</sup> The diversity of Se species that can result have been previously detailed in the context of nanoparticle synthesis.<sup>47–51</sup> We

find that organometallic principles are descriptive of the reactivity that we observe for selenium under these conditions. This analogy is consistent with the range of oxidation states that Se can adopt and its possession of both electrophilic and nucleophilic 4p orbitals.<sup>52</sup>

Allotropic Se can perform oxidative addition with a  $C(sp^3)$ -H bond of 1-ODE that are further detailed in Scheme 4.1.<sup>53,54</sup> Oxidative addition increases the coordination number and oxidation state of a redox-active centre by two. The selenide hydride that results can then proceed to  $\beta$ -hydride elimination, generating an internal alkene and H<sub>2</sub>Se. Alternatively, allotropic Se can also perform oxidative addition with a  $C(sp^2)$ -H bond of 1-ODE which generates a vinylic selenide that is further detailed in Scheme 2. The Se-H bond can insert at the 1,2- or 2,1-position of the terminal alkene of 1-ODE and yields a linear or branched alkyl substituent, respectively. We refer to these species as R<sub>2</sub>Se where R indicates a sp<sup>2</sup>- or sp<sup>3</sup>hybridized carbon substituent.

> 1. Oxidative Addition: C(*sp*<sup>3</sup> - H) 2. β-Hydride Elimination



**Scheme 4.1.** (*left*) The oxidative addition, with respect to the  $C(sp^3 - H)$  bond of 1-ODE where R' =  $C_{13}H_{22}$ , and an allotrope of Se. (*right*) The  $\beta$ -hydride elimination, with respect to the selenide hydride of the preceding oxidative addition.



Scheme 4.2. (*left*) The oxidative addition, with respect to the  $C(sp^2 - H)$  bond of 1-ODE where  $R = C_{16}H_{33}$ , and an allotrope of Se. (*right*) The olefin insertion that can occur with either 1,2- or 2,1-regiochemistry.

We consider the impact of the contrasting Lewis acid-base properties of  $H_2Se$  and  $R_2Se$  towards the formation of Cu<sub>3</sub>PSe<sub>4</sub>. To start, we monitor the Se monomers and the distinct olefin

products from both Scheme 4.1 and Scheme 4.2 by a suite of characterization methods. Control experiments of individual reagent behaviour in 1-ODE under reaction conditions (20 min at 300 °C) were compared to the total reaction solution. The experiments included 1-ODE (tech grade), 1-ODE + Se, and 1-ODE + Cu<sub>3</sub>P NPs. Neither heating 1-ODE on its own or with Cu<sub>3</sub>P to reaction conditions resulted in transformations in the individual reagents. Of note, the 1-ODE + Se control resulted in the growth of peaks at 1.61 ppm and 5.41 ppm in the <sup>1</sup>H NMR spectra. The 1.61 ppm shift could be a result of convoluted Se speciation, which warrants the tracking of alkene proton shifts instead. The unsaturated hydrocarbons that result from the mechanism in Scheme 4.1 and Scheme 4.2 are differentiated by the topology of its olefin groups. The sensitivity of the <sup>1</sup>H NMR signal C(sp<sup>2</sup>)-H groups to their chemical environment enables assignment of reaction pathway details by the following <sup>1</sup>H NMR spectra. The signal at 5.41 ppm is distinct from the terminal alkene peaks at 5.80 and 4.95 ppm for 1-ODE. This preliminary reaction is corroborated with the red shift of the  $C(sp^2) - H$  bend from 994 to 976 cm<sup>-1</sup> in the IR spectrum of the reaction solution.<sup>55</sup> The products that result from the initial speciation provided by oxidative addition are detailed in the context of chalcogen bonding later in the discussion.

Indirect characterization of the H<sub>2</sub>Se monomer, as exemplified by several reports of the synthesis of CdE (E = S or Se), was implemented for our total reaction to consider the assignment of H<sub>2</sub>Se as the active Se reagent in the NP synthesis of Cu<sub>3</sub>PSe<sub>4</sub>.<sup>49,55–57</sup> Two methods were explored to probe the addition of selenium species to the overall reaction: cannula transfer of the Se/1-ODE headspace to a dispersion of Cu<sub>3</sub>P NPs in 1-ODE (Figure 4.2, *Indirect A*) and the direct addition of H<sub>2</sub>Se to Cu<sub>3</sub>P NPs in 1-ODE (Figure 4.2, *Indirect B*). To deconvolute the different interactions between the reaction species over the reaction progress, we used <sup>1</sup>H NMR and IR spectroscopy to monitor organic transformations and XRD to resolve bulk and crystalline phases through ex situ, timed aliquots. The Se group of H<sub>2</sub>Se is best classified as

Lewis basic which allows us to probe the impact of its hydrogen bonding ability on the speciation of the reaction conditions. While H<sub>2</sub>Se is a weak hydrogen bond donor due to the low electronegativity of Se we note that this noncovalent interaction is directly related to its classification as a proton donor, as illustrated in Figure 4.1. If H<sub>2</sub>Se, formed from Se/1-ODE, is the active chalcogenide species in the transformation of Cu<sub>3</sub>P NPs to Cu<sub>3</sub>PSe<sub>4</sub> NPs, then cannula transfer of the gaseous species from a chalcogenide precursor flask (Se and 1-ODE only) to a dispersion of Cu<sub>3</sub>P NPs in 1-ODE should yield Cu<sub>3</sub>PSe<sub>4</sub> (*Indirect A*). For standard reaction conditions (20 min at 300 °C), no transformation of the starting reagent, Cu<sub>3</sub>P NPs, was observed via XRD, and no changes were observed for the solution system via <sup>1</sup>H NMR or IR spectra as well.



**Figure 4.2.** Cartoon diagrams illustrating two methods for identifying the active Se precursor: cannula transfer of the Se/1-ODE headspace to a flask of Cu<sub>3</sub>P NPs in 1-ODE (*Indirect A*) and the direct addition of  $H_2Se$  to a flask of Cu<sub>3</sub>P in 1-ODE (*Indirect B*). Highlighted are appropriate characterization methods for describing specific areas of the reaction flask. Complementary techniques are important to gain a broad perspective of multiple, simultaneous phases and to prevent speculation of processes beyond the data that one technique suggests.

The first noted changes were observed at 1 h. Changes in the <sup>1</sup>H NMR and IR spectra corresponded to what was expected if the total reaction proceeded. Temporally, this was also

the first indication of new crystalline phases in which there is growth of Cu-Se binaries alongside unidentifiable shoulders at 45- and 47-degrees, the highest intensity peaks, in the XRD pattern. Ultimately, no ternary product was observed. This is notable as the results suggest that the reaction progress towards the synthesis of ternary Cu<sub>3</sub>PSe<sub>4</sub> NPs from Cu<sub>3</sub>P NPs is not as straightforward as the synthesis of binary Cd chalcogenide NPs, which is often used as a prototypical model for nanoparticle syntheses.<sup>56,58</sup> A solution of Cd cations can directly react with chalcogenide species available in the appropriate oxidation state. The ternary case would require all Cu-P bonds to be broken and rearranged into Cu-Se and Se-P bonds.<sup>33</sup> While this could be a result of diverse Se speciation in the gaseous headspace, perhaps the concentration of H<sub>2</sub>Se released to the headspace was not sufficient for reaction.

Time at 300 °C	XRD (phases)	<sup>1</sup> H NMR Shift, H <sub>a-c</sub> (ppm)	IR Wavenumber, C-H (cm <sup>-1</sup> )
20 min	Cu <sub>3</sub> P	No transformation	No transformation
1 h	Cu <sub>3</sub> P, Cu <sub>2</sub> Se <sub>x</sub>	1.61, 5.40	978
2 h	Cu <sub>3</sub> P, Cu <sub>2</sub> Se <sub>x</sub> , Cu <sub>2-x</sub> Se	1.61, 5.40	978
4 h	Cu <sub>2-x</sub> Se	1.61, 5.40	978

 Table 4.1 Temporal aliquot characterization for Indirect A

If the success of the ternary reaction was indeed due to a specific species, H<sub>2</sub>Se, it could be directly added to a dispersion of Cu<sub>3</sub>P and 1-ODE to form Cu<sub>3</sub>PSe<sub>4</sub> (*Indirect B*). XRD patterns indicated the formation of Cu<sub>2-x</sub>Se after 1 min at 300°C with no indication of solution transformation via <sup>1</sup>H NMR and IR. This suggests that H<sub>2</sub>Se is not the species responsible for the synthesis of Cu<sub>3</sub>PSe<sub>4</sub>. Instead, it is simply a by-product of Se reduction by 1-ODE as noted in Scheme 4.1, and its use as a reagent mostly impacts the reaction's equilibrium. The formation of Cu<sub>7</sub>PSe<sub>6</sub>, a phosphorus-deficient ternary phase compared to Cu<sub>3</sub>PSe<sub>4</sub>, was observed after 20 min, and is associated with minimal transformation of the alkene group of the solvent. The
absence of  $Cu_3PSe_4$  with direct addition of  $H_2Se$  suggests that  $H_2Se$  is not the sole participant, if at all, in the total synthesis of  $Cu_3PSe_4$  NPs.

Time at 300 °C	XRD (phases)	<sup>1</sup> H NMR Shift, H <sub>a-c</sub> (ppm)	IR, C-H (cm <sup>-1</sup> )
1 min	Cu <sub>2-x</sub> Se	No transformation	No transformation
5 min	Cu <sub>2-x</sub> Se, Cu <sub>7</sub> PSe <sub>6</sub>	No transformation	No transformation
10 min	Cu <sub>2-x</sub> Se, Cu <sub>7</sub> PSe <sub>6</sub>	1.61, 5.40	978
20 min	Cu <sub>2-x</sub> Se,Cu <sub>7</sub> PSe <sub>6</sub> , Cu <sub>3</sub> PSe <sub>4</sub>	1.61, 5.40	978

Table 4.2 Temporal aliquot characterization for Indirect B

Ultimately, we establish that the nanoparticle synthesis of  $Cu_3PSe_4$  is not strictly dependent on the presence of  $H_2Se$  and its noncovalent interaction of hydrogen bonding. Intuitively, a Lewis basic Se source is not conducive for the formation of P-Se bonds from phosphide. Likely, the success of the phase pure  $Cu_3PSe_4$  reaction is dependent on the reaction system. While  $H_2Se$ can react directly with  $Cu_3P$ , this species directs a different route as compared to the route that forms  $Cu_3PSe_4$ . Instead,  $R_2Se$  is hypothesized to have a much more significant role in the total reaction.

We pivoted our strategy toward direct identification of specific active monomers by <sup>1</sup>H NMR and GC-MS complemented with exploration of bond formations via computation. Of excitement was the direct characterization of  $H_2Se$  and( $C_{18}H_{35}$ )Se( $C_{18}H_{37}$ ), the two monomers of interest. However, while our preliminary results seem to be consistent with the diversity and complexity of Se speciation one might expect at elevated temperatures and in an organic solvent, the identification of these species did not necessarily elucidate their roles as relevant participants or innocuous bystanders to direct the reaction pathway toward  $Cu_3PSe_4$ . To deconvolute Se monomer characterization and identify the roles of the different Se monomers to ultimately direct a pathway toward the targeted ternary NP product, computational methods

were used as a bridge.<sup>59,60</sup> Further, computation is shown here to be a powerful tool for modelling molecular level processes that may not be observed directly.

# 4.4.2 Theoretical Assignment of Chalcogen Bonding

Selenides are established chalcogen bond donors, a type of noncovalent interaction that is analogous to the hydrogen bonding of H<sub>2</sub>Se.<sup>59</sup> Due to an anisotropic electron distribution, chalcogen atoms are electrophilic along their covalent bond axis, enabling close contacts with nucleophiles. We use the Cambridge Structural Database (CSD) to assign the separation and orientation between the selenium atoms of two selenide groups (R<sub>2</sub>Se) that is illustrated in Figure 4.3.<sup>61</sup> In this instance, selenium is both a chalcogen bond donor and acceptor and is consistant with its ambiphilic character. Their close contacts ( $\leq 1.00 \text{ R } \Sigma v dW^{-1}$ ) are anisotropic and favor a parallel alignment with a seleniumcarbon bond. The angle is converted to its value of 1-cos $\theta$  to address the polar flattening that occurs at 180°.<sup>62</sup> This preferential orientation rapidly decays with their increased separation. An accurate model of chalcogen bonding must address these distinct features of their angular dependence.<sup>63</sup>

We investigate the chalcogen bonding ability of a group of substituted ethylene selenide molecules,  $(C_2H_3)$ Se-X where X = CH<sub>3</sub> or H, as models for the Se products of Scheme 4.1 and Scheme 4.2. We employ trimethyl phosphine, P(CH<sub>3</sub>)<sub>3</sub>, as a chalcogen bond acceptor that approximates the nucleophilicity of the experimental phosphide, Cu<sub>3</sub>.P The overlap between the phosphine lone pair and  $\sigma^*$ -antibonding orbital of chalcogen and hydrogen bonding selenium groups are included in Figure 4.4.<sup>38,64</sup> The Lewis acidic Se of the representative selenide, (C<sub>2</sub>H<sub>3</sub>)Se-CH<sub>3</sub> overlaps with the phosphine group, P(CH<sub>3</sub>)<sub>3</sub>, which concurrently weakens the C<sub>2</sub>H<sub>3</sub>-Se bond. In contrast, H<sub>2</sub>Se possesses a Lewis basic Se group that can display hydrogen bonding with the adjacent phosphine which is consistent with its classification as a proton donor. In other words, *chalcogen bonding favours the formation of P-Se bonds, like those ultimately observed in Cu<sub>3</sub>PSe<sub>4</sub>*. We, thus, expect (C<sub>2</sub>H<sub>3</sub>)Se-X to be the active Se monomer and contrast it to its analogous hydrogen bonding counterpart. The potential energy surface of the hydrogen or chalcogen bonding interactions between  $P(CH_3)_3$  and  $H_2Se$  or  $(C_2H_3)Se-CH_3$ , respectively, is shown in Figure 4.4. The chalcogen bonding interaction occurs along the  $C_2H_3$ -Se bond axis due to the greater electronegativity of sp<sup>2</sup>-hybridized carbon.



**Figure 4.3.** The separation between the selenium groups ( $d_{Se-Se}$ ) as a factor of R  $\Sigma vdW^{-1}$ . The angle is in units of 1-cos $\theta$ . A depiction of the favored conformation of selenides at separations contracted from 1.00  $\Sigma vdW^{-1}$  is shown below.

The interaction energy ( $E_{int}$ ) of the hydrogen and chalcogen bonding structures are -2.24 and -3.07 kcal mol<sup>-1</sup>, respectively. The smaller magnitude of the hydrogen bonding interaction is anticipated from the low electronegativity of selenium.<sup>65</sup> The equilibrium P-Se separation of the hydrogen and chalcogen bonding interactions are a factor of 1.13 and 0.98 when scaled with respect to the sum of their van der Waals radii (R  $\Sigma vdW^{-1}$ ), respectively. Of note, while the hydrogen bonding strength of a Se group is invariant, the equilibrium separation observed for chalcogen bonding can be decreased with electron-withdrawing substituents.<sup>66–68</sup> This posits chalcogen bonding as a bond templating method by giving insight on what monomers could be judiciously selected for the synthesis of a target material.



**Figure 4.4** (*top*) The DLPNO-CCSD(T)/aug-cc-pVTZ potential energy surface of the chalcogen (ChB) and hydrogen bonding (HB) interaction of  $(C_2H_3)$ Se-CH<sub>3</sub> and H<sub>2</sub>Se, respectively, with P(CH<sub>3</sub>)<sub>3</sub>. (*middle*) The chalcogen and hydrogen bonding interaction of  $(C_2H_3)$ Se-CH<sub>3</sub> and H<sub>2</sub>Se, respectively, with PMe<sub>3</sub>. (*bottom*) The overlap (*S*<sub>ab</sub>) between the phosphine lone pair and  $\sigma^*$ -antibonding orbital of H<sub>2</sub>Se and (C<sub>2</sub>H<sub>3</sub>)Se-CH<sub>3</sub> where the colors orange and red indicate a negative and positive value, respectively.

Chalcogen bonding is traditionally aligned with the favorable electrostatics of the  $\sigma$ -hole model, where chalcogenides are electron-deficient along their covalent bond axis.<sup>69,70</sup> Electrostatics possess an R<sup>-1</sup> distance dependence that would maintain linear chalcogen bonds well-past 1.0 R  $\Sigma$ vdW<sup>-1</sup> that is irreconcilable with the structural data collected in Figure 4.3. Recent reports have argued a charge transfer interaction with the  $\sigma$ \*-antibonding orbital of the chalcogenide bond as the origin of chalcogen bonding. We perform an energy decomposition analysis with the DLPNO-CCSD(T)-based Local Energy Decomposition (LED) module where we focus on the kinetic and potential energy components of their Hartree-Fock interaction energy.<sup>71–73</sup> Potential energy is descriptive of the electrostatics and polarization effects argued by the  $\sigma$ -hole model. Alternatively, kinetic energy should illustrate the bond formation associated with the  $\sigma^*$ -model that is inspired by Ruedenberg's pivotal work on chemical bonding.<sup>74,75</sup>



**Figure 4.5.** The angular dependence of the energies of the chalcogen bonding interaction between  $(C_2H_3)$ Se-CH<sub>3</sub> and P(CH<sub>3</sub>)<sub>3</sub>. An angle of 180 and 90° corresponds to the orientation of the phosphine lone pair with the Se-R bond axis and selenium lone pair, respectively. The kinetic and potential energies are obtained from the Hartree-Fock interaction energy of the detailed Local Energy Decomposition (LED) module. The E<sub>int</sub> was obtained at the DLPNO-CCSD(T)/aug-cc-pVTZ level-of-theory.

We consider the fluctuation in the intermolecular potential and kinetic energy as a function of angle at the equilibrium separation of the (C<sub>2</sub>H<sub>3</sub>)Se-CH<sub>3</sub> system detailed above. At an angle of 180° and 90° the phosphine lone pair is oriented with the axis of the Se-R bond or the selenium lone pair, respectively. The DLPNO-CCSD(T) energies assigns that the strength of the noncovalent goes from net-attractive to -repulsive in reorienting the phosphine lone pair. Surprisingly, the potential energy of the system *decreases* and is most favorable when the phosphine and selenium lone pairs are directed towards each other. The kinetic energy of the system concurrently *increases* with contraction of the chalcogen bonding angle, its repulsive contributions always greater than the stabilization provided by the potential energy. We attribute the greater potential attraction to electrostatic penetration whose impact has recently been highlighted with respect to the conformations of  $\pi$ - $\pi$  interactions.<sup>76</sup> We align the destabilizing kinetic energy to an increase in exchange repulsion. The orthogonalization of occupied orbitals required by the exclusion principle introduces a node into the system that increases

the gradient, raises the kinetic energy, of the coherent wavefunctions. When oriented along the Se-R bond axis this is lessened due to the resonance contributions of Se-P bond formation that is illustrated in Figure 4.1.

#### 4.4.3 *Mechanistic Insight to P-Se Bond* Formation

Following chalcogen bonding, the formation of a P-Se bond from  $(C_2H_3)$ Se-X requires the loss of its substituents and a reduction of its Se centre. This process is descriptive of a reductive elimination, a reaction where the oxidation state and coordination number of a redox-active group decreases by two. A covalent bond between the eliminated groups is subsequently formed and is further illustrated in Scheme 4.3.<sup>52</sup>



cis (Z): 43% trans (E): 57%

Scheme 4.3 Chalcogen bonding and subsequent reductive elimination between  $(C_2H_3)$ Se-X and  $P(CH_3)_3$  to form P-Se bonds.

We consider the reaction barriers of the reductive elimination of  $C_2H_3Se-X$  in the absence and presence of  $P(CH_3)_3$ ; the results are summarized in Table 4.3. We report that the enthalpy of activation  $(\Delta H^{\ddagger})$  decreases by 6.39 and 9.82 kcal mol<sup>-1</sup> for  $X = CH_3$  and H, respectively, in the presence of phosphine due to its ability to participate in chalcogen bonding with selenide species. Thus, chalcogen bonding interactions can aid in the reactivity displayed in Se-containing species. The products of both reaction mechanisms are a selenophosphine, SeP(CH\_3)\_3, and an unsaturated hydrocarbon. This reaction pathway is inaccessible to H<sub>2</sub>Se that would formally yield H<sub>2</sub><sup>2-</sup>.

**Table 4.3** The calculated enthalpy of activation ( $\Delta H^{\ddagger}$ ) for the reductive elimination of (C<sub>2</sub>H<sub>3</sub>)Se-X at 300 °C in the presence or absence of P(CH<sub>3</sub>)<sub>3</sub>.

Х	P(CH <sub>3</sub> ) <sub>3</sub>	$\Delta H^{\ddagger}$ (kcal mol <sup>-1</sup> )
CH <sub>3</sub>	Yes	61.47
CH <sub>3</sub>	No	67.86
Н	Yes	35.39
Н	No	45.20

Chalcogen bonding stabilizes the transition state associated with the reductive elimination of the considered selenide species. While the  $E_{int}$  of chalcogen bonding is marginal at their equilibrium separations, the reduced strain provided by its complementary Lewis acid-base character is magnified at the contracted distances associated with bond formation. The Cu<sub>3</sub>PSe<sub>4</sub> reaction pathway that follows reductive elimination will yield an extended unsaturated hydrocarbon whose formula is  $C_{36}H_{72}$ . Reductive elimination is preceded by a 1,2- or 2,1-olefin insertion whose products are linear and branched hydrocarbons, respectively. The product of the 2,1-olefin insertion can be further classified as cis-(Z) or trans-(E) stereoisomers. To probe for these products, the <sup>1</sup>H NMR spectra of various reaction solutions were reinvestigated including those of the controls (1-ODE, 1-ODE + Se, 1-ODE +  $Cu_3P$ ), indirect studies, and the total reaction solution (Figure 4.6). All the samples were collected after the completion of the respective experiments then cooled, typically subjected to the total reaction conditions (300 °C for 20 min) with exceptions noted. For *Indirect A*, both the Se/1-ODE transfer flask and Cu<sub>3</sub>P/transferred Se species/1-ODE reaction flask were considered. Previously for these studies, potential convolutions such as the ability of 1-ODE to autopolymerize at elevated temperatures and over extended periods of time,<sup>77</sup> and the isomerization of 1-ODE by Se<sup>47</sup> were identified, but these nuances were not necessarily deconvoluted.

We consider the alkene signal of the <sup>1</sup>H NMR spectrum at 5.41 ppm of the total reaction solution to help resolve the mechanism associated with the synthesis of Cu<sub>3</sub>PSe<sub>4</sub>. Various oxidative addition, olefin insertion, and reductive elimination transition states and products were computed to confirm the feasibility of this pathway. The asymmetry of the apparent quartet observed from the total reaction conditions suggests that the signal results from overlapping vinylic 1:2:1 triplets of near-equivalent chemical environments. This pattern is satisfied through a reductive elimination that follows a 2,1olefin insertion and yields a non-racemic mixture of the E- and Z-stereoisomers. The barrier for 2,1insertion was computed to be 8.0 kcal mol<sup>-1</sup> lower than for 1,2-insertion. The experimental spectrum is reproduced for a 47:53 mixture of the E- and Z-stereoisomers each of whose single alkene proton is weakly coupled to the adjacent methylene group.



**Figure 4.6** Reinvestigation of the <sup>1</sup>H NMR spectra for the potential alkene products by  $\beta$ -hydride elimination or reductive elimination. Asterisks indicate signals associated with tech grade 1-ODE.

The control reaction of Se and 1-ODE similarly yields a 47:53 ratio of the E- and Z-stereoisomers assigned as the product of the proposed reductive elimination, respectively. Distinct to the total reaction conditions, the ratio of the reductive elimination product with respect to 1-ODE increases by a factor of 2.75 with the addition of  $Cu_3P$ . This result is consistent with our calculations that chalcogen bonding stabilizes the transition state.

The alkene peak at 5.4 for Se/1-ODE (*Indirect A*) is distinct from 1-ODE+Se control experiments. While the 1-ODE + Se control was subjected to standard reaction conditions, the Se/1-ODE (*Indirect A*) flask was subjected to 300 °C for 4 h while its gaseous species were continuously transferred via cannula into another reaction flask containing Cu<sub>3</sub>P and 1-ODE. This could have resulted in reaction equilibrium shifts, most of the 1-ODE to be transferred by extended reflux, and/or extensive reactions between Se and 1-ODE. The alkene <sup>1</sup>H NMR signal for Se/1-ODE *Indirect A* models as an internal alkene that would follow  $\beta$ -hydride elimination. The vinylic C(sp<sup>2</sup>)-H protons are coupled to both each other and their adjacent methylene group. Our findings suggest that the noncovalent interaction that occurs between Cu<sub>3</sub>P and R<sub>2</sub>Se facilitates distinct reactivity of the selenide group.



**Figure 4.7** (top) The experimental (black) and calculated (red) <sup>1</sup>H NMR signal from 5.3-5.5 ppm of the total reaction mixture of 1-ODE, Se, and Cu<sub>3</sub>P. (bottom) The reductive elimination that occurs from the speciation of Se detailed in Scheme 4.2

Overall, our results suggest that chalcogen bonding templates the reactants along its reaction coordinate and drives the P-Se bond formation ultimately observed in the speciation of Cu<sub>3</sub>PSe<sub>4</sub> through reductive elimination. The Lewis basic lone pair of the phosphine group of the P-Se product remains reactive towards Lewis acidic R<sub>2</sub>Se which could cascade toward the synthesis of an extended material, such as Cu<sub>3</sub>PSe<sub>4</sub>, illustrated in Figure 4.8. Our calculated  $\Delta H^{\ddagger}$  are larger than analogous organometallic processes but is consistant with the approximate kinetics of the current experiment that is further detailed in the Experimental. We note that our current computational framework is limited in that it approximates the experimental phosphide  $(Cu_3P)$  as a phosphine and does not account for the bonding interaction between Se<sup>-1</sup> and Cu<sup>+1</sup> following formation of the P-Se bond.



**Figure 4.8**. Our proposed mechanism for the generation of P-Se and Se-Cu bonds that are experimentally observed in  $Cu_3PSe_4$ . The first two successive reductive eliminations that will generate the molecular unit of  $Cu_3PSe_4$  is shown.

#### 4.5 Conclusion

We exploit a rich chemistry by probing the Se precursor to monomer transformation in the presence of 1-ODE and Cu<sub>3</sub>P. Nanoparticle syntheses are inherently complex, and processes beyond nucleation and growth can also occur. Studies to describe these processes start with the characterization of the diverse reaction speciation and the mindfulness that these species can exist beyond what is in solution such as in the headspace of the reaction flask. A toolkit of complementary characterization and computational techniques and multidisciplinary chemistries can help gain a broad perspective of multiple, simultaneous components.

Our experimental and theoretical characterizations detail the molecular level transformations that can facilitate the synthesis of Cu<sub>3</sub>PSe<sub>4</sub>. The interaction of Se powder precursor in 1-ODE leads to a diversity of Se species with correspondingly diverse roles. We directed our attention to the role of H-Se and R-Se groups, considering their contrasting Lewis acidic and basic properties, on the advent of P-Se bonds. These monomers were characterized by indirect methods, <sup>1</sup>H NMR, and GC-MS; and their delivery and assembly into the extended structure were probed by computation. Our findings demonstrate that chalcogen bonding stabilizes the transition state of the reductive elimination of selenide species which facilitates P-Se bond formation. We suggest that noncovalent interactions can serve as a template for bond formations of seemingly antagonistic groups. The HSAB principles described by Pearson serve as first order approximations for materials development, but on their own are not sufficient to predict precursors to use for synthesis. Rather than treat Lewis acidity and basicity as global properties determining reactivity, we additionally considered a directional dependence of orbitals that results from a non-uniform electronic distribution. Established organometallic mechanisms could generally be applied to aid in the synthesis of Se- and Te-based materials. While elegant NP syntheses exist for both material systems, mechanistic detail of compositionally complex systems are emergent and strategies to plan and control these syntheses remain more elusive.

Chalcogen bonding interactions are tunable based on solvent- and substituent-identity and could be applied to these systems to further lower the activation energy associated with main group element and selenium bond formation. In this way, a methodology merging computation and experiment was used to correlate selenization reagents to supramolecular assembly in which precursors (or more aptly monomers due to the interaction of solvent) could be judicially selected via retrosynthesis. Thus, selection of a solvent for colloidal nanoparticle syntheses should also be made carefully when developing a synthesis. Solvents can undergo transformations themselves in the presence of different reagents, impacting precursor reactivities and the identities of different monomers, and can serve as reagents.

Our current findings assign established organometallic-based principles as a possible design strategy for Cu<sub>3</sub>PSe<sub>4</sub> and related materials, building a multidisciplinary toolkit for NP synthesis to satisfy its interdisciplinary nature. Ultimately, the expansion of molecular level reaction principles to nanoparticle synthesis must build off the characterization of active species generated under reaction conditions and subsequent description of how they interact and are assembled. By understanding the

speciation, precursors and solvents can be aptly selected to yield the monomers required for a desired material. This could lead to general strategies for designing the synthesis of materials of a diverse composition.

#### 4.6 Experimental

The following calculations were performed with the Gaussian16 electronic structure software package.<sup>78</sup> The geometries were optimized with the M06-2X hybrid DFT functional<sup>79</sup> with a def2-TZVPP basis set.<sup>80</sup> We employed the parameterized GD3 empirical dispersion correction<sup>81</sup> and a 1-hexene solvent environment ( $\varepsilon = 2.072$ ) with the polarizable continuum model.<sup>82</sup> The C-Se-P and Se-H-P bond angles were constrained as linear in the optimization of the chalcogen and hydrogen bonding adduct of SeMe<sub>2</sub> and SeH<sub>2</sub> – PMe<sub>3</sub>, respectively. The stationary points of the SeMe<sub>2</sub> – PMe<sub>3</sub> reaction coordinate was assigned as minima or saddle points by the identification of zero or one harmonic vibrational frequency, respectively. An internal reaction coordinate was performed that identified Se=PMe<sub>3</sub> and C<sub>2</sub>H<sub>6</sub> as the production of the provided transition state. The zero-point energy corrections were calculated at the same level-of-theory while the thermal corrections were evaluated at a temperature of 573.15 K.

The following calculations were performed with the ORCA 4.1 electronic structure software package.<sup>83</sup> The unrelaxed potential energy surface of the noncovalent interactions between PMe<sub>3</sub> and SeMe<sub>2</sub> or SeH<sub>2</sub> were performed with the DLPNO-CCSD(T) functional<sup>84,85</sup> and the aug-cc-pVTZ basis set and its associated auxiliary basis set, within RIJK approach.<sup>86,87</sup> The calculations were performed with TightSCF and TightPNO convergence settings.<sup>88,89</sup> The interactions were corrected for their basis set superposition error (BSSE) a counterpoise correction.<sup>90</sup> The <sup>1</sup>H – NMR chemical shifts were calculated with the DSD-PBEP86 double-hybrid DFT functional<sup>91</sup> with its RI-approximation with the basis set previously described.<sup>92</sup> GD3BJ empirical dispersion correction was applied. The chemical shifts are referenced with respect to a tetramethylsilane (TMS).

The orbital overlap plots in Figure 4.4 were generated with the DLPNO-CCSD natural orbitals from the ORCA 4.2 electronic structure software. Each orbital was generated as an isolated fragment so that the orbitals remained non-orthogonal. The overlap is the integral of the product of a pair of orbitals that was treated in the context of their Gaussian cubes.

Assuming the reaction is 90% complete in 20 minutes at 300°C, the 2<sup>nd</sup> order Eyring activation free energy is estimated as 40 kcal/mol (octadecene assume to be at a constant 3.1 M concentration)

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# Chapter 5 Electronic Structures of Cr(III) and V(II) Polypyridyl Systems: Undertones in an Isoelectronic Analogy<sup>3</sup>

# 5.1 Outline

A recently reported description of the photophysical properties of V<sup>2+</sup> polypyridyl systems has highlighted several distinctions between isoelectronic, d<sup>3</sup>, Cr<sup>3+</sup> and V<sup>2+</sup> tris-homoleptic polypyridyl complexes of 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen). Here, we combine theory and experimental data to elucidate the differences in electronic structures. We provide the first crystallographic structures of the V<sup>2+</sup> complexes [V(bpy)<sub>3</sub>](BPh<sub>4</sub>)<sub>2</sub> (**V1b**) and [V(phen)<sub>3</sub>](OTf)<sub>2</sub> (**V2**), and observe pronounced trigonal distortion relative to analogous Cr<sup>3+</sup> complexes. We use electronic absorption spectroscopy in tandem with TD-DFT computations to assign metal-ligand charge transfer (MLCT) properties of **V1b** and **V2** that are unique from the intra-ligand transitions, <sup>4</sup>(<sup>3</sup>IL), solely observed in Cr<sup>3+</sup> analogues. Our newly developed Natural Transition Spin Density (NTp<sup> $\alpha,\beta$ </sup>) plots characterize both the Cr<sup>3+</sup> and V<sup>2+</sup> absorbance properties. A multi-determinant approach to DFT assigns the energy of the <sup>2</sup>E state of V1b as stabilized through electron delocalization. We find that the profound differences in excited state lifetimes for Cr<sup>3+</sup> and V<sup>2+</sup> polypyridyls arise from differences in the characters of their lowest doublet states and pathways for intersystem crossing, both of which stem from trigonal structural distortion and metal-ligand  $\pi$ -covalency

#### **5.2 Division of Labor**

The following Chapter was a collaborative effort. Unless otherwise stated, the computational work was done by Justin P. Joyce. Unless otherwise stated, the experimental work was done by Romeo I. Portillo. The crystallographic structure of [V(bpy)<sub>3</sub>](BPh<sub>4</sub>)<sub>2</sub> was collected by Michael P. Nguyen. The

<sup>&</sup>lt;sup>3</sup> Joyce, J.P.<sup>‡</sup>; Portillo, R.I.<sup>‡</sup>; Nite, C.M.; Nite, J.M.; Nguyen, M.P.; Rappé, A.K.; Shores, M.P. *Inorg. Chem.* **2021**, *60*, 12823. Reproduced in part by permission of the American Chemical Society.

SORCI calculations were performed by Jacob M. Nite. The Franck-Condon-Herzberg-Teller was performed by Collette M. Nite.



**Figure 5.1** The distinct photophysical properties of  $Cr^{3+}$  and  $V^{2+}$  polypyridyls are assigned to their degree of trigonal distortion, intertwining their geometric and electronic structures. Our analysis is applied to probe impacts on ground and excited state properties of both d<sup>3</sup> transition metal systems.

#### **5.3 Introduction**

Octahedral  $Cr^{3+}$  complexes have received intense research interest due to their attractive photophysical properties and the relative natural abundance of chromium.<sup>1,2</sup> The interpretation of their absorption spectra was foundational in the advancement of both crystal and ligand field theories, and the spectra themselves provide critical benchmarks for computational methods.<sup>3–6</sup> The long-lived excited state of  $Cr^{3+}$  complexes is attributed to the minimal geometric distortion and hence minimal non-radiative decay associated with the spin-flip nature of the low-lying <sup>2</sup>E state (using  $O_h$  symmetry notation).<sup>7</sup> Since the energy of the <sup>2</sup>E state for  $Cr^{3+}$  is approximately independent of ligand field, being dominantly impacted by interelectronic repulsion, it is anticipated that slow emission is an innate property of d<sup>3</sup> systems, and this attribute should transfer to the isoelectronic V<sup>2+</sup> analogues—but it does not.<sup>8–10</sup> Thus, elucidating a more nuanced understanding of the electronic properties of d<sup>3</sup> polypyridyls is essential for the hopeful application of these coordination complexes in photovoltaic devices and photocatalytic processes.

Herzog and König reported the initial comparison of  $[V(bpy)_3]^{2+}$  and  $[Cr(bpy)_3]^{3+}$  in 1970. Their analysis treated V<sup>2+</sup> and Cr<sup>3+</sup> absorbances interchangeably in the context of ligand field transitions.<sup>11,12</sup> This isoelectronic analogy was strained by inconsistencies with respect to the magnitude of molar absorptivities, relative ligand field strengths (10 Dq), and metal-centered exchange interaction energies (B). Findings by Maverick and co-workers in the late 1980s further shook the equivalency of these isoelectronic species, when they reported that  $[V(bpy)_3]^{2+}$  has an excited state lifetime of 0.5 ns, that pales in comparison to the 400 µs lifetime of its Cr<sup>3+</sup> analogue.<sup>13,14</sup> While <sup>2</sup>E states of V<sup>2+</sup> polypyridyl complexes evade a precise energetic assignment, Dill et al. recently refined our understanding of these species through a detailed spectroscopic study and characterization of the role of charge transfer in their excited state manifold.<sup>15</sup>

Herein, we focus on the distinctions between the geometric and electronic structures of the ground and excited states of isoelectronic  $Cr^{3+}$  and  $V^{2+}$  polypyridyl systems to discern the source(s) of their divergent physicochemical properties. The manuscript is organized as follows. First, we disclose novel crystallographic analyses of the first  $V^{2+}$  polypyridyl systems, and compare their structures with analogous  $Cr^{3+}$  systems from literature; we characterize the trigonal distortion of the  $V^{2+}$  complexes using the continuous shape measurement (CShM) Second, we present a multi-reference electronic structure description, including spin orbit coupling, for the manifold of metal-centered excited states for a small model complex. Third, we use DFT computations to analyze the electronic structures of the metal- and ligand-orbitals of both  $V^{2+}$  and  $Cr^{3+}$  polypyridyl complexes. Fourth, we assign the experimentally observed visible-light absorbance of  $V^{2+}$  and  $Cr^{3+}$  polypyridyls using TD-DFT, and illustrate changes with a newly developed density display procedure. Finally, we assign the low-lying doublet excited states of  $Cr^{3+}$  and  $V^{2+}$  polypyridyl complexes.

#### 5.4 Results and Discussion

### 5.4.1 Geometric Structural Analyses

Six-coordinate d<sup>3</sup> metal complexes are anticipated to have well-defined near-octahedral geometries due to an isotropic electronic configuration and large ligand field stabilization energy. The Cambridge Crystallographic Structural Database (CSD) reports 22 Cr<sup>3+</sup> polypyridyl complexes that we refer to as  $[Cr(NN)_3]^{3+,16}$  The average Cr-N distance in this set is 2.048(7) Å, equivalent to a factor of 0.975(3) when scaled with respect to the sum of their covalent radii, R  $\Sigma r_{cov}^{-1,17,18}$  The octahedral coordination environment is quantified with the Continuous Shape Measure (CShM) approach. This procedure assigns the angular distortional distance between the experimental structure and a reference polyhedra, providing a quantitative assessment of a metal center's coordination geometry. We report a small average value of 0.779, where deviation from zero indicates geometric distortion.<sup>19</sup> Of interest is that the Cr<sup>3+</sup> complexes closely reside at one end of the distortion pathway between octahedral (OC-6) and trigonal prismatic (TRP-6) geometries, approximately 21 % ( $\phi_{OC \rightarrow TRP}$ ), a distortion known as a Bailar twist.<sup>20</sup>

We introduce the first crystallographic characterizations of V<sup>2+</sup> polypyridyl complexes. The V<sup>2+</sup> complex in [V(bpy)<sub>3</sub>](BPh<sub>4</sub>)<sub>2</sub> (**V1b**) has an average V-N bond distance of 2.133(5) Å that is contracted relative to the [Cr(NN)<sub>3</sub>]<sup>3+</sup> structures when scaled with respect to their covalent radii, 0.952(1) R  $\Sigma r_{cov}^{-1}$ . Meanwhile, [V(phen)<sub>3</sub>](OTf)<sub>2</sub> (**V2**) possesses a very similar average V-N bond length of 2.177(8) Å with a sum of covalent radii equal to 0.951(2) R  $\Sigma r_{cov}^{-1}$ . We equate the contracted bond length in vanadium analogues with greater metal-ligand covalency, consistent with greater nuclear shielding and larger size of the 3d orbitals of V<sup>2+</sup>. **V1b** has an OC-6 measure of 1.82 that is associated with a  $\phi_{OC \rightarrow TRP}$  of 32.1%. The largest Bailar twist conversion reported for a tris-bidentate d<sup>3</sup> system is 38%, highlighting the significant magnitude of the structural distortion of **V1b**.<sup>21</sup> A similar, though less-pronounced, distortion is observed for **V2** with an S(OC-6) of 1.20 and  $\phi_{OC \rightarrow TRP}$  of 26.6%. Their

crystal structures are presented alongside their minimal distortion pathway in Figure 5.2 indicating that  $V^{2+}$  polypyridyls possess greater trigonal distortion than their Cr<sup>3+</sup> analogues.



Figure 5.2. The continuous shape measure (CShM) correlation between trigonal prismatic (TPR-6) and octahedral (OC-6) geometries (solid line) for the  $[Cr(NN)_3]^{3+}$  data set (open black squares) and our reported structures for V1b (red circle) and V2 (blue diamond). Crystal structures for the cationic complexes in V1b and V2 are shown at right, where hydrogen atoms, anions, and co-crystallized solvent molecules are omitted for clarity. Thermal ellipsoids are set to 40%.

## 5.4.2 Electronic Structural Analyses

The isoelectronic V<sup>2+</sup> and Cr<sup>3+</sup> free ions have <sup>4</sup>F ground states and low lying <sup>2</sup>G excited states with experimental J-averaged excitation energies of 1.46 eV (11,800 cm<sup>-1</sup>) and 1.82 eV (14,700 cm<sup>-1</sup>), respectively.<sup>22</sup> In an octahedral environment, the nine-fold degenerate <sup>2</sup>G state splits into <sup>2</sup>E, <sup>2</sup>T<sub>2</sub>, <sup>2</sup>T<sub>1</sub>, and <sup>2</sup>A states, see the Tanabe-Sugano diagram in Figure 5.3. Emission is not observed for  $[V(bpy)_3]^{2+}$  while for  $[Cr(bpy)_3]^{3+}$ , emission from the <sup>2</sup>E excited state occurs at 1.78 eV (14,300 cm<sup>-1</sup>).<sup>15,23</sup> Computationally, the  $[V(bpy)_3]^{2+}$  E state is reported to range between 0.90 eV (7,300 cm<sup>-1</sup>) and 1.16 eV (9,360 cm<sup>-1</sup>), while comparable methods place the <sup>2</sup>E  $[Cr^{3+}(bpy)_3]$  at 1.6 eV (13,000 cm<sup>-1</sup>).<sup>15</sup>

Non-observation of emission could either be due to a lack of formation or a rapid non-radiative decay of the emissive excited state. Excitation of the  ${}^{4}A_{2}$  ground state to the  ${}^{4}T_{2}$  excited state ( $t_{2g}^{2} - e_{g}^{*1}$ ) can result in geometric distortion that can provide a mechanism for intersystem crossing (ISC) to the doublet manifold. As discussed above, for a d<sup>3</sup> system, in an octahedral or near octahedral field there

are nine potentially low-lying metal-centered doublet states, most of which are multi-configurational and hence are not accessible to TD-DFT.



**Figure 5.3** Simplified Tanabe-Sugano diagram for a  $d^3$  transition metal center in an O<sub>h</sub> coordination where blue and orange denote a quartet and doublet state, respectively.

To examine the distortion hypothesis we use a multi-configurational Spectroscopy Oriented Configuration Interaction (SORCI) method<sup>24</sup> to provide a balanced description of the full manifold of low lying metal-centered excited states along the TD-DFT-based structural distortion pathway between the <sup>4</sup>A<sub>2</sub> and <sup>4</sup>T<sub>1</sub> states. The significant increase in computational resource utilization for SORCI led us to study the model complexes [Cr(PDO)<sub>3</sub>] and [V(PDO)<sub>3</sub>], where PDO = 1,3-propanedionato.<sup>25</sup> PDO provides a 3-fold symmetric ligand field with a modest  $\pi$ -system. The overall charge of the model complexes is 0 and -1 for the Cr<sup>3+</sup> and V<sup>2+</sup> species, respectively. The active space utilized three electrons and five d orbitals. Inclusion of spin-orbit coupling results in significant mixing between the doublet and quartet state manifolds in [Cr(PDO)<sub>3</sub>].<sup>26–28</sup> In contrast, a crossing point is *not* observed between the excited quartet and metal-centered doublet state manifolds of the corresponding V<sup>2+</sup> complex. The lowered energy of the doublet manifold for V<sup>2+</sup> relative to Cr<sup>3+</sup> provides this energetic

separation. Thus, intersystem crossing to the doublet manifold in V<sup>2+</sup> complexes *via* geometric distortion from the  ${}^{4}T_{2} \leftarrow {}^{4}A_{2}$  transition is not likely without significant ligand  $\pi$ -system intervention.



**Figure 5.4** Plots of metal-centered excited states of  $[Cr^{3+}(PDO)_3]$  (left) and  $[V^{2+}(PDO)_3]^-$  (middle) along a linear distortion reaction coordinate between the  ${}^{4}A_{2g}$  and  ${}^{4}T_{2g}$  optimized geometries that are defined as 0 and 1, respectively. The blue and orange lines represent the quartet and doublet states, respectively. Right: structure of the model  $[M(PDO)_3]^n$  complexes.

#### 5.4.3 $M(bpy)_3$ structural distortion

Further computational discussion is centered on  $[Cr(bpy)_3]^{3+}$  and  $[V(bpy)_3]^{2+}$  complexes, where DFT calculations were performed with the APFD hybrid-DFT functional that we have previously used for the analysis of  $Cr^{3+}$  and  $V^{2+}$  octahedral complexes.<sup>15,29</sup> We note that the *S*(OC-6) values of the optimized structures are in quantitative agreement with the experimental structures discussed above. The calculated  $[Cr(bpy)_3]^{3+}$  and  $[V(bpy)_3]^{2+}$ structures are closely aligned with the structural parameters gathered from the CSD that validates the current method can accurately reproduce the primary coordination sphere of octahedral transition metal complexes. The optimized structure of  $[V(phen)_3]^{2+}$ does not display the same magnitude of distortion present in the experimental structure of **V1b**, possessing an S(OC-6) of 1.270. While our sample size is small, it suggests that the degree of trigonal distortion for V<sup>2+</sup>polypyridyl complexes can be appreciably altered through intermolecular interactions that agrees with their proximity to the minimal distortion pathway. The phenanthroline-containing complexes  $[Cr(phen)_3]^{3+}$  and  $[V(phen)_3]^{2+}$  have more well-defined octahedral geometries with an S(OC-6) of 0.498 and 0.996, respectively, that suggests ligand architecture can modulate distortion. There is little variation in the structural parameters for the 4,4'-substituted bipyridine complexes, inferring minimal steric impact. The 3d orbitals of the  $Cr^{3+}$  complex display the classic  $t_{2g} - e_g^*$  ligand field splitting anticipated for a near octahedral coordination environment—despite the ligand-imposed reduction in symmetry to  $D_3$  that is shown in Figure 5.5.



**Figure 5.5** (*left*) The qualitative orbital diagram for  $[Cr(bpy)_3]^{3+}$  where the vertical axis is energy. (*right*) Representative orbitals of the triply degenerate  $t_{2g}$  and  $\pi^*$ -orbitals of  $[Cr(bpy)_3]^{3+}$ .

Although it is commonly classified as a  $\pi^*$ -acceptor, we emphasize here that bipyridine is poised as a  $\pi$ -donor with respect to the Cr<sup>3+</sup> metal-center, in agreement with the Angular Overlap Model (AOM) that assigns ligand field properties, such as  $\sigma$ - and  $\pi$ -bonding ability, based on the orbital overlap between a metal center and its ligands.<sup>30,31</sup> It has previously been reported that, for Cr<sup>3+</sup> complexes, bipyridine is a weaker-field ligand in the spectrochemical series than ethylenediamine, a ligand of pure  $\sigma$ -character.<sup>32,33</sup> This distinction is important since increasing the ligand field strength of Cr<sup>3+</sup> octahedral complexes represents an effective strategy to inhibit back-intersystem crossing, in order to maximize excited state lifetimes.<sup>34–37</sup>

In agreement with the crystal structure for **V1b**, there is a reduction in symmetry from  $O_h$  to  $D_3$  for the computed structure for  $[V(bpy)_3]^{2+}$  that alleviates the three-fold degeneracy of the  $t_{2g}$  set into  $a_1 + e$  sets. The e orbitals engage in both donor *and* acceptor interactions with the  $\pi$  and  $\pi^*$ -orbitals of the polypyridyl ligand set. The metal-centered e orbitals are destabilized relative to the  $a_1$  orbital and are in a predominantly non-bonding arrangement with the bipyridyl  $\pi$  system, we refer to this pair as  $e_{\delta}$ . The complementary ligand e set is stabilized upon structural distortion—providing the electronic basis for the structural distortion. Analogous bonding properties of bipyridine have been recently reported for low-spin Fe<sup>2+</sup> complexes.<sup>38,39</sup> Our findings are complementary to an earlier report by Dobson and Taube, that V<sup>2+</sup> polypyridyls possess minimal  $\pi^*$ -backbonding despite the sensitivity of their reduction potential to ligand identity.<sup>40</sup>

The associated qualitative orbital diagram and pertinent orbitals for  $[V(bpy)_3]^{2+}$  are presented in Figure 5.6. Collectively, these electronic structure properties corroborate the trigonal distortion that is observed crystallographically for  $[V(bpy)_3]^{2+}$  relative to  $[Cr(bpy)_3]^{3+}$ . As discussed below, the higher lying/larger d orbitals of V<sup>2+</sup> provide greater covalency to the interactions with the bipyridyl ligands. While geometric and electronic structures are inseparable, we maintain that the  $\pi$ -interactions described above predicate the trigonal distortion of the complex.



**Figure 5.6.** (*left*) The qualitative orbital diagram for  $[V(bpy)_3]^{2+}$  where the vertical axis is energy; the  $V^{2+}$  " $e_g^*$ " orbitals are omitted from the diagram. (*right*) Representative orbitals of the doubly degenerate  $e_{\delta}$  and  $e_{\pi^*}$  orbitals of  $[V(bpy)_3]^{2+}$ .

Figure 5.7 presents Natural Transition Spin Density  $(NT\rho^{\alpha,\beta})$  plots for the lowest metal-based quartet excitations of  $[Cr(NH_3)_4(bpy)]^{3+}$  and  $[V(NH_3)_4(bpy)]^{2+}$ . The model complexes displayed in Figure 5.7-Figure 5.10 are provided strictly for visual clarity, and we note that their transition energies and characters are interchangeable with the corresponding tris-bidentate polypyridyl complexes. In these plots, the TD-DFT calculated  $\alpha$  and  $\beta$  spin densities of an excited state are subtracted from the respective spin densities of its ground state. Blue denotes a positive value that is attributed to an increase of  $\alpha$ -electron density in the excited state or a decrease of  $\beta$ -electron density in the ground state. Green is the negative value associated with an increase of  $\beta$ -electron density in the excited state or loss of  $\alpha$ -electron density in the ground state. The NT $\rho^{\alpha,\beta}$  plots in Figure 5.7 illustrate the archetypal  $e_g^* \leftarrow$  $t_{2g}$  d-d ligand field processes. We note that the NT $\rho^{\alpha,\beta}$  plot of  $[V(bpy)(NH_3)_4]^{2+}$  shows greater metalligand covalency, descriptive of the nephelauxetic effect, and significant ligand  $\pi$ -character that will be detailed further below.



**Figure 5.7** (*top*) The NT $\rho^{\alpha,\beta}$  plots, described above, of the ligand field transitions for  $[Cr(bpy)(NH_3)_4]^{3+}$  (*left*) and  $[V(bpy)(NH_3)_4]^{2+}$ . Green denotes the loss of  $\alpha$ -electron density in the ground state. Blue represents the increase of  $\alpha$ -electron density in the excited state (*right*). Their ligand field strength (10 Dq) and wavelength ( $\lambda$ ) computed from TD-DFT are provided. Their associated qualitative orbital energy diagrams are presented below with respect to O<sub>h</sub>-symmetry.

# 5.4.4 Intraligand excitation

The NT $\rho^{\alpha,\beta}$  plots associated with near-UV ( $\lambda_{max} = 307 \text{ nm}$ ) and visible light ( $\lambda_{max} = 425 \text{ nm}$ ) absorbance of [Cr(bpy)(NH<sub>3</sub>)<sub>4</sub>]<sup>3+</sup> are presented in Figure 5.8. Both transitions display dominantly ligand character with complementary relative spin densities. The visible light absorbance has been previously assigned as an intra-ligand,  $\pi^* \leftarrow \pi$ , transition at lower energy than the intraligand singlet transition <sup>4</sup>(<sup>1</sup>IL).<sup>41</sup> This suggests that the visible-light absorbance is associated with a triplet excitation of the coordinated bipyridine, <sup>4</sup>(<sup>3</sup>IL). Despite extensive characterization, the visible light absorbance of Cr<sup>3+</sup> continues to evade a definite classification.<sup>42,43</sup> The <sup>4</sup>(<sup>3</sup>IL) description of the electronic

absorbance of  $Cr^{3+}$  polypyridyls was originally offered by Ohno et. al. upon discounting its assignment as a ligand field transition.<sup>44</sup> Herein, we provide a computational characterization of the <sup>4</sup>(<sup>3</sup>IL).

The two-electron spin eigenfunctions of the bipyridine triplet and singlet electronic configurations in terms of  $\alpha$  and  $\beta$  spins are provided in Eq. 5.1-Eq. 5.4 and correspond to the ligand excited state. Spin eigenfunctions are combinations of individual electron spin determinants that form proper S and  $M_{\rm s}$  representations. The ligand triplet states exhibit magnetic exchange interactions with the paramagnetic metal center Eq. 5.5-Eq. 5.8 for the quartet spin eigenfunctions) to yield a Heisenberg-Dirac-van Vleck (HDvV) spin ladder of sextet, quartet, and doublet states. The sextet and doublet states can be thought of as parallel (ferromagnetic) and anti-parallel (antiferromagnetic) coupling between a metal-centered quartet pseudospin and a ligand centered triplet pseudospin. If the doublet HDvV state is lowest in energy it is said that there is antiferromagnetic coupling, while of the sextet state is lowest in energy the system is said to be ferromagnetically coupled. While the sextet can be described with a single determinant a proper description of the doublet state requires 10 spin determinants—in DFT this is approximated a simple broken symmetry model of indeterminant spin.<sup>45,46</sup> The intermediate quartet state (neither ferro nor antiferromagnetically coupled) is associated with the observed 425 nm transition whose dominant five-spin determinant representation is provided in Eq. 5.11 and illustrated in Figure 5.8. It consists the negative combination of the  $M_{\rm S} = 0$  triplet spin eigenfunction of the ligand and  $M_s = 3/2$  metal-centered quartet state with the  $M_s = 1/2$  metal-centered quartet spin eigenfunction and the  $M_s = 1$  triplet spin eigenfunction of the ligand. The multireference *n*-Electron Valence State Perturbation Theory NEVPT2(5,7) method is used <sup>47–49</sup> to compute the spin energetics and analysis.

> (Eq. 5.1) ( $\alpha\alpha$ ) Ligand-based Triplet:  $M_s = 1$ (Eq. 5.2) ( $\alpha\beta+\beta\alpha$ ) Ligand-based Triplet:  $M_s = 0$ (Eq. 5.3) ( $\beta\beta$ ) Ligand-based Triplet:  $M_s = -1$ (Eq. 5.4) ( $\alpha\beta-\beta\alpha$ ) Ligand-based Singlet:  $M_s = 0$

# (Eq. 5.5) ( $\alpha\alpha\alpha$ ) Metal-centered Quartet: $M_s=3/2$



**Figure 5.8.** The electronic absorbance spectrum of  $[Cr(bpy)_3]^{3+}$  as calculated by TD-DFT. For clarity, the NT $\rho^{\alpha,\beta}$  are shown with the corresponding transition of  $[Cr(bpy)(NH_3)_4]^{3+}$ . The orbital diagrams provided below offer a multi-determinant representation of the labeled transitions.

The intermediate coupling of the ligand triplet to the unpaired electrons on the metal center provides a mechanism for the spin-forbidden triplet excitation to have intensity. The  ${}^{4}({}^{3}IL)$  excitation in the experimental electronic absorption spectrum of  $[Cr(bpy)_{3}]^{3+}$  exhibits feature that are resolved by approximately 520 cm<sup>-1</sup>, suggested to correspond to the C<sub>py</sub>-C<sub>py</sub> stretching modes of the *cis*conformation of bipyridine. Optimization of the excited state geometry and inclusion of vibronic coupling between the ground and lowest-lying quartet excited state leads to a computed spectrum that displays this vibrational feature. In addition, projecting the excited state structural distortion onto the vibrational modes supports the C<sub>py</sub>-C<sub>py</sub> stretching mode assignment. In addition to providing an absorption pathway, modest spin-orbit coupling between the states of the Heisenberg spin ladder provides a viable pathway for the  ${}^{4}({}^{3}IL)$  excited state to undergo intersystem crossing (ISC) to the potential energy surface of the associated doublet state for Cr<sup>3+</sup>. The coupling constant between the paramagnetic metal center and ligand triplet-excited state were calculated with a HDvV model Hamiltonian that simplifies to the following equation for a two-center interaction where  $S_1$  and  $S_2$  refer to the proper  $M_S$  of spin center one and two, respectively, Eq. 5.13.

(Eq. 5.13) 
$$J = \frac{E(S_1) - E(S_2)}{S_1(S_1+1) - S_2(S_2+1)}$$

Spin center one has the larger spin value so that positive and negative coupling values refer to ferro- and antiferromagnetic exchange interactions, respectively. NEVPT2(5,7) classifies the  ${}^{4}({}^{3}\text{IL})$  of  $[Cr(bpy)(NH_3)_4]^{3+}$  as an antiferromagnetic interaction with  $J = -126 \text{ cm}^{-1}$ . We also report the presence of a  ${}^{4}({}^{3}\text{IL})$  transition in  $[V(bpy)(NH_3)_4]^{2+}$  that has a smaller antiferromagnetic coupling ( $J = -75.3 \text{ cm}^{-1}$ ) and is red-shifted with respect to its Cr<sup>3+</sup> analogue. We note that this model does not distinguish the competing ferro- and antiferromagnetic interactions that define the  ${}^{4}({}^{3}\text{IL})$  state that is illustrated in Figure 5.8.

# 5.4.5 MLCT Transitions

As described above, electronic absorbance spectra of V<sup>2+</sup> polypyridyl complexes show significant absorbance in the visible region that are associated with a metal-to-ligand charge transfer transition (MLCT) at  $\lambda_{max}$  of 643 nm, whereas similar events for Cr<sup>3+</sup> are not observed.<sup>15</sup> The experimental absorbance spectra of the Cr<sup>3+</sup> and V<sup>2+</sup> polypyridyl complexes are provided in Figure 5.10. The NTp<sup>α,β</sup> plot shown in Figure 5.9 provides an unambiguous description as a  $\pi^* \leftarrow e_\delta$  transition centered at 605 nm that is modestly blue-shifted with respect to experiment. Symmetry-breaking of the t<sub>2g</sub> set of V<sup>2+</sup> polypyridyls, that destabilizes the e<sub>δ</sub> orbitals, lowers the energy of the MLCT. The transitions centered at approximately 400 nm are MLCT bands that result in population of upperlying  $\pi^*$ -orbitals: we suggest that the symmetry-breaking trigonal distortion based on metal-ligand covalency leads to the increased intensity of the visible light absorbance for V<sup>2+</sup> polypyridyls. We note that the <sup>4</sup>(<sup>3</sup>IL) of [V(bpy)(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> described above is buried within this series of MLCT bands of greater intensity. This suggests that the <sup>4</sup>(<sup>3</sup>IL) is not an accessible pathway for intersystem crossing for V<sup>2+</sup> polypyridyls. Our findings are consistent with the previous assignment of an MLCT transition as the pathway for intersystem crossing for V<sup>2+</sup> polypyridyls.



**Figure 5.9**. The absorbance spectra of  $[V(bpy)_3]^{2+}$  as calculated by TD-DFT. For clarity, the NT $\rho^{\alpha,\beta}$  of the MLCT absorbances are shown for the corresponding transition of  $[V(bpy)(NH_3)_4]^{2+}$ , noting that their energies are modestly red-shifted by approximately 400 cm<sup>-1</sup>.

# 5.4.6 Substituent Impact

It is of interest to probe the impact of ligand architecture on the electronic properties of d<sup>3</sup> systems. We performed calculations on -CH<sub>3</sub>, -*t*-But, -CF<sub>3</sub>, and -CO<sub>2</sub>Me at the 4,4'-positions of the bipyridine ligand sets. The substituents are *para*- with respect to the donor nitrogens and their electronic impact should be dominated by resonance. We report no relationship between the calculated energy of both the LMCT and  $^{4}(^{3}IL)$  and their Hammett parameter ( $\sigma_{para}$ ) for the Cr<sup>3+</sup> complexes. We note that the transitions of the -CO<sub>2</sub>Me-substituted species are red-shifted by approximately 0.20 eV. There is negligible distinction with respect to the phen ligand environment, both experimentally and computationally. The calculated energy of the  $^{2}E$  excited state is invariant to substituent identity of the Cr<sup>3+</sup> series that corroborates its metal-centered and ligand-field independent character. These results are consistent with previous substituent studies performed by us and others.<sup>41,50,51</sup>



**Figure 5.10.** The electronic absorption spectra of  $[V(bpy)_3(OTf)_2]$  (V1a; black),  $[V(phen)_3(OTf)_2]$  (V2; red),  $[Cr(bpy)_3](BF_4)_3$  (Cr1; gray), and  $[Cr(phen)_3](BF_4)_3$  (Cr2; purple) collected in CH<sub>3</sub>CN

The calculated MLCT of the V<sup>2+</sup> complexes do not display a relationship with any reported substituent parameters. There is no significant differentiation between the calculated transition energy of the -CH<sub>3</sub>, -*t*-Bu, and -CF<sub>3</sub> substituted species and the parent complex. Due to the dual  $\pi$ -donor and  $\pi^*$ -acceptor character of the ligand set, the electronic impact of the substituents approximately cancels.  $\pi^* \leftarrow e_{\delta}$  and the higher energy MLCT absorbances of the -CO<sub>2</sub>Me-substituted complex are red-shifted

by 0.12 and 0.42 eV, respectively, suggesting that charge transfer states of V<sup>2+</sup> polypyridyl complexes can be stabilized by expansion of the  $\pi$ -system. The use of the phen ligand set does not impact the MLCT of **V2**.

**Table 5.1.** Visible absorbance peaks,  $\lambda_{max}$  (nm), and molar absorptivities,  $\epsilon$  (M<sup>-1</sup> cm<sup>-1</sup>), of the complexes in the UV-Vis spectra of Cr<sup>3+</sup> and V<sup>2+</sup> polypyridyls in Figure 5.10.

	Visible Absorbance Peaks, $\lambda_{max}$ (nm) ( $\epsilon$ )
[Cr(bpy) <sub>3</sub> ](BF <sub>4</sub> ) <sub>3</sub> (Cr1)	346 (8100), 360 (5680), 402 (950), 428 (682), 458 (291)
$[Cr(phen)_3](BF_4)_3 (Cr2)$	342 (6810), 358 (3710), 405 (821), 435 (558), 454 (285)
[V(bpy) <sub>3</sub> ](OTf) <sub>2</sub> (V1a)	404 (3460), 643 (5890)
$[V(phen)_3](OTf)_2 (V2)$	349 (3300), 640 (7980)

#### 5.4.7 Assignment of Lowest Excited State

The change in spin density associated with the excitation from the  ${}^{4}A_{2}$  ground state ( $\rho_{4_{A}}^{\alpha,\beta}$ ) to the  ${}^{2}E$  excited state ( $\rho_{2_{E}}^{\alpha,\beta}$ ) of [Cr(bpy)<sub>3</sub>]<sup>3+</sup> is shown in the  $\Delta \rho^{\alpha,\beta}$  plot in Figure 5.9. The plot illustrates that one component of the  ${}^{2}E$  state is merely a spin flip within the non-bonding metal-centered,  $t_{2g}$ , orbital set relative to the ground state. This suggests minimal excited state geometric distortion and minimal non-radiative decay. We compute a  ${}^{2}E$  excitation energy of 1.62 eV (13,100 cm<sup>-1</sup>), using a multi-determinant approach to DFT in agreement with the experimental value of 1.70 eV (13,700 cm<sup>-1</sup>). The optimized geometry of the  ${}^{2}E$  state confirms minimal distortion of the primary coordination sphere,  $\Delta S(OC-6) = 0.055$ . Collectively, the data suggest the excited state lifetime of Cr<sup>3+</sup> polypyridyls is attributable to minimal non-radiative decay of its spin-flip excited state.

While  $[V(bpy)_3]^{2+}$  is non-emissive, as discussed above, the  $\Delta \rho^{\alpha,\beta}$  plot Figure 5.9 shows that the lowest energy transition, the spin flipped doublet, involves an  $e_{\delta}$  orbital. The transition is computed to occur at an energy of 1.10 eV (8,870 cm<sup>-1</sup>), outside the range of our detectors. The plot also suggests that the  $[V^{2+}(bpy)_3]$  <sup>2</sup>E state is not entirely metal-centered, as the  $\beta \leftarrow \alpha$  spin flip delocalizes onto perpendicular pyridine groups, which is consistent with its greater trigonal distortion and metal-ligand covalency. The delocalization of the excited state reduces the overlap between the electron densities
of the metal-centered orbitals, that in turn decreases the magnitude of its exchange interactions, lowering the energy of the <sup>2</sup>E excited state. TD-DFT calculations indicate a broad and intense near-IR absorbance in the doublet manifold, which the NT $\rho^{\alpha,\beta}$  assigns as a  $\beta$ -transition of <sup>2</sup>MLCT character (Figure 5.10).



**Figure 5.9.** The spin density of the  ${}^{4}A_{2}$  (top row) and  ${}^{2}E$  state (middle row) of  $[Cr^{3+}(bpy)_{3}]$  (left column) and  $[V^{2+}(bpy)_{3}]$  (right column) where blue and green denote  $\alpha$  and  $\beta$  spin, respectively. The difference of the excited state with respect to the ground state,  $\Delta \rho^{\alpha,\beta}$ , (bottom row) is presented below where green is associated with a  $\beta \leftarrow \alpha$  spin flip

We consider the role of nonradiative decay and optimize the <sup>2</sup>E of the complexes. Both  $[Cr(bpy)_3]^{3+}$  and  $[V(bpy)_3]^{2+}$  display minimal distortion in their primary coordination sphere. The Cr<sup>3+</sup> complex

has a  $\Delta S(OC-6)$  and  $\Delta \phi_{OC \rightarrow TRP}$  of 0.055 and 0.8 %, respectively, where a positive sign indicates distortion from octahedral geometry. In contrast, V<sup>2+</sup> distorts towards octahedral geometry with a  $\Delta S(OC-6)$  of -0.061 and  $\Delta \phi_{OC \rightarrow TRP}$  of -0.7%. For the phen-containing complexes, Cr<sup>3+</sup> displays no distortion of its <sup>2</sup>E state while V<sup>2+</sup> has changes in its primary coordination sphere consistant with  $[V(bpy)_3]^{2+}$ . The pyridine groups engaged in the spin flip of the e<sub>8</sub> orbital of the <sup>2</sup>E state of  $[V(bpy)_3]^{2+}$ contract by approximately 0.04 Å in their excited state geometry.



**Figure 5.10.** TD-DFT calculated absorbance of the quartet (black) and doublet (red) state of  $[V (bpy)_3]^{2+}$ , their energies with respect to the quartet ground state. The inset is the NT $\rho^{\alpha,\beta}$  that corresponds to the third doublet excited state.

Previously,<sup>15</sup> some of us suggested that the lowest doublet state should be an admixture of the <sup>2</sup>E (<sup>2</sup>MC) and <sup>2</sup>MLCT states. These states should be near-degenerate and possess the same symmetry, coupling between them lowers the energy of the <sup>2</sup>MC state relative to a pure metal-centered <sup>2</sup>E excited state, Figure 5.10. This is further supported by the broadness of the transition.

In addition, the symmetry mixing associated with the observed trigonal distortion reported here also increases the ligand character of the V<sup>2+ 2</sup>E state, which should also increase the coupling between the metal-centered doublet, <sup>2</sup>MC, and the lowest <sup>2</sup>MLCT states. This is functionally equivalent to suggesting an increase in covalency between the metal and ligand arises from the greater trigonal distortion of V<sup>2+</sup> polypyridyls, see Figure 5.12. As suggested previously, the geometric distortion of

the  ${}^{2}MC/{}^{2}MLCT$  state due to admixture of ligand character should facilitate intersystem crossing to the ground state and shorten the lifetime of the  ${}^{2}MC/{}^{2}MLCT$  state.



**Figure 5.11.** The adiabatic coupling between doublet states of dominant metal-character ( ${}^{2}\text{E}$  or  ${}^{2}\text{MC}$ ) and the metal-ligand charge transfer ( ${}^{2}\text{MLCT}$ ). This resonance results in a symmetric and antisymmetric combination of their states that splits their energies with respect to the average of their isolated states.



**Figure 5.12.** The symmetric linear combination of the singles excitations of the metal-centered spinflip,  $(t_{2\alpha} \leftarrow \pi)$  and  $(\pi^* \leftarrow t_{2\alpha})$  character that are descriptive of greater metal-ligand covalency.

We lastly consider the importance of the polypyridyl ligand environment. If the geometry of the quartet state is optimized for the series  $[V(bpy)_n(NH_3)_{6n-2}]^{2+}$ , where we sequentially substitute bipyridine with *cis*-coordinated amines, the trigonal distortion of the complex increases with the number of coordinated polypyridyls. We attribute this systematic distortion to metal-ligand  $\pi$ -covalency that is absent for NH<sub>3</sub>  $\sigma$ -donor ligands. In addition, we find an inverse relationship between the  $\phi_{OC \rightarrow TRP}$  distortion and the calculated <sup>2</sup>E excitation energy as shown in Figure 5.13. This suggests that the trigonal distortion of V<sup>2+</sup> polypyridyls is a result of metal-ligand  $\pi$  interactions discussed above and that the accompanying delocalization of the metal-centered electrons stabilizing the <sup>2</sup>E state.

### 5.5 Conclusion

Rather than the analogous ground and excited-state properties anticipated from the isoelectronic  $(d^3)$  structure of Cr<sup>3+</sup> and V<sup>2+</sup> polypyridyl complexes, we report stark contrasts. The destabilized and expanded nature of the 3d-orbitals of V<sup>2+</sup> results in ligand  $\pi$ -metal t<sub>2g</sub> orbital mixing and a pronounced

trigonal distortion, compared to the metal-ligand isolation and more rigorously octahedral coordination geometry of  $Cr^{3+}$  polypyridyls. This orbital mixing and trigonal geometric distortion delocalize the spin density of the paramagnetic metal center onto the ligand  $\pi^*$  orbitals. Through DFT and multireference calculations, we find that the visible light absorbance of  $Cr^{3+}$  polypyridyl complexes results from an anti-ferromagnetic exchange interaction between the paramagnetic metal center and a ligandcentered triplet-excited state. Due to the extensive metal-ligand charge transfer (MLCT) character of the quartet and doublet manifolds of V<sup>2+</sup> polypyridyls, this pathway for intersystem crossing (ISC) is suppressed. Instead, significant delocalization of the <sup>2</sup>E state of the V<sup>2+</sup> complexes reduce the magnitude of its excitation energy that can be further stabilized by an adiabatic coupling with its neardegenerate <sup>2</sup>MLCT state. Collectively, our findings complement the recent spectroscopic characterization of V<sup>2+</sup> polypyridyls and provides context for its diminished excited-state lifetimes compared to the robust photophysical properties of their Cr<sup>3+</sup> analogues. In addition, they support an important emerging role for metal-ligand covalency in structural distortion and excited state tuning.



**Figure 5.13.** The APFD multi-determinant corrected <sup>2</sup>E excitation energy of the  $[V(bpy)_n(NH_3)_{6-2x}]^{2+}$  as a function of the distortion pathway between octahedral and trigonal prismatic geometry.

#### 5.6 Experimental

The  ${}^{4}A_{2}$  structures of the  $[Cr(PDO)_{3}]^{3+}$  and  $[V(PDO)_{3}]^{2+}$  complexes (PDO is 1,3-propanedionate) were optimized with the APFD functional<sup>53</sup> and the cc-pVTZ basis set<sup>54</sup> using the Gaussian09 software package.<sup>55</sup> The structure for the  ${}^{4}A_{2}$  ground state was also used to represent the  ${}^{2}E$  state. The  ${}^{4}T_{2}$  excited

state structures were calculated by promoting an electron from the  $t_{2g}$  orbital to an  $e_g^*$  orbital, its geometry constrained as  $C_2$ -symmetric. The excited state was further optimized without the symmetry restriction resulting in the vibrational minimum structure that we define as the  ${}^4T_2$ . A linearly interpolated path between the  ${}^2E$  and  ${}^4T_2$  states was obtained following the method of Miller et al.<sup>56</sup>

The excited state energies for the interpolated path structures were calculated with the SORCI method with a CAS(3,5) zeroth-order wavefunction.<sup>24</sup> The cc-pCVTZ<sup>57</sup> and cc-pVDZ basis sets were used for the metal-center and the remaining atoms, respectively. The active space of the SORCI calculation was expanded to include the metal-center 3p orbitals. Spin-orbit coupling was calculated for structures within the 0.50-0.75 range of the distortion pathway. All SORCI related calculations were performed using the ORCA electronic structure software package version 3.0.3.<sup>58</sup>

The ground state (<sup>4</sup>A<sub>2</sub>) structures of compounds [M<sup>n+</sup>(4,4'-X-bpy)<sub>3</sub>] (M = Cr<sup>3+</sup> and V<sup>2+</sup>; X = H, CH<sub>3</sub>, *tert*-butyl, CF<sub>3</sub>, and CO<sub>2</sub>Me) were optimized using DFT with the APFD functional and the 6-311+G\* basis set<sup>59</sup> in a PCM acetonitrile continuum solvent.<sup>60</sup> An analogous procedure was used for the optimization of the model complexes [Cr(NH<sub>3</sub>)<sub>4</sub>(bpy)]<sup>3+</sup> and [V(NH<sub>3</sub>)<sub>6-n</sub>(bpy)<sub>n</sub>]<sup>2+</sup>. All DFT calculations utilized the Gaussian 16 software suite.<sup>61</sup> An unrestricted wavefunction was used coupled with a stability analysis to verify the wavefunction as the lowest of a given *M*<sub>5</sub>. The geometries for the <sup>2</sup>E excited state of [Cr(bpy)<sub>3</sub>]<sup>3+</sup> and [V(bpy)<sub>3</sub>]<sup>2+</sup> were optimized as well, about their stable wavefunction. TD-DFT calculations<sup>62</sup> and Natural Transition Orbital (NTO)<sup>63</sup> and Natural Transition Spin Density (NTp<sup>a,β</sup>) analyses were performed on the quartet and doublet state of the Cr<sup>3+</sup> and V<sup>2+</sup> polypyridyl complexes. The electronic absorption spectra were generated using the oscillator strengths and peak positions from the corresponding TD-DFT calculation. Each electronic state was convoluted with a Gaussian line shape with a 0.219 eV line width.

The following calculations were performed with the ORCA 4.0 electronic structure software program.<sup>64</sup> The molecular orbitals and qualitative energies presented in Figure 5.5 and Figure 5.6 were generated with the B3LYP functional<sup>65</sup> and the def2-TZVP basis set<sup>66</sup> and the previously detailed

D3(Ar<sub>2</sub>) empirical dispersion correction.<sup>65</sup> The spin determinants of the CAS(5,7) wavefunction of  $[Cr(bpy)(NH_3)_4]^{3+}$  and  $[V(bpy)(NH_3)_4]^{2+}$  were determined with the def2-TZVP basis set and the corresponding auxiliary basis sets. The active space was defined as the metal-centered t<sub>2g</sub> and e<sub>g</sub><sup>\*</sup> orbitals and the ligand-based  $\pi$  and  $\pi^*$  orbitals. The final energies for the excited states were obtained with the NEVPT2(5,7) technique.<sup>49,67,68</sup>

The vibronic spectrum of [Cr(bpy)(NH3)<sub>4</sub>]<sup>3+</sup> was calculated with the APFD functional and 6-311+g(d) basis set with the Gaussian16 software. The geometry of the lowest-lying quartet excited state via TD-DFT was optimized. Frequency calculations of the ground and the corresponding excited states were performed. As previously described by Santoro et al, the vibronic spectrum was generated by Franck-Condon-Herzberg-Teller analysis for a one photon absorption between the ground and excited state.<sup>69</sup>

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# Chapter 6 Visualizing and Quantifying Magnetic Interactions in Multielectron Systems

#### 6.1 Outline

Herein, we present a procedure to visualize different electron-electron interactions: coulomb integrals ( $J_{ab}$ ,  $J_{aa}$ , and  $J_{bb}$ ), exchange integrals ( $K_{ab}$ ), and orbital overlap ( $S_{ab}$ ). The different terms can be plotted as a potential or an integrand that provides new insight for open-shell systems. We develop our method and its application with respect to the allotropes of oxygen, O<sub>2</sub> and O<sub>3</sub>. We refer to our method as Heisenberg-Dirac-van Vleck-Strongly Orthogonal (HDvV-SO) model. Our method similarly provides quantitative insight that accurately assigns the sign and magnitude of magnetic interactions. We present the method as an auxiliary quantum chemistry code for most current electronic structure software packages. Our model extends to systems, irrespective of the total multiplicity, when implemented with CASSCF calculations.

#### 6.2 Division of Labor

All work in this Chapter was performed by Justin P. Joyce.

# **6.3 Introduction**

Molecules can possess near-degenerate states of distinct electron spin multiplicity. This can result in desirable magnetic properties where bistability between different spin states can engender molecular switches.<sup>1–4</sup> Electron spin is also a controlling factor in electron spectroscopy where spin conservation engenders photon absorption and spin change is the basis of phosphorescence.<sup>5</sup> More generally, this is a latent property of all molecules where homolytic bond cleavage generates two unpaired electrons, different spin states possessing different reactivities.<sup>6–9</sup> An understanding of the interactions between unpaired electrons and its impact on their spin state energies are invaluable to the study of magnetism, electronic spectroscopy, and reaction mechanisms. These systems have inherently challenged theoretical models because of the small magnitude of their energetic differentiation and their multideterminant character. This difficulty has incited the advancement of computational techniques to address these complex electronic structures.<sup>10–13</sup> Our focus and motivation here are to understand how unquenched electronic spins interact, this earnest ambition being pivotal to scientific progress. Herein, we develop the Heisenberg-Dirac-van Vleck-Strongly Orthogonal (HDvV-SO) model that provides visual and quantitative insight to the electron-electron interactions that constitute the relative energies of their magnetic states. We use the allotropes of oxygen (O<sub>2</sub> and O<sub>3</sub>) to introduce the foundational concepts of electronic structure and spin. The oxygen allotropes are diradical systems that can display ferro- or antiferromagnetic coupling for a triplet and singlet ground state, respectively. While seemingly trivial, each of these chemicals remain problematic for the full suite of theoretical methods and continue as a source of active inquiry in the field.<sup>14–16</sup> These systems and their excited states are not only valuable computational benchmarks, but are active participants in atmospheric and photochemistry.<sup>17–20</sup>

#### 6.4 Results and Discussion

#### 6.4.1 Hund's First Rule

The generalized valence bond (GVB) diagram of diatomic oxygen (O<sub>2</sub>) is presented in Figure 6.1.<sup>21</sup> The circle and lobes of the GVB diagram denote the localized p-orbitals that are oriented perpendicular  $(2p_x)$  and parallel  $(2p_y \text{ and } 2p_z)$  to the plane of the page. The singly occupied orbitals along the z-axis form a  $\sigma$ -bond that we represent with a solid line in Figure 6.1. (*bottom*). We arrange the remaining unpaired electrons of O<sub>2</sub> to occupy perpendicular p-orbitals on separate atomic centers.<sup>22</sup> The Pauli Exclusion principle prohibits two electrons of the same spin from occupying the same orbital. The resonance structure satisfies this constraint and delocalizes the unpaired electron between the atomic centers. Figure 6.1 is consistant with the charge-shift bond model developed by Shaik and Hibberty.<sup>23</sup>

GVB diagrams represent electrons as dots that do not assign  $\alpha$  or  $\beta$  spin. O<sub>2</sub> is ferromagnetically coupled and possesses a  ${}^{3}\Sigma^{-}$  ground state that is stabilized by 0.98 eV with respect to the  ${}^{1}\Delta_{g}$  excited

state that is referred to as singlet oxygen.<sup>24</sup> The wavefunction and energy expressions for the lowest lying triplet and singlet state of  $O_2$  are provided in Figure 6.2 and Figure 6.3 and Eq. 6.1 and Eq. 6.4, respectively. The equations refer to orbitals *a* and *b* that are occupied with electrons *1* and 2. The energy expressions are with respect to the one-electron operators (h<sub>ii</sub>), the two-center and two-electron coulomb (J<sub>ii</sub>) and exchange integrals (K<sub>ii</sub>).

**O**<sub>2</sub>: 
$${}^{3}\Sigma - \& {}^{1}\Delta_{q}$$



**Figure 6.1**. The generalized valence bond (GVB) diagram of diatomic oxygen (O<sub>2</sub>) that emphasizes the resonance associated with the three-electron  $\pi$ -bonds. The orbital representation of the  $\sigma$ -bonding interaction is explicitly drawn in the top and represented with a line in the bottom.



Figure 6.2. The  $M_s = 0$  spin eigenfunction of a two-electron triplet state.

(Eq. 6.1) 
$$\psi_{\rm T} = [\phi_{\rm a}(1)\phi_{\rm b}(2) - \phi_{\rm a}(2)\phi_{\rm b}(1)][\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$
  
(Eq. 6.2)  $E_{\rm T} = h_{\rm aa} + h_{\rm bb} + J_{\rm ab} - K_{\rm ab}$   
 $\underline{4} - \underline{7} - \underline{7} - \underline{7}$ 

Figure 6.3. The  $M_s = 0$  spin eigenfunction of a two-electron singlet state

(Eq. 6.3) 
$$\psi_{S_2} = [\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$
  
(Eq. 6.4)  $E_{S_2} = h_{aa} + h_{bb} + J_{ab} + K_{ab}$ 

We reference the spin density of the lowest-lying singlet excited state to the corresponding triplet ground state in our  $\Delta \rho^{\alpha,\beta}$  plot in Figure 6.4. We classify the  ${}^{1}\Delta_{g}$  state as a spin-flip excited state where the unpaired electrons are triplet and singlet coupled for the  ${}^{3}\Sigma^{-}$  ground state and  ${}^{1}\Delta_{g}$  excited states,

respectively. The spin density and spin density difference plots are illustrated in Figure 6.4. The oneelectron operators and coulomb integrals are independent of spin, their energies being nearly constant between the two states. The difference in energy between the  ${}^{3}\Sigma^{-}$  ground state and  ${}^{1}\Delta_{g}$  excited states is dominantly due to two-electron exchange interactions.



**Figure 6.4**. The spin density differences  $(\Delta \rho^{\alpha,\beta})$  for the lowest-lying triplet and singlet states of O<sub>2</sub> obtained at the Hartree-Fock level-of-theory with an unrestricted wavefunction.

(Eq. 6.5) 
$$\Delta E_{T-S_2} = -2K_{ab}$$

The two-electron exchange interaction between a pair of electrons is a positive integral (repulsive interaction) so that the  ${}^{3}\Sigma^{-}$  is stabilized with respect to the  ${}^{1}\Delta_{g}$  state due to the negative sign. Electrons of the same spin cannot occupy the same location due to the Pauli Exclusion principle. Electron correlation refers to the concerted relationship of the motion and position between electrons, their spatial and spin wavefunctions being dependent on those of its neighbors. This type of electron correlation is addressed in Hartree-Fock theory by the antisymmetry of the Slater determinant and is referred to as Fermi correlation. If the unpaired electrons are restricted by symmetry from overlapping, then exchange is the sole resource of stabilization.

There are two remaining singlet states that result from the linear combination of the alternant double and empty occupation of the  $2p_y$  and  $2p_z$  orbitals. We refer to these states as  $S_1$  and  $S_3$  and they are equivalent to the bonding and antibonding orbitals provided by Molecular Orbital (MO) theory, respectively, or the ionic states of Valence Bond (VB) theory. The corresponding wavefunctions can

be described with a Generalized Valence Bond-Perfect Pair  $(\text{GVB-PP})^{25}$  or a two-configuration configuration interaction (CI) representation.<sup>26</sup> The coefficients,  $c_1$  and  $c_2$ , are normalized and solved variationally, providing the lowest energy singlet state (S<sub>1</sub>) with respect to the two-electron basis. Because the singly occupied orbitals are degenerate and orthogonal for O<sub>2</sub>, the coefficients are equivalent. The one-center two-electron coulomb integrals, J<sub>aa</sub> and J<sub>bb</sub>, are associated with fulloccupation of orbital *a* and *b*, respectively, and each contributes more electrostatic repulsion than J<sub>ab</sub> due to the smaller separation between electrons.

$$\left[\begin{array}{ccc} c_1 & \downarrow \\ \hline \end{array} & \hline \\ c_2 & \downarrow \\ \hline \end{array}\right]$$

Figure 6.5. The wavefunction of the S<sub>1</sub> singlet state

$$(Eq. 6.6) \quad S_{1} = \left[c_{1} \phi_{a}(1)\phi_{a}(2) - c_{2}\phi_{b}(1)\phi_{b}(2)\right] \left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

$$(Eq. 6.7) \quad S_{1} = \frac{1}{\sqrt{2}} \left[\phi_{a}(1)\phi_{a}(2) - \phi_{b}(1)\phi_{b}(2)\right] \left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

$$(Eq. 6.8) \quad E(S_{1}) = h_{aa} + h_{bb} + \frac{J_{aa} + J_{bb}}{2} - K_{ab}$$

$$\left[c_{2} \underline{4} + c_{1} \underline{4}\right]$$

Figure 6.6. The wavefunction of the S<sub>3</sub> singlet state

(Eq. 6.9) 
$$S_3 = [c_2\phi_a(1)\phi_a(2) + c_1\phi_b(1)\phi_b(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$
  
(Eq. 6.10)  $S_3 = \frac{1}{\sqrt{2}} [\phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]$   
(Eq. 6.11)  $E(S_3) = h_{aa} + h_{bb} + \frac{J_{aa} + J_{bb}}{2} + K_{ab}$ 

The stabilization to the total energy provided by including an additional electronic configuration is referred to as resonance, or static correlation.<sup>27</sup> Resonance stabilizes and destabilizes the S<sub>1</sub> and S<sub>3</sub> state by a single exchange interaction that is detailed in Eq. 6.12. The triplet ground state predicted with Hund's first Rule can be equally attributed to the electron correlation provided by resonance (static) or the Pauli exclusion principle (Fermi).

(Eq. 6.12) 
$$\Delta E_{S_1-S_3} = -2K_{ab}$$

The stabilization of the triplet state (T) relative to the lowest singlet state ( $S_1$ ) can be described by the difference in the two- and average of the one-center coulomb integrals as detailed in Eq. 6.16.



**Figure 6.7.** The relative energy diagrams for the three singlet and one triplet state of a two-electron system with respect to their coulomb and exchange integrals.

In this chapter we present a model that incorporates anti-ferromagnetic coupling and provides numerical as well as visual insight into the two-electron integrals that are foundational to electronic structure theory. We refer to our method as the Heisenberg-Dirac-van Vleck Strongly Orthogonal (HDvV-SO) model and it provides an unambiguous description of discrete electron-electron interactions. The energy expressions are developed from the GVB-SO method previously reported by Goddard and Bobrowicz.<sup>28,29</sup> We illustrate our procedure by plotting the integrands of coulomb and exchange integrals for O<sub>2</sub>. The only required input is a system's singly occupied orbitals in the format of a Gaussian cube file---there is no restriction as to which electronic structure software package our

method is paired with. This has tremendous utility in that its expense scales with respect to the density of an orbitals grid rather than the total number of electrons in the system. Our current focus is directed towards the graphical opportunities that HDvV-SO provides for the comprehension of electronelectron interactions that comprise the lowest-common-denominator of electronic structure.

Provided below is the coulomb integral  $(J_{ab})$  whose impact on the energy of the electronic states we have detailed above.  $J_{ab}$  denotes the electrostatic or coulombic repulsion, between the charge or electron densities of each electron ( $\rho_a$  and  $\rho_b$ ). Each electron provides a field that acts on the charge density of each additional electron, the coulomb integral being the summation of the interactions between a pair of electrons. This is illustrative of an electrostatic potential and it is a repulsive contribution to the energy of a system since both electrons possess a negative charge. Below we plot the three-dimensional potential of electrons one and two on the surface of the charge densities of two and one, respectively. Blue indicates a positive, repulsive, potential whose magnitude is invoked by its shading. As a product, electron densities do not retain the phases of their respective orbital wavefunction, so there is no symmetry restriction to inhibit overlap Figure 6.8 illustrates that  $J_{ab}$  is concentrated in the areas where their densities overlap, despite the orbitals being orthogonal.

The potentials, densities, and integrands displayed are obtained from the manipulation of orbitals in the format of a Gaussian cube. Our method is pairwise, formally considering the interactions between electrons 1 and 2 that occupy orbitals a and b. The following procedure extends across the corresponding one- and two-center coulombic ( $J_{aa}$ ,  $J_{bb}$ ,  $J_{ab}$ , and  $J_{ba}$ ) and exchange ( $K_{ab}$ ) interactions that are detailed in Eq. 6.17-Eq. 6.27.

(Eq. 6.17) 
$$J_{ab} = \int \phi_a(1)\phi_a(1) \left[ \int \frac{\phi_b(2)\phi_b(2)}{r_{12}} dr_2 \right] dr_1$$
  
(Eq. 6.18)  $J_{ab} = \int \rho_a(1) \left[ \int \frac{\rho_b(2)}{r_{12}} dr_2 \right] dr_1$   
(Eq. 6.19)  $J_{ba} = \int \phi_b(1)\phi_b(1) \left[ \int \frac{\phi_a(2)\phi_a(2)}{r_{12}} dr_2 \right] dr_1$ 



**Figure 6.8.** (*top*) The CASSCF(8,6) natural orbitals of the equilibrium geometry of  $O_2$  that are presented to Eq. X. (*bottom*) The potential of the  $J_{ab}$  and  $J_{ba}$  coulomb integral plotted on the electron density of orbital a and b, respectively, oriented along the  $O_2$  bond axis.

(Eq. 6.22) 
$$J_{aa} = \int \phi_a(1)\phi_a(1) \left[ \int \frac{\phi_a(2)\phi_a(2)}{r_{12}} dr_2 \right] dr_1$$
  
(Eq. 6.23)  $J_{aa} = \int \rho_a(1) \left[ \int \frac{\rho_a(2)}{r_{12}} dr_2 \right] dr_1$ 

The corresponding plots of  $J_{aa}$  and  $J_{bb}$  are provided in Figure 6.9 and Figure 6.10. Since an orbital has perfect overlap with itself the potential is evenly distributed across the density. The electrostatic potential is proportional to the separation between the electrons ( $R_{12}$ ) so that  $J_{aa}$  and  $J_{bb}$  self-terms are always larger than the corresponding value of  $J_{12}$ . The only distinction between  $J_{aa}$  and  $J_{bb}$  in oxygen atom is their orientations, the two terms being equivalent.



**Figure 6.9.** (*top*) The CASSCF(8,6) natural orbitals of the equilibrium geometry of  $O_2$  that are presented to Eq. X. (*bottom*) The potential of the  $J_{aa}$  coulomb integral *is* plotted on the electron density of orbital *a* and oriented along the  $O_2$  bond axis.



**Figure 6.10.** (*top*) The CASSCF(8,6) natural orbitals of the equilibrium geometry of  $O_2$  that are presented to Eq. X. (*bottom*) The potential of the J<sub>bb</sub> coulomb integral *is* plotted on the electron density of orbital b and oriented along the  $O_2$  bond axis.

While coulombic interactions have a classical definition, exchange is a purely quantum phenomenon that derives from the resonance between a pair of electrons. The exchange integrand is provided in Figure 6.11 where we highlight that it maintains the formalism of an electrostatic potential. Exchange is distinct from our discussion of coulombic interactions in that its potential derives from the interference between a pair of orbitals, rather than tangible electron densities. Borrowing notation developed by Dougherty, we refer to the area of coherence between wavefunctions as the overlap functional ( $f_{ab}$ ) and will demonstrate its utility in assigning magnetic properties continually throughout this chapter.<sup>30</sup> We note that sign is arbitrary with respect to Figure 6.11 and strictly indicates that the overlap is in-phase (blue) or out-of-phase (red). For our current system, the amount of in-phase and out-of-phase overlap is the same indicating that the orbitals are orthogonal. Since its potential is squared prior to integration exchange is a repulsive term, the spin of the respective electrons determining whether it's a source of strain or stability.

(Eq. 6.26) 
$$K_{ab} = \int \phi_a(1)\phi_b(1) \left[ \int \frac{\phi_a(2)\phi_b(2)}{r_{12}} dr_2 \right] dr_1$$
  
(Eq. 6.27)  $K_{ab} = \int f_{ab}(1) \left[ \int \frac{f_{ab}(2)}{r_{12}} dr_2 \right] dr_1$ 

The potential of a coulomb interaction is calculated by summing the electron density at each point of each cubic grid element in its Gaussian cube that is detailed in Eq. 6.28-Eq. 6.33. Our procedure extends to exchange interactions in considering overlap densities rather than electron densities.



**Figure 6.11.** (*top*) The CASSCF(8,6) natural orbitals of the equilibrium geometry of  $O_2$  that are presented to Eq. 6.26 (*bottom*) The potential of the exchange integral is plotted on the overlap functional of orbital a and b and oriented along the  $O_2$  bond axis.

$$(Eq. 6.28) \quad \Delta \rho_{a}^{j} = \phi_{a} \left( x_{j} + \Delta x_{j}, y_{j} + \Delta y_{j}, z_{j} + \Delta z_{j} \right) \phi_{a} \left( x_{j} + \Delta x_{j}, y_{j} + \Delta y_{j}, z_{j} + \Delta z_{j} \right)$$

$$(Eq. 6.29) \quad \Delta \rho_{b}^{j} = \phi_{b} \left( x_{j} + \Delta x_{j}, y_{j} + \Delta y_{j}, z_{j} + \Delta z_{j} \right) \phi_{b} \left( x_{j} + \Delta x_{j}, y_{j} + \Delta y_{j}, z_{j} + \Delta z_{j} \right)$$

$$(Eq. 6.30) \quad \Delta f_{ab}^{j} = \phi_{a} \left( x_{j} + \Delta x_{j}, y_{j} + \Delta y_{j}, z_{j} + \Delta z_{j} \right) \phi_{b} \left( x_{j} + \Delta x_{j}, y_{j} + \Delta y_{j}, z_{j} + \Delta z_{j} \right)$$

$$(Eq. 6.31) \quad \Delta V_{a} \left( x_{i}, y_{i}, z_{i} \right) = \sum_{j} \frac{\Delta \rho_{a}^{j}}{\sqrt{\left( x_{j} - x_{j} \right)^{2} + \left( z_{i} - z_{j} \right)^{2}}} \Delta x_{j} \Delta y_{j} \Delta z_{j}$$

$$(Eq. 6.32) \quad \Delta V_{b} \left( x_{i}, y_{i}, z_{i} \right) = \sum_{j} \frac{\Delta \rho_{b}^{j}}{\sqrt{\left( x_{j} - x_{j} \right)^{2} + \left( z_{i} - z_{j} \right)^{2}}} \Delta x_{j} \Delta y_{j} \Delta z_{j}$$

$$(Eq. 6.33) \quad \Delta V_{ab} \left( x_{i}, y_{i}, z_{i} \right) = \sum_{j} \frac{\Delta f_{ab}^{j}}{\sqrt{\left( x_{j} - x_{j} \right)^{2} + \left( z_{i} - z_{j} \right)^{2}}} \Delta x_{j} \Delta y_{j} \Delta z_{j}$$

The density of a coulomb interaction is obtained with multiplying the potential by the electron density of its corresponding electron. The product is the integrand, and the summation is the integral that is showed in Eq. 6.34-Eq. 6.38.

(Eq. 6.34) 
$$J_{ab} = \sum_k \Delta \rho_a^k \Delta V_b^k$$

(Eq. 6.35) 
$$J_{ba} = \sum_{k} \Delta \rho_{b}^{k} \Delta V_{a}^{k}$$
  
(Eq. 6.36)  $J_{a} = \sum_{k} \Delta \rho_{a}^{k} \Delta V_{a}^{k}$   
(Eq. 6.37)  $J_{b} = \sum_{k} \Delta \rho_{b}^{k} \Delta V_{b}^{k}$   
(Eq. 6.38)  $K_{ab} = \sum_{k} \Delta f_{ab}^{k} \Delta V_{ab}^{k}$ 

The integral of the HDvV-SO method with respect to the  $\pi^*$ -antibonding orbitals of O<sub>2</sub> exaggerates the magnitude of exchange and assigns the <sup>1</sup>Δ<sub>g</sub> excited state an energy of 1.31 eV. We attribute the error due to the approximation that the three-electron  $\pi$ -bonds of O<sub>2</sub> are independent unpaired electrons. Static correlation can be formally included in a system through the multireference technique of complete active space-self consistant field (CASSCF). We subtract the electron density ( $\rho$ ) of the <sup>3</sup>Σ<sup>-</sup> of O<sub>2</sub> where its active space is expanded to include its  $\pi$ -bonding orbitals, (6,4), relative to a twoconfiguration description used in its HDvV pair, (2,2). This is illustrated in Figure 6.12 where the colors blue and green denote an accumulation and loss of electron density. Inclusion of the  $\pi$ -bonding orbitals reduces the overlap between the electron densities, thus lowering exchange.



**Figure 6.12.** The electron density of the lowest-lying triplet state of the CASSCF(6,4) wavefunction of  $O_2$  with respect to its CASSCF(2,2) active space.

Mulliken interpreted the absorbance spectrum of  $O_2$  in 1928 with molecular orbital (MO) theory that he had previously developed with Hund.<sup>31</sup> The proper assignment of the triplet ground state of  $O_2$ provided an important validation of MO theory. The MO diagram is provided in Figure 6.13 and illustrates that the  $\pi^*$ -antibonding orbitals of  $O_2$  are singly occupied. Because the energies of the  $\pi^*$ antibonding orbitals of  $O_2$  are degenerate the state of higher multiplicity is the electronic ground state that is consistant with Hund's first rule. While the energy expressions of the  $M_s = 1$  and  $M_s = 0$  triplet state are equivalent, the spin function of the  $M_s = 0$  state does not permute.<sup>32</sup> While MO theory is rooted in spectroscopy it systematically underestimates the transition energy of the lowest-lying singlet state of O<sub>2</sub> by a factor of two.

The singlet biradical states of  $O_2$  cannot be defined by single-determinant, real wavefunctions that are the basis of density functional and Hartree-Fock theory. The energy expressions of the  $M_s = 1$  and  $M_s = 0$  states provided below. The  $M_S = 1$  state is stabilized by a single exchange interaction, underestimating the excitation energy by a factor of two. As we have previously detailed, the spin state energetics obtained from single-reference methods can be systematically improved by scaling with respect to the change in exchange interactions <sup>33–35</sup> This procedure strictly applies to unpaired electrons that conform with Hund's first rule; its accuracy ultimately dependent on the suitability of the exchange functional employed.



**Figure 6.13.** The molecular orbital (MO) diagram of the equilibrium geometry of  $O_2$  from the CASSCF(8,6) wavefunction.

$$\frac{1}{\pi_{x}^{*}} \frac{1}{\pi_{y}^{*}}$$

Figure 6.14. The electronic configuration of the  $M_s = 1$  state of a DFT or Hartree-Fock wavefunction.

(Eq. 6.39) 
$$\psi_{M_s=1} = [\phi_a(1)\phi_b(2)][\alpha(1)\alpha(2)]$$
  
(Eq. 6.40)  $E_{M_s=1} = h_{aa} + h_{bb} + J_{ab} - K_{ab}$   
 $\frac{4}{\pi_x^*} \frac{1}{\pi_y^*}$ 

Figure 6.15. The electronic configuration of the  $M_s = 0$  state of a DFT or Hartree-Fock wavefunction.

(Eq. 6.41)  $\Psi_{M_s=0} = [\phi_a(1)\phi_b(2)][\alpha(1)\beta(2)]$ (Eq. 6.42)  $E_{M_s=0} = h_{aa} + h_{bb} + J_{ab}$ (Eq. 6.43)  $\Delta E_{(M_s=1 - M_s=0)} = -K_{ab}$ (Eq. 6.44)  $\Delta E_{T-S_2} = 2\Delta E_{M_c=1-M_c=0}$ 

We briefly illustrate the ability of DFT to treat different spin states using the excited states of  $O_2$  as a model. We strictly consider the TPSSh hybrid-DFT functional that has been prescribed for complex magnetic systems that include spin-crossover complexes<sup>38</sup> and enzymatic clusters<sup>39</sup>. TPSSh underestimates the ferromagnetic coupling in  $O_2$ , assigning a <sup>1</sup> $\Delta$  excited state of 0.36 eV. Our few-determinant DFT procedure improves its performance and provides a 0.72 eV excitation energy. This finding is surprising because hybrid-DFT functionals are routinely cited to *over stabilize* the high spin state in spin crossover complexes.<sup>40,41</sup> This has been attributed to overestimating metal-centered exchange interactions or increasing charge transfer in the description of the metal-ligand bond.<sup>42</sup>The equation for the TPSSh functional is provided below.<sup>43,44</sup>

(Eq. 6.45) 
$$E_{xc}^{TPSSh} = aE_x^{exact} + (1-a)E_x^{TPSS} + E_c^{TPSS}$$

TPSSh is classified as a hybrid-DFT functional because it contains a fractional amount (a) of Hartree-Fock exact exchange ( $E_x^{exact}$ ) in addition to a DFT exchange functional ( $E_x^{TPSS}$ ). In Figure 6.16 we

graph the  ${}^{1}\Delta_{g}$  excitation energy of O<sub>2</sub> as a function of the a-variable. A direct linear relationship is observed that suggests that an a-variable of 0.50 for TPSSh would reproduce the observed excitation energy of O<sub>2</sub>. A similar trend has been reported for the B3LYP functional with respect to Fe<sup>2+</sup> spin state energetics.<sup>45</sup> We similarly integrated the explicit electron-electron terms associated with the singly occupied  $\pi^*$ -orbitals of O<sub>2</sub> for a range of a-parameter values. These terms are largely invariant suggesting the excitation energy is not changing due to greater Fermi or static correlation between unpaired electrons.



**Figure 6.16.** The  ${}^{1}\Delta_{g}$  excited state energy of O<sub>2</sub> calculated with our detailed FD-DFT and HDvV-PP procedure with respect to the TPSSh hybrid-DFT functional with a variable fractional amount of Hartree-Fock exact exchange.

## 6.4.2 Antiferromagnetic Coupling

Extending our discuss to ozone. The dominant resonance structures of ozone (O<sub>3</sub>) are presented in the GVB diagram in Figure 6.17.<sup>46</sup> We direct our focus on the biradical electronic configuration that has been shown as a lead component of its electronic ground state.<sup>47–52</sup> O<sub>3</sub> is distinct from the other allotropes of oxygen because it possesses a singlet (<sup>1</sup>A<sub>1</sub>) ground state that is stabilized by approximately 1.2 eV with respect to its triplet (<sup>3</sup>B<sub>2</sub>) excited state.<sup>53,54</sup> We will detail how nonorthogonal orbitals can expand upon Hund's first rule, rather than invalidate it, to account for antiferromagnetic systems of which O<sub>3</sub> is representative.<sup>55</sup>



**Figure 6.17.** The GVB diagrams of the resonance structures of the three-center four-electron  $\pi$ -bond of O<sub>3</sub>.

 $O_3$  is described as a three-center four-electron  $\pi$ -bond whose respective nonbonding and antibonding orbitals are shown in Figure 6.18. The coulomb potential is concentrated where the charge densities of the central oxygen  $\pi$ -lone pair and the  $\pi$ -radicals of the singly occupied oxygen atoms overlap. The J<sub>ab</sub> potential is shown in Figure 6.18 and its integral is equal to 13.60 eV. The one-center coulomb potentials, J<sub>aa</sub> and J<sub>bb</sub>, are also provided. We refer to the difference between the two-center coulomb integral and the average of the one-center coulomb integrals as K<sub>J</sub> that is detailed in the figure below. The exchange potential is concentrated on the  $\pi$ -orbitals of the terminal oxygen atoms that illustrates areas where both unpaired electrons are localized. The exclusion principle requires that for two electrons to occupy separate orbitals at the same location their spins must be parallel and are referred to as coextensive.<sup>56</sup>

Because the S<sub>1</sub> and S<sub>3</sub> states have the same ( $\pi$ ) symmetry they are coupled. The resonance between S<sub>1</sub> and S<sub>3</sub> makes a state that is stabilized (S<sub>-</sub>) and destabilized (S<sub>+</sub>) with respect to their average energies. The energy expressions for the S<sub>-</sub> and S<sub>+</sub> states are provided in Eq. 6.46 and Eq. 6.49. The electronic coupling (H<sub>12</sub>) between the pure singlet states is equal to the exchange integral, K<sub>ab</sub>. The magnitude of the resonance is also dependent on the energy difference between the pure singlet states ( $\Delta$ ). The collected integrals assign O<sub>3</sub> a singlet ground state that is stabilized by 0.60 eV. Our HDvV-SO method accurately reproduces the sign and magnitude of magnetic interactions.

(Eq. 6.46) 
$$E_{S_{\pm}} = \frac{(H_{11}+H_{22}) \pm \sqrt{(H_{11}-H_{22})^2 + 4H_{12}^2}}{2}$$
  
(Eq. 6.47)  $\sum = 2h_{aa} + 2h_{bb} + J_{aa} + J_{bb}$   
(Eq. 6.48)  $\Delta = 2(\epsilon_{aa} - \epsilon_{bb}) + (J_{aa} - J_{bb})$   
(Eq. 6.49)  $E_{S_{\pm}} = \frac{\sum \pm \sqrt{\Delta^2 + 4K_{ab}^2}}{2}$ 

We reference the energy of the triplet state  $(E_T)$  with respect to the singlet ground state  $(E_S)$ . An antiferromagnetic interaction is observed if the proportionality in Eq. 6.50 is valid.

(Eq. 6.50) 
$$\Delta > 2\sqrt{K_J(K_J + K_{ab})}$$
  
(Eq. 6.51)  $K_J = J_{ab} - \frac{J_{aa} + J_{bb}}{2}$ 

The pair-coefficients,  $c_1$  and  $c_2$ , are solved variationally with respect to the lowest energy singlet state. The pair coefficients are normalized and related to the orbital overlap that is detailed in Eq. 6.52-Eq. 6.56. Orbitals that have larger overlap will have stronger antiferromagnetic coupling whose limit is descriptive of a covalent bond. We can convert the orthogonal natural orbitals into their corresponding non-orthogonal, GVB, orbitals based on their pair-coefficients that is detailed in Eq. 6.57 and Eq. 6.58. The resulting GVB orbitals in Figure 6.19 show the resonance of the three-center four-electron  $\pi$ -bond of O<sub>3</sub>. The corresponding overlap functional show that the GVB orbitals are inphase (pink) on the terminal oxygen atoms and out-of-phase (green) at the  $\pi$ -lone pair of the central oxygen. Because the Pauli principle requires that the unpaired electrons are orthogonal to the  $\pi$ -lone pair they are made non-orthogonal to each other. This is known as a 'through-bond' interaction that classifies the  $\pi$ -lone pair as an 'antiferromagnetic coupling unit'.<sup>30,57,58</sup>



Figure 6.18. (top) The CASSCF(12,10) natural orbitals of O<sub>3</sub>. (bottom) The potentials plotted on their respective densities for J<sub>ab</sub>, J<sub>aa</sub>, J<sub>bb</sub>, and K<sub>ab</sub>. The value of the integral is included in parenthesis.



Figure 6.19. (top) The HDvV-SO orbitals that are transformed from the CASSCF(12,10) natural orbitals of O<sub>3</sub>. The overlap between the non-orthogonal HDvV-SO orbitals is included in parenthesis. (bottom) The overlap function of the non-orthogonal HDvV-SO orbitals above where pink and green refer to a positive and negative interference.

(Eq. 6.52) 
$$\gamma = \frac{E_{\text{S}} - H_{11}}{H_{12}}$$
  
(Eq. 6.53)  $c_1 = \frac{1}{\sqrt{1 + \gamma^2}}$   
(Eq. 6.54)  $c_2 = \frac{\gamma}{\sqrt{1 + \gamma^2}}$   
(Eq. 6.55)  $c_1^2 + c_2^2 = 1$ 

-

(Eq. 6.56) 
$$S = \frac{c_1 - c_2}{c_1 + c_2}$$
  
(Eq. 6.57)  $\phi_x = \frac{\sqrt{c_1}\phi_a + \sqrt{c_2}\phi_b}{\sqrt{c_1 + c_2}}$   
(Eq. 6.58)  $\phi_y = \frac{\sqrt{c_1}\phi_a - \sqrt{c_2}\phi_b}{\sqrt{c_1 + c_2}}$ 

#### 6.4.3 Bond Dissociation of O<sub>3</sub>: 4-electron Case

We consider the change in the magnetic interactions of O<sub>3</sub> associated with its bond dissociation. The photodissociation of ozone occurs from 220-310 nm, the Hartley band, that is principally responsible for the absorbance of harmful UV-radiation.<sup>59,60</sup> The products are O<sub>2</sub> and atomic oxygen that have four unpaired electrons. There are two spin eigenfunctions for four electrons to adopt a singlet state. The Y<sub>1</sub> and Y<sub>2</sub> states are illustrated in the Tableau Diagrams of Figure 6.20 where ferro- and antiferromagnetic interactions are represented with a vertical and horizontal arrangement of oneelectron wavefunctions, respectively.<sup>61</sup> The Y<sub>1</sub> spin eigenfunction is made with the singlet-coupling between a set of non-orthogonal orbitals whose overlap is described by the pair-coefficients c<sub>1</sub> and c<sub>2</sub> ( $\sigma$ -) and c<sub>3</sub> and c<sub>4</sub> ( $\pi$ -type). The Perfect Pairing model only considers the contribution of the Y<sub>1</sub> spin eigenfunction to describe the singlet state. The Y<sub>2</sub> spin eigenfunction describes the antiferromagnetic arrangement between the triplet-coupled electrons centered on both O<sub>2</sub> and O that is illustrated in Figure 6.20. The Strongly Orthogonal model optimizes the contribution of the Y<sub>1</sub> and Y<sub>2</sub> states with the respective spin-coefficients  $\varepsilon_1$  and  $\varepsilon_2$ . There is a large deviation between the GVB-PP and GVB-SO model at distances intermediate of bond dissociation and formation.<sup>28,29</sup>

(Eq. 6.59)

$$Y_{1} = \frac{1}{\sqrt{4}} \begin{bmatrix} \alpha(1)\beta(2)\alpha(3)\beta(4) - \alpha(1)\beta(2)\beta(3)\alpha(4) - \beta(1)\alpha(2)\alpha(3)\beta(4) \\ + \beta(1)\alpha(2)\beta(3)\alpha(4) \end{bmatrix}$$

(Eq. 6.60)

$$Y_{2} = \frac{1}{\sqrt{12}} [2\alpha(1)\alpha(2)\beta(3)\beta(4) - \beta(1)\alpha(2)\beta(3)\alpha(4) - \alpha(1)\beta(2)\beta(3)\alpha(4) - \alpha(1)\beta(2)\alpha(3)\beta(4) + 2\beta(1)\beta(2)\alpha(3)\alpha(4) - \beta(1)\alpha(2)\alpha(3)\beta(4)]$$



Figure 6.20. The GVB diagrams and spin-eigenfunctions in the form of a Tableau diagram for the singlet states of a four-electron system.

$$\begin{aligned} (\text{Eq. 6.61}) \quad \psi_{\text{GVB-SO}} &= \varepsilon_1 \{ \left[ c_1 \phi_a(1) \phi_a(2) - c_2 \phi_b(1) \phi_b(2) \right] \left[ c_3 \phi_c(1) \phi_c(2) - c_4 \phi_d(1) \phi_d(2) \right] \} + \\ &= \varepsilon_2 \{ \left[ \left( \phi_a(1) \phi_b(2) - \phi_b(1) \phi_a(2) \right] \left[ \phi_c(1) \phi_d(2) - \phi_d(1) \phi_c(2) \right] \} \right] \\ (\text{Eq. 6.62}) \quad \psi_{\text{GVB-SO}} &= A_1 \left[ \phi_a(1) \phi_a(2) \phi_c(3) \phi_c(4) \right] + A_2 \left[ \phi_a(1) \phi_a(2) \phi_d(3) \phi_d(4) \right] \\ &+ A_3 \left[ \phi_b(1) \phi_b(2) \phi_c(3) \phi_c(4) \right] + A_4 \left[ \phi_b(1) \phi_b(2) \phi_d(3) \phi_d(4) \right] + A_5 \left[ \phi_a(1) \phi_b(2) \phi_c(3) \phi_d(4) \right] \\ &= (\text{Eq. 6.63}) \quad A_1 = c_1 c_3 \varepsilon_1 \\ &= (\text{Eq. 6.64}) \quad A_2 = -c_1 c_4 \varepsilon_1 \\ &= (\text{Eq. 6.65}) \quad A_3 = -c_2 c_3 \varepsilon_1 \\ &= (\text{Eq. 6.66}) \quad A_4 = c_2 c_4 \varepsilon_1 \\ &= (\text{Eq. 6.67}) \quad A_5 = \varepsilon_2 \\ &= (\text{Eq. 6.68}) \quad c_1 = \sqrt{\frac{A_1^2}{A_1^2 + A_3^2}} = \sqrt{\frac{A_2^3}{A_2^2 + A_4^2}} \\ &= (\text{Eq. 6.69}) \quad c_2 = \sqrt{1 - c_1^2} \\ &= (\text{Eq. 6.70}) \quad c_3 = \sqrt{\frac{A_1^2}{A_1^2 + A_2^2}} = \sqrt{\frac{A_3^3}{A_3^2 + A_4^2}} \end{aligned}$$

(Eq. 6.71) 
$$c_4 = \sqrt{1 - c_3^2}$$
  
(Eq. 6.72)  $c_4 = \sqrt{\frac{A_2^2}{A_1^2 + A_2^2}}$   
(Eq. 6.73)  $\varepsilon_1 = \frac{A_1}{c_1 c_3} = \frac{A_2}{c_1 c_4} = \frac{A_3}{c_2 c_3} = \frac{A_4}{c_2 c_4}$   
(Eq. 6.74)  $\varepsilon_2 = \sqrt{1 - \varepsilon_1^2}$ 

The spin and pair-coefficients are combined to make spin-pair coefficients in the SO-GVB framework that are detailed in Eq. 6.61 and Eq. 6.62. The spin-pair coefficients are obtained from the coefficients of the lowest-energy singlet state of the corresponding CAS(4,4) wavefunction. We plot the fractional contribution of the  $Y_1$  and  $Y_2$  states to the total wavefunction as a function of distance in Figure 6.21. The  $Y_2$  spin eigenfunction is a significant feature of the bond dissociation process. This second configuration stabilizes the singlet state but lowers the overlap between the non-orthogonal orbitals. We include the overlap functionals at a range of separations for the  $\pi$ -type bonding interaction that are collected in Figure 6.22. At large distances, the  $\pi$ -orbital of atomic oxygen is out-of-phase with that of  $O_2$ . This is consistant with the  $Y_2$  state where the oxygen-centered electrons are triplet-coupled. This orbital illustrates a  $\pi$ -bonding interaction with the adjacent oxygen atom at intermediate separations. This is distinct from the antiferromagnetic coupling between the terminal oxygen atoms that we detailed for the equilibrium geometry above.

#### 6.5 Conclusion

We use the different multiplet states allotropes of oxygen to develop our HDvV-SO method that provides qualitative and quantitative insight to discrete electron-electron interactions. This provides a method to calculate the electron-electron coulomb and exchange integrals. The corresponding energy expressions reproduce the sign and magnitude, ferro- or antiferromagnetic, for discrete electronelectron interactions. The energies give the variational coefficients that are associated with the overlap between an electron pair.



**Figure 6.21.** The weighted coefficient for the  $Y_1$  and  $Y_2$  singlet spin eigenfunctions as a function of distance between  $O_2$  and O.



**Figure 6.22.** The two GVB-SO orbitals and overlap functional for the  $\pi$ -bonding interactions between a fragment of O<sub>2</sub> and atomic oxygen. The closest distance between O<sub>2</sub> and O are provided with their orbital overlap in parenthesis.

Our current interest is the qualitative insight provided with the visualization of the potential associated with the coulomb and exchange integrals and the integrand of the overlap functional. The variational coefficients can also be used to change orthogonal natural orbitals to non-orthogonal GVB-orbitals. Because our method treats electron-electron interactions in pairwise terms it can be extended to systems irrespective of the total spin. This is unique from usual DFT-based Broken-Symmetry

methods that treat the cumulative impact of competing magnetic interactions on the relative energies of the state of largest and smallest multiplicity. Extending from magnetism, this provides new descriptors for chemical bond breaking processes.

The input required for our procedure is a single-occupied molecular orbital in the format of a Gaussian cube. The computational time is proportional to the density of the Gaussian cube and the number of electron-pairs rather than the total number of electrons. The corresponding auxiliary quantum chemistry code can be implemented with any electronic structure software package. We are confident that our procedure can further extend to more complex chemical systems whose size would typically prohibit multi-reference calculations.

#### 6.6 Experimental

The following calculations were performed with the ORCA 4.1 electronic structure software package.<sup>62</sup> The literature values for the geometries of  $O_2$  and  $O_3$  were used.<sup>58</sup> The reported CASSCF electronic structure calculations were performed with the aug-cc-pVTZ basis set.<sup>63</sup> The final energies for the excited states were obtained with the NEVPT2 technique with the same active space and conditions.<sup>64–66</sup> The spin-pair coefficients for the bond dissociation of  $O_3$  were obtained from the CASSCF(12,9) optimization of the lowest-lying doublet state.

For atomic oxygen an active space of (6, 4) active space was used that consisted of the 2s and 2p orbitals.

For O<sub>2</sub> we implemented the following active spaces for the CASSCF wavefunctions:

(2, 2): The singly occupied  $\pi^*$ -orbitals.

(6, 4): The bonding and anti-bonding combination of the doubly degenerate  $\pi$  and  $\pi^*$  orbitals

(8,6): The bonding and anti-bonding combination of the doubly degenerate  $\pi$  and  $\pi^*$  orbitals and the  $\sigma$  and  $\sigma^*$  orbitals.

For  $O_3$  an active space of (12,9) was used that has been previously detailed by Ruedenberg.<sup>67</sup> The HDvV-SO integrals were calculated with the orbitals from the CASSCF wavefunction. This corresponded to the (8,6) active space for  $O_2$ . The integrals and surfaces were calculated with a 50x50x50 grid size that were generated using in-house FORTRAN codes.

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# Chapter 7 Doublet Ground State in a Vanadium(II) Complex: Redox and Coordinative Noninnocence of Tripodal Ligand Architecture<sup>4</sup>

# 7.1 Outlook

We report on the geometric and electronic structures of a series of V<sup>2+/3+</sup> redox-noninnocent trenbridged iminopyridine complexes that we respectively refer to as  $[V(py)_3 tren](OTf)_2$  (1-H), [V(py)] $_3$ tren](OTf)<sub>3</sub> (2-H), and [V(5-CO<sub>2</sub>Me-py)<sub>3</sub>tren](OTf)<sub>2</sub> (1-CO<sub>2</sub>Me). The ester-appended complex 1-**CO<sub>2</sub>Me** possesses a doublet ( $M_s = 1/2$ ) electronic ground state that is unprecedented for a nominally 3d<sup>3</sup>-system, owing to electron transfer between metal and ligand, that classifies as valence tautomerism. While 1-H is an octahedral coordination complex, both 2-H and 1-CO<sub>2</sub>Me display capped octahedral geometries in their crystallographic structures, forming a seventh coordinate covalent bond with the tren scaffold. To help understand this inversion in spin state we present a new visualization method that we refer to as the Heisenberg-Dirac-van Vleck-Strongly Orthogonal (HDvV-SO) model that allows quantification of the discrete electron-electron interactions, focusing on exchange, that dictate excited state energies in open-shell systems. We attribute the doublet ground state to several factors: (i) strong metal-ligand  $\pi$ -covalency that lowers the exchange stabilization of the anticipated quartet ground state that is detailed for 1-H; (ii) hypervalency with the bridgehead nitrogen of the tren-scaffold for a  $V^{3+}$  oxidation state that is detailed with respect to 2-H; and (iii) iminopyridine redox non-innocence of  $1-CO_2Me$ , the resulting antiferromagnetic coupling providing resonance stabilization to the doublet state.

#### 7.2 Division of Labor

The following Chapter was a collaborative effort. The computational work was done by Justin P. Joyce. The experimental work was done by Romeo I. Portillo.

<sup>&</sup>lt;sup>4</sup> This chapter has been submitted, in part, as a manuscript to *Inorganic Chemistry*: Joyce, J.P.<sup>‡</sup>; Portillo, R.I.<sup>‡</sup>; Shores, M.P.; Rappé, A.K. *Submitted*.

# 7.3 Introduction

Growing efforts have been directed towards the integration of first-row transition metal ions into photocatalytic processes that are traditionally associated with precious congeners.<sup>1–10</sup> Earth-abundant coordination complexes strain confinement by the chemical properties of their noble-metal analogues. Attributable to the weakened covalency of their metal-ligand bonds, 3d complexes possess many low-lying excited states that can have distinct electronic spin multiplicities. While these near-degenerate states are advantageous with respect to molecular magnetism<sup>11–14</sup>, they convolute direct mechanistic pathways for catalytic transformations.<sup>15–24</sup> Octahedral Cr<sup>3+</sup> polypyridyl complexes have been demonstrated to facilitate photocatalytic and photoredox processes.<sup>25–29</sup> The low-lying <sup>2</sup>E excited state of d<sup>3</sup> complexes is classified as a spin-flip transition whose energy is approximately independent of ligand field strength, but proportional to the interelectronic repulsion between its metal-centred electrons.<sup>30,31</sup> Reducing the interelectronic repulsion, *via* metal-ligand covalency, has been recently demonstrated by Wenger and Piaguet as a robust design principle to impact the energy of the <sup>2</sup>E state of a Cr<sup>3+</sup> complex.<sup>32</sup> The ability to modulate the energetics amongst the densely populated excited state manifolds of first-row transition metals are critical to their success in catalysis.

Despite potential environmental advantages, photocatalysis has not been extended to the isoelectronic (d<sup>3</sup>) V<sup>2+</sup>analogue due to greater  $\pi$ -bonding with its polypyridyl ligand set.<sup>33–35</sup> With these principles in mind, we report the observation of an inversion between the quartet ground and doublet excited state typical for d<sup>3</sup> transition metal systems.<sup>36–38</sup> This inversion occurs in a V<sup>2+</sup> treniminopyridine system whose ligand environment stabilizes the low-spin state through several dramatic changes in the covalency of the system that are illustrated in Figure 7.1 and detailed as Results and Discussion. Our system provides a unique opportunity to directly characterize the catalytically relevant doublet state of 3d<sup>3</sup> complexes that has only previously been accessible through transient spectroscopic and computational techniques.<sup>38–41</sup> Herein, we combine spectroscopic and theoretical methods to address the unique electronic and geometric structures of our vanadium tripodal complexes. We present a model that provides visual and quantitative insight to the discrete electron-electron interactions of open-shell systems. This Heisenberg-Dirac-van Vleck-Strongly Orthogonal (HDvV-SO) model cultivates an understanding through 3D graphics of the structural properties that impact the energy of spin-flip excited states. This has been a recent focus of d<sup>2</sup> and d<sup>3</sup> transition metal systems<sup>6,43-47</sup> Our approach is a natural extension of the General Valence Bond (GVB) treatment of small open-shell molecules developed by Goddard and Bobrowicz<sup>48–50</sup> and finding further articulation with research from Dunning and Cooper.<sup>51–53</sup> Our HDvV-SO model can be extended to systems irrespective of the total number of unpaired electrons or competing magnetic interactions that provides new insight to the root causes of ferro- and antiferromagnetic coupling.



**Figure 7.1.** The illustrated geometric structures, chosen notation and abbreviations, and multiplicities of the three vanadium tren-iminopyridine complexes detailed in our report.

# 7.4 Results and Discussion

# 7.4.1 $V^{2+}$ -Iminopyridine: Metal-Ligand, $\pi$ -Covalency

Firstly, we detail the strong metal-ligand  $\pi$ -covalency between the V<sup>2+</sup> metal-centre and the iminopyridine ligand set in complex **1-H**. The subsequent reduction in the interelectronic repulsion between the unpaired electrons on the paramagnetic metal centre decreases the gap between the doublet excited and quartet ground states. This is manifested as a 0.09 eV reduction in exchange with respect to its bipyridyl analogue, that helps facilitate the doublet ground state that we will detail with respect to **1-CO<sub>2</sub>Me**.

Diffraction quality single crystals of **1-H** are obtained by the slow-diffusion of diethyl ether into acetonitrile, and the structure is shown in Figure 7.2. Key bond distances and structural parameters are collected in Table 7.1. The imine and pyridine donor atoms possess near equivalent bond lengths, and structure displays a V<sup>2+</sup>-N<sub>bridge</sub> distance that is intermediate between a coordinate covalent bond and a noncovalent interaction, when scaled with respect to the sum of their covalent radii, R  $\Sigma cov^{-1} = 1.41$ .<sup>54</sup>

The separation between the bridgehead nitrogen (N<sub>bridge</sub>) of the tren scaffold and the transition metal centre is established to be dependent on the oxidation and spin state.<sup>55–60</sup> We have previously reported that the N<sub>bridge</sub> conformation impacts the local electronic structure of its transition metal centre with respect to the photophysics of Cr<sup>3+</sup> and the molecular magnetism of Co<sup>2+</sup> complexes.<sup>61,62</sup> The geometry of the primary coordination sphere is best classified as distorted octahedral by the Continuous Shape Measure (CShM), S(OC-6) = 1.480, which computes the "distance" between idealized and observed structures.<sup>63</sup> This is increased with respect to our previous analysis of the polypyridyl analogue [V(bpy)<sub>3</sub>]<sup>2+</sup> whose DFT-optimized structure has an S(OC-6) of 1.27.<sup>64</sup> This suggests greater metal-ligand  $\pi$ -covalency for the iminopyridine coordination environment because of the loss of degeneracy in the nominally non-bonding t<sub>2g</sub> orbitals as the complex distorts toward a trigonal, *C*<sub>3</sub>-symmetric, environment.



**Figure 7.2.** The experimental molecular structures of **1-H**, **2-H**, and **1-CO<sub>2</sub>Me**, as determined by X-ray crystallography, where hydrogen atoms, anions, and co-crystallized solvent molecules are omitted for clarity. Thermal ellipsoids are set to 40%. Assigned coordination geometries, pertinent bond distances, and interatomic separations (in Å) are provided.

The electronic absorbance spectra of **1-H** and its polypyridyl analogue,  $[V(bpy)_3](OTf)_2$ , are included in Figure 7.3. **1-H** exhibits a broad electronic absorbance at approximately 750 nm that we assign as a metal-to-ligand charge transfer (MLCT). This is consistent with the transition's large molar absorptivity ( $\epsilon$ ).<sup>34,65</sup> The MLCT is red shifted by 0.28 eV with respect to the polypyridyl analogue, that we attribute to greater metal-ligand  $\pi$ -covalency in the iminopyridine ligand set.

The computed electronic ground state of **1-H** is a quartet ( $M_s = 3/2$ ), the <sup>4</sup>A<sub>2</sub> state common for d<sup>3</sup> systems in an octahedral coordination environment.<sup>31</sup> The lowest-lying doublet state is the <sup>2</sup>E that our detailed multi-determinant DFT computation assigns as 0.96 eV above the ground state for **1-H**.<sup>66</sup>

Comparatively, we have reported that  $[V(bpy)_3]^{2+}$  should have a <sup>2</sup>E excited state of 1.10 eV.<sup>64</sup> We reference the spin density of the <sup>2</sup>E of **1-H** to its <sup>4</sup>A<sub>2</sub> ground state in our  $\Delta\rho^{\alpha,\beta}$  plot in Figure 7.4. While the <sup>2</sup>E state is traditionally characterized as a metal-centred spin flip, the  $\Delta\rho^{\alpha,\beta}$  plot shows that it is significantly delocalized onto the iminopyridine ligand set for **1-H**. This is consistent with the greater octahedral distortion and the red shift in the absorbance of the MLCT that we observe in **1-H** with respect to our previous characterization of  $[V(bpy)_3]^{2+.64}$ 



**Figure 7.3.** (*top*) Electronic absorption spectra of **1-H**, **2-H**, and **1-CO<sub>2</sub>Me**, collected in acetonitrile. The corresponding spectrum of  $[V(bpy)_3](OTf)_2^{35}$  is provided as a reference to the impact of the iminopyridine ligand environment. (*bottom*) Orbital energy depiction of the ground and excited states of the  ${}^2({}^3IL)$  transition.

The impact of metal-ligand covalency on the <sup>2</sup>E excited state energy is that it decreases the interelectronic repulsion (*B*) between the singly-occupied metal-centred orbitals.<sup>67–69</sup> The unpaired electrons of the <sup>4</sup>A<sub>2</sub> state of **1-H** occupy orbitals that are orthogonal and nearly degenerate so that Hund's first rule applies.<sup>70–72</sup> The basis for a quartet ground state is the three favourable exchange interactions between parallel electrons (K<sub>ab</sub>), we have detailed elsewhere.<sup>73–75</sup> The Pauli Exclusion principle prohibits electrons of the same spin from

occupying the same location, thus reducing a system's interelectronic repulsion *via* electron correlation. If the unpaired electrons are restricted by symmetry from bonding, then exchange is the sole resource of stabilization.



**Figure 7.4.** (*top*) The electronic configuration of the lowest-lying quartet and doublet state for octahedral d<sup>3</sup> complexes, where the quotation marks denote its singlet-determinant description in the context of DFT. (*bottom*) The APFD spin density of the lowest-lying doublet state of the vanadium complex of **1-H** referenced against its lowest-lying quartet state for our  $\Delta \rho^{\alpha,\beta}$  plot.

7.4.2 Introducing the Heisenberg-Dirac-van Vleck-Strongly Orthogonal (HDvV-SO)

# Model

To visualize the impact of exchange on state energy differences, we present a model that provides 3D-graphical representations of electron-electron interactions that we refer to as the Heisenberg-Dirac-van Vleck-Strongly Orthogonal (HDvV-SO) model. While our current focus is the exchange interactions, our procedure similarly extends to coulombic and more complex interelectronic interactions.  $K_{ab}$  possesses the form of an electrostatic potential (R<sup>-1</sup>) that is detailed in Eq. 7.1. While the coulombic interaction between a pair of electron occurs with their physically measurable charge densities,  $K_{ab}$  is the electrostatic repulsion that occurs in the unmeasurable regions where the orbitals overlap. *Exchange is a classical interaction with a*  *quantum mechanical origin*. Dougherty has previously referred to areas of interference between orbitals as the overlap functional ( $f_{ab}$ ) that is illustrated in Figure 7.5.<sup>76</sup>

(Eq. 7.1) 
$$K_{ab} = \int \int \frac{\phi_a(1)\phi_b(2)\phi_a(2)\phi_b(1)}{R_{12}} dr_1 dr_2$$
  
(Eq. 7.2)  $K_{ab} = \int \int \frac{f_{ab}^2}{R_{12}} dr_1 dr_2$ 

In Figure 7.5 we plot a representative exchange interaction between a pair of singly occupied metalcentred orbitals of **1-H** as an electrostatic potential overlayed on the surface density of the respective  $f_{ab}$ .<sup>77</sup> The exchange interaction is dominantly metal centred because there is little overlap between the respective orbitals where they are delocalized on the ligand set. Here, blue and red coloring refer to areas where the interference between the singly occupied orbitals displays positive and negative coherence, respectively. Because the current orbitals are orthogonal, the amount of in-phase and outof-phase overlap will be equal.

Overall,  $K_{ab}$  is a repulsive interaction whose energetic impact on the system depends on the orientation of the electron spins that is favorable for aligned spins. Metal-ligand  $\pi$ -covalency delocalizes the singly occupied V<sup>2+</sup> orbitals onto the ligand, thus reducing the  $f_{ab}$  overlap functional and the magnitude of their exchange interactions. We note that  $K_{ab}$  can be similarly plotted as a surface density, descriptive of the integrand in Eq. 7.1, providing a quantitative numerical value. Our HDvV-SO model provides both visual and quantitative values for discrete electron-electron interactions. This is distinct from Figure 7.4 in that it illustrates the magnitude of the spin-flip excited state energy and suggests that exchange interactions can be modulated *via* established synthetic principles for metal-ligand covalency.

#### 7.4.3 Hypervalency with Tren Scaffold

Oxidation of **1-H** with silver triflate (AgOTf) produces the V<sup>3+</sup> complex **2-H**. The structure (Figure 7.3) features a seventh coordinate covalent bond, now involving the tertiary amine (N<sub>bridge</sub>) of the tren backbone. Relative to **1-H**, the V- N<sub>bridge</sub> distance for **2-H** contracts by 0.92 Å to 2.228(5) Å, which is

smaller than the sum of their covalent radii, R  $\Sigma cov^{-1} = 0.995(2)$ .<sup>54</sup> As shown in Table 7.1, whereas **1- H** shows relatively equal V-N distances, for **2-H**, significant deviation is apparent in the metal-ligand bond lengths of the imine and pyridine donor atoms.



**Figure 7.5.** (*top*) The two lowest-lying singly occupied molecular orbitals of the vanadium complex of **1-H**. The orbitals are obtained from the corresponding CAS(3,8) wavefunction. (*bottom*) The exchange potential ( $K_{ab}$ ) and the corresponding value between the labelled orbitals obtained with our HDvV-SO model.

Complex 2-H displays the shortest metal-bridgehead nitrogen contact amongst reported tren systems. The structure of 2-H is well-defined by the CShM for capped octahedral geometry, S(COC-7) = 0.791, an arrangement that is favored in tren-containing systems but relatively anomalous in the full catalogue of heptacoordinate complexes.<sup>78</sup> While analogous  $Mn^{2+}$  complex geometries have been assigned as capped octahedral, the separation from the N<sub>bridge</sub> is primarily an impact of crystal packing forces.<sup>79–81</sup> In contrast, as we will outline below, heptacoordination is a source of stability for the d<sup>2</sup> electronic configuration of V<sup>3+</sup>, that will help facilitate the doublet ground state we observe for 1-CO<sub>2</sub>Me.

Heptacoordination can be understood in terms of the hybridization between the metal d-orbitals. Independent of metal identity, the  $\sigma$ -bonding abilities of the five d-orbitals are inequivalent, and greatest for the d<sub>z<sup>2</sup></sub> orbital. In octahedral symmetry the solitary d<sub>z<sup>2</sup></sub> orbital points along a metal-ligand bond axis. Interestingly, the symmetric linear combination of the octahedral non-bonding t<sub>2g</sub> orbitals (d<sub>xz</sub>, d<sub>yz</sub>, and d<sub>xy</sub>) forms a hybridized orbital of pure d-orbital and  $\sigma$ -symmetry character along a 3-fold octahedral axis, facilitating hypervalency. We refer to this orbital as d<sub> $\sigma$ </sub> and a plot of it is shown in Figure 7.6.<sup>82,83</sup> We can consider the strength of the hypervalent metal-ligand bond involving d<sub> $\sigma$ </sub> using principles of orbital orthogonality that stem from the classic work of Pauling, and later refined by Landis.<sup>84–88</sup> Eq. 7.3 details the overlap between the d<sub> $\sigma$ </sub> and d<sub>z<sup>2</sup></sub> orbital based on the angle between the seventh ligand and the adjacent metal-ligand bond.

(Eq. 7.3) 
$$S_{12} = \left| \frac{3\cos^2 \theta - 1}{4} \right|$$

At an angle of 54.7° the orbitals are orthogonal so that the  $d_{\sigma}$  orbital has equivalent bonding properties to the  $d_{z^2}$  orbital.<sup>89</sup> Due to interelectronic repulsion between the metal-ligand  $\sigma$ -bonds, the angle expands to approximately 72° as reported by Hoffmann, Muetterties and co-workers, and illustrated in Figure 7.6.<sup>90</sup> This is consistent with the structure of **2-H** that displays an average  $\angle N_{bridge}$ -V-N<sub>imine</sub> bond angle of 71.5(3)° corresponding to an S<sub>12</sub> value of 0.35. To maintain orthogonality, these angular distortions are accompanied by a rehybridization of the nominally nonbonding t<sub>2g</sub> orbitals so that we define the covalency of the d<sub> $\sigma$ </sub> orbital as the deviation in overlap from unity that we refer to as  $\Delta_3$ . This posits that the strength of the hypervalent V-N<sub>bridge</sub> bond of **2-H** is a factor of 0.65 with respect to the remaining metal-ligand  $\sigma$ -bonds of the octahedral coordination environment.

The ligand field transitions of the electronic absorbance spectrum of **2-H** are centred at 774 nm and 506 nm, and illustrated with our previously detailed Natural Transition Spin Density ( $NT\rho^{\alpha,\beta}$ ) plots in Figure 7.7.<sup>64</sup> These ligand field transitions are descriptive of the *C*<sub>3</sub>-symmetry of the tripodal scaffold

that reduces the three-fold degeneracy of  $t_{2g} \rightarrow e + a_1^*$ . This reduction in symmetry shifts the reference energy (barycenter) of the complex, stabilizing the lower- and upper-lying e-orbitals. The difference in energy between the  $d_{\sigma}(a_1^*)$  and lowest-lying e-orbitals relative to the octahedral ligand field splitting is equal to our  $\Delta_3$  parameter as shown in Eq. 7.4.



**Figure 7.6.** (*top*) The symmetric hybridization between the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals that constitute the  $t_{2g}$  set with respect to an octahedral coordination environment. This generates a  $d_{\sigma}$  orbital that is equivalent to the  $d_{z2}$  orbital but rotated 54.7° along its nodal zone. (*bottom*) The rehybridization of the  $d_{\sigma}$ -orbital from the ideal bond angle of 54.7° to the experimental bond angle of 72.0° to remove its area of overlap with the  $d_{z2}$  orbital.

Eq. 7.5 provides the change in ligand field stabilization energy ( $\Delta$ LFSE) associated with a d<sup>n</sup> metal center adopting a capped octahedral geometry with respect to the corresponding octahedral complex. The experimental bond angle for **2-H** of 72° suggests that heptacoordination stabilizes the complex by -2.6 Dq. This converts to a hypervalent bond strength of 14.8 kcal mol<sup>-1</sup> if we assume that contraction of the bridgehead nitrogen strictly impacts the energy of the  $a_1^*$  orbital. The experimental ligand field transition of  $a_1^* \leftarrow e$  suggests that coordination of the bridgehead nitrogen stabilizes **2-H** by an identical value of 14.8 kcal mol<sup>-1</sup> that provides validation to our current structural model. Comparatively, a capped octahedral geometry is not anticipated for **1-H** because the d<sub> $\sigma$ </sub> orbital is populated, heptacoordination destabilizes the complex by +2.6 Dq.



**Figure 7.7.** Natural Transition Spin Density  $(NT\rho^{\alpha,\beta})$  plots of the ligand field transitions of the vanadium complex of **2-H** that illustrate the loss-of-degeneracy associated with heptacoordination with the tren-scaffold.

(Eq. 7.4) 
$$1 - S_{12} = \left(\frac{a_1^* \leftarrow e}{e^* \leftarrow e}\right) = \Delta_3$$
  
(Eq. 7.5)  $\Delta LFSE (Dq) = 2\Delta_3 [4N(a_1^*) - N(e^*) - N(e)]$ 

Electrochemical experiments further support stabilization from oxidation-activated hypervalency. The cyclic voltammogram of **1-H** in Figure 7.8 displays a reversible 3+/2+ oxidation at -0.51 V vs Fc<sup>+</sup>/Fc<sup>0</sup> in CH<sub>3</sub>CN, along with ligand reductions at -1.09 V, -1.64 V, and -1.98 V vs Fc<sup>+</sup>/Fc<sup>0</sup>. Compound **2-H** displays identical redox properties except that the 3+/2+ couple lacks reversibility. This difference suggests a considerable reorganization of **2-H** between the two oxidation states, consistent with a change in coordination number. The corresponding V<sup>2+</sup> bipyridine complex exhibits an  $E_{1/2}(3+/2+)$  of 0.08 V which suggests the tren-scaffold stabilizes the V<sup>3+</sup> oxidation state by 0.59 eV, in agreement with the  $\Delta$ LFSE values calculated above. It is interesting to note that the same trend in the electrochemical reversibility of the  $E_{1/2}(3+/2+)$  value based on coordination geometry has been previously reported in characterizing spin-labile Fe<sup>2+</sup> tren-iminopyridine complexes.<sup>91,92</sup>



**Figure 7.8.** Cyclic voltammograms (0.1 V sec<sup>-1</sup>) of the cathodic reduction potentials for **1-H**, **2-H**, **1- CO<sub>2</sub>Me** and  $[V(bpy)_3](OTf)_2^{35}$ . The experiment was performed 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN.

For the vanadium complexes reported herein, *hypervalency is a redox-mediated process*. The transition between OC-6 and COC-7 has not been previously reported. While spin-labile Fe<sup>2+</sup> complexes will exhibit a contraction of the tren-scaffold when undergoing a low- to high-spin transition, the Fe-N<sub>bridge</sub> separation does not approach the sum of their covalent radii.<sup>93,94</sup> Halcrow has previously reported that spin crossover is inhibited in these complexes by deviations in the Fe<sup>2+</sup> -N<sub>bridge</sub> separation that exceed 0.5 Å between spin states.<sup>95</sup> Similar to the above discussion of Mn<sup>2+</sup>, the equilibrium position of the N<sub>bridge</sub> of the tren-scaffold of high-spin Fe<sup>2+</sup> complexes is principally an impact of crystal packing forces.

# 7.4.4 Doublet Ground State in 1-CO<sub>2</sub>Me

Lastly, we detail the roles of heptacoordination, and redox non-innocence play on the formation of an unexpected doublet ground state for **1-CO<sub>2</sub>Me**. For comparison with previously reported tren structures,<sup>79</sup> we installed an ester substituent that is located *meta*- and *para*- with respect to the pyridine and imine donor atoms, respectively, that we refer to as  $[V(5-CO_2Mepy)_3tren](OTf)_2$  (**1-CO<sub>2</sub>Me**). The isovalent Cr<sup>2+</sup> complex displayed redox non-innocence with an iminopyridine moiety that is descriptive of its triplet ground state.<sup>96</sup> We would anticipate this behavior to be more accessible for V<sup>2+</sup> systems because of its smaller ionization potential with respect to  $Cr^{2+}$  (29.31 eV versus 30.96 eV). In addition, heptacoordination recuperates some of the loss of LFSE associated with removing an electron from a  $t_{2g}$  orbital.

In agreement, the crystal structure of **1-CO<sub>2</sub>Me** in Figure 7.2 displays structural properties that are consistent with a V<sup>3+</sup> species, rather than a V<sup>2+</sup>, oxidation state (Table 1). The V-N<sub>bridge</sub> separation of **1-CO<sub>2</sub>Me** is 2.213(9) Å, equal to 0.988(4)  $R \Sigma \text{cov}^{-1}$ . CShM classifies **1-CO<sub>2</sub>Me** as a capped octahedral geometry where *S*(COC-7) is equal to 0.908 and more distorted than **2-H**.

The anticipated  $C_3$ -symmetry is not observed for **1-CO<sub>2</sub>Me**, as the V-N<sub>imine</sub> and V-N<sub>pyridine</sub> bond lengths of the trigonal ligand set are inequivalent. Two of the coordinated groups have average V-N<sub>imine</sub> and V-N<sub>pyridine</sub> bond lengths of 2.10(1) and 2.20(4) Å, respectively, that are consistent with a V<sup>3+</sup> metal centre. In those two iminopyridine ligand arms, the C<sub>imine</sub>-C<sub>pyridine</sub> bond distance is 1.42(1) Å. The C<sub>imine</sub>-C<sub>pyridine</sub> bond length of the remaining iminopyridine group contracts from 1.38(2) Å, suggestive of the partial double-bond character that accompanies a one-electron reduction.<sup>97</sup> The N-donor atoms display contracted bond lengths of V-Nimine and V-Npyridine as 1.976(9) Å and 2.112(7) Å, respectively, attributable to greater coulombic attraction between the cationic transition metal centre and anionic ligand radical. The ester substituents are in the plane of the iminopyridine groups,  $\varphi = 14(4)^{\circ}$ , whose  $\pi^*$ - orbitals of the ester functional group are conjugated with that of the aromatic ligand set.

**Table 7.1.** The key metric parameters of detailed vanadium complexes where bond lengths are reported in Å and S(OC-6) and S(COC-7) refer to the SHAPE values for octahedral and capped octahedral coordination geometries, respectively.

	1-H	2-Н	1-CO <sub>2</sub> Me
V-N <sub>bridge</sub>	3.151	2.228(5)	2.213(9)
V-N <sub>imine</sub>	2.127(7)	2.094(4)	2.10(1)
V-(N <sub>imine</sub> ) <sup>-</sup>			1.976(9)
V-N <sub>pyridine</sub>	2.146(5)	2.206(4)	2.20(4)
V-(N <sub>pyridine</sub> ) <sup>-</sup>			2.112(7)
<i>S</i> (OC-6)	1.480	2.503	2.521
<i>S</i> (COC-7)	3.055	0.792	0.943

Collectively, the structural features of  $1-CO_2Me$  are consistent with a V<sup>3+</sup> metal centre resulting from redox non-innocence of an iminopyridine moiety. Literature precedent suggests that the spin centers should be antiferromagnetically coupled resulting in a doublet ground state.<sup>98,99</sup>. To support this spin assignment, we analyzed the magnetic susceptibility of  $1-CO_2Me$  as a function of temperature in Figure 7.9. At low temperatures, the  $\chi_M T$  value gives a minimum value of 0.41 cm<sup>3</sup> K<sup>-1</sup> mol<sup>-1</sup>, suggesting an isotropic S = 1/2 state. This conclusively illustrates that this nominally d<sup>3</sup> system does not possess a quartet ground state. We are surprised to find that the  $\chi_M T$  value increases linearly with temperature above 50 K, inconsistent with the curvature anticipated for (weaker) antiferromagnetic exchange coupling between metal and ligand spin centers. We attribute the linear response to temperature independent magnetism (TIP) that results from second-order Zeeman coupling between the ground and excited states. While the TIP value is 15-20 times larger than is traditionally assigned to representative octahedral Co<sup>3+</sup> complexes,<sup>100</sup> our assignment is consistent with previous reports of Mn<sup>2+/4+</sup>catecholate and Ti<sup>3+</sup> and V<sup>4+</sup> octahedral diimine systems whose anomalous magnetic properties were attributed to trigonal distortion.<sup>101-104</sup> The magnitude of TIP is inversely proportional to the excited state energies. Because of the redox- active transition metal centre and ligand sets, 1-CO2Me has a densely populated excited state manifold. This is detailed with respect to the NEVPT2(3,8) multireference calculations of 1-CO<sub>2</sub>Me.



**Figure 7.9.** Temperature dependence of magnetic susceptibility for a powdered sample of **1-CO<sub>2</sub>Me**, collected with a 1 kOe measuring field.

The UV-Vis spectra of 1-H, 2-H, 1-CO2Me, and our previously detailed polypyridyl analogue, [V(bpy)<sub>3</sub>](OTf)<sub>2</sub>, are collected in Figure 7.3.<sup>34,64</sup> Along with the ligand field transitions detailed above, **2-H** contains a high energy MLCT at 378 nm, consistent with the large ionization energy of the V<sup>3+</sup> ion. The broad peak observed in the near-IR is indicative of a  $\pi^* \leftarrow \pi^*$  transition of a ligand radical that is consistent with the crystallographic structure of **1-CO<sub>2</sub>Me**. Similarly, we assign the absorbance with  $\lambda_{max}$  at 397 nm to the V<sup>3+</sup> MLCT that is red-shifted with respect to the unsubstituted complex, **2-**H.

Interestingly, we find that **1-CO<sub>2</sub>Me** displays spectroscopic signatures that are diagnostic of both  $V^{2+}$  and  $V^{3+}$  formal oxidation states. The intense absorbance at 785 nm resembles the MLCT of **1-H** whose energy is red-shifted by 0.12 eV. We interpret from that data that both the <sup>4</sup>A<sub>2</sub> and crystallographically and magnetically observed <sup>2</sup>MLCT state are present in solution, classifying **1-CO<sub>2</sub>Me** as a valence tautomer. The thermodynamic properties of valence tautomers have been established as being sensitive to the solvent identity, the enthalpy between the states being qualitatively related to solvent polarity while being unobserved in the solid-state.<sup>105–108</sup>

The experimental absorbance at 467 nm is distinct to **1-CO<sub>2</sub>Me**. The corresponding TD-DFT calculation of the doublet excited state manifold assigns this transition to a ligand  $\pi^* \leftarrow \pi$  transition of an unreduced iminopyridine. The low energy of the transition suggests that the excitation is of triplet, rather than singlet, character that is magnetically coupled to the three-electron paramagnetic system. We follow up the TD-DFT study with an NEVPT2(5,5) study to address the multireference character of this transition. The resulting spin eigenfunctions for this excited state suggest that the reduced iminopyridine undergoes a spin flip during the transition that changes its magnetic coupling with the V<sup>3+</sup> metal centre from an antiferromagnetic (<sup>2</sup>MLCT) to a ferromagnetic (<sup>4</sup>MLCT) interaction (Figure 7.3, *bottom*). The <sup>4</sup>MLCT state antiferromagnetically couples with the intraligand transition (<sup>3</sup>IL) resulting in an overall doublet state whose absorbance is spin allowed: we refer to it as <sup>2</sup>(<sup>3</sup>IL).

The cyclic voltammogram of **1-CO<sub>2</sub>Me** shown in Figure 7.8 resembles **1-H** and **2-H**. **1-CO<sub>2</sub>Me** is oxidized at -0.39 V and reduced at -0.73 V vs Fc<sup>+</sup>/Fc<sup>0</sup>. The  $E_{1/2}(3+/2+)$  and  $E_{1/2}(2+/1+)$  redox events of compound **1-CO<sub>2</sub>Me** are 0.12 V and 0.36 V anodic relative to the parent compounds, respectively, which we attribute to the electron-withdrawing properties of the ester substituents. Importantly, the open circuit potential does not sit at the  $E_{1/2}$  of the observed peaks which assures that there is one dominant species in solution and no impurity, such as a di- and tri-cationic reduced-oxidized pair. The  $E_{1/2}(3+/2+)$  redox event displays quasi-reversibility, consistent with the electrochemical behaviour of **2-H**. This suggests that **1-CO<sub>2</sub>Me** maintains the crystallographically-observed capped octahedral geometry in solution. The similar electrochemical properties suggest that the products of both reduction and oxidation of **1-H** and **1-CO<sub>2</sub>Me** are analogous, which is supported by spectroelectrochemistry data. The data suggest that the structural features of **1-H** and **1-CO<sub>2</sub>Me** are attributable to different electronic states of the +2 system, that respectively correspond to the lowest-lying quartet (<sup>4</sup>A<sub>2</sub>) and doublet (<sup>2</sup>MLCT) states of a d<sup>3</sup> system.

#### 7.4.5 Treatment of Multi-electron Antiferromagnetism with the HDvV-SO Model

To understand this complex spin system, we expand upon Hund's first rule and consider that the electronic structure of the <sup>2</sup>MLCT ground state of **1-CO<sub>2</sub>Me** that can be described in local terms as a  $V^{3+}$  (d<sup>2</sup>) metal centre and anionic ligand radical ( $\pi^*$ ).

The metal center's two unpaired electrons and anionic ligand radical occupy non-degenerate orbitals that can be antiferromagnetically coupled, the doublet being lower in energy than the quartet state. Both solid-state and molecular models of antiferromagnetic coupling require overlap between magnetic orbitals.<sup>109–112</sup> Orbital orthogonality is a requirement of most electronic structure methods— spin unrestricted broken symmetry models being the exception.<sup>113–115</sup> The overlap of antiferromagnetic interactions can be accounted for in multi-determinant methods. Multireference NEVPT2(3,8)

calculations suggest that the doublet ground state is stabilized by 0.55 eV with respect to the <sup>4</sup>MLCT state that is equal to a magnetic coupling of  $J = -1480 \text{ cm}^{-1}$ .<sup>116,117</sup>

We describe an antiferromagnetic interaction as a configuration interaction where the metalcentred ( $\phi_a$ ) and an anionic ligand radical ( $\phi_b$ ) orbital are partially occupied. <sup>49,50,118,119</sup> This is detailed in Eq. 7.6 where the coefficients ( $c_1$  and  $c_2$ ) are solved variationally with respect to the lowest energy doublet state. Our HDvV-SO model expands on this conventional description of two electrons<sup>120</sup> by addressing the spin recoupling involving the remaining metal-centred orbital ( $\phi_c$ ).<sup>121</sup> This recoupling is accomplished with a final configuration included in Eq. 7.6 where  $\phi_a$  and  $\phi_b$  are triplet coupled *via* their magnetic interaction with  $\phi_c$ .

(Eq. 7.6) 
$$\psi$$
(SO-GVB) = $\varepsilon_1 [(c_1 \phi_a \phi_a - c_2 \phi_b \phi_b) \phi_c] (\alpha \beta - \beta \alpha) \alpha + \varepsilon_2 [(\phi_a \phi_b - \phi_b \phi_a) \phi_c] (2\alpha \alpha \beta - \alpha \beta \alpha - \beta \alpha \alpha)$ 

The coupling between this configuration and a perfect pairing model is provided by the metaexchange interaction ( $M_c$ ) in Eq. 7.7 and Eq. 7.8. This electron-electron interaction reflects the overlap between the overlap functionals that involve the third unpaired electron ( $f_{ac}$  and  $f_{bc}$ ). If the three orbitals are mutually orthogonal then the energy expression of Eq. 7.6. simplifies to the <sup>2</sup>E excited state energy detailed with respect to **1-H**.

(Eq. 7.7) 
$$M_c = \int \int \frac{\phi_a(1)\phi_c(1)\phi_b(2)\phi_c(2)}{R_{12}} dr_1 dr_2$$
  
(Eq. 7.8)  $M_c = \int \int \frac{f_{ac}f_{bc}}{R_{12}} dr_1 dr_2$ 

For visualization and insight, the two paired orbitals  $\phi_a$  and  $\phi_b$  can be transformed to equivalent overlapping orbitals,  $\phi_x$  and  $\phi_y$ , as detailed in Eq. 7.9-Eq. 7.10. The resulting overlap of  $\phi_x$  and  $\phi_y$  in the HDvV-SO wavefunction is 0.23 that classifies **1-CO<sub>2</sub>Me** as an antiferromagnetic coupling, rather than a covalent bond, between its V<sup>3+</sup> metal centre and anionic ligand radical. Our calculated nonorthogonal orbitals of **1-CO<sub>2</sub>Me** are presented in Figure 7.10 along with their originating orthogonal orbitals of the SCF framework. Our HDvV-SO method assigns an antiferromagnetic coupling of J = -1490 cm<sup>-1</sup> that accurately reproduces the sign and magnitude of the magnetic coupling of **1-CO<sub>2</sub>Me**, the energy expressions being further detailed in Appendix (A 1).

(Eq. 7.9) 
$$\phi_{x} = \frac{\sqrt{c_{1}}\phi_{a} + \sqrt{c_{2}}\phi_{t}}{\sqrt{c_{1} + c_{2}}}$$
  
(Eq. 7.10)  $\phi_{y} = \frac{\sqrt{c_{1}}\phi_{a} - \sqrt{c_{2}}\phi_{b}}{\sqrt{c_{1} + c_{2}}}$   
(Eq. 7.11)  $S = \frac{c_{1} - c_{2}}{c_{1} + c_{2}}$ 

The observance of a doublet electronic configuration as the ground state is unique to **1**-**CO<sub>2</sub>Me** with respect to **1-H**. To help understand this we consider the NEVPT2(3,8) transitions of the quartet optimized geometry of **1-CO<sub>2</sub>Me** which is consistent with a local V<sup>2+</sup>-metal centre, analogous to the crystallographic structure of **1-H**. Based on Cr<sup>3+</sup> complexes we would expect to observe five near-degenerate low-lying doublets that are attributed to the metal-centred <sup>2</sup>E and <sup>2</sup>T<sub>1</sub> states of a d<sup>3</sup> system. However, as previously reported for  $[V(bpy)_3]^{2+}$  we calculate six doublet states that are below approximately 1.5 eV for both **1-H** and **1-CO<sub>2</sub>Me**.<sup>34</sup> The states exhibit significant multireference mixing between the metal-centred and  $\pi^*$ -orbitals that is descriptive of resonance stabilization, or static correlation. Rather than dominantly metal-based states, the doublet excited states exhibit coupling between their metal-centred and charge-transfer states that we refer to as <sup>2</sup>MC/<sup>2</sup>MLCT.<sup>34</sup> The lowest-lying <sup>2</sup>MC/<sup>2</sup>MLCT states of **1-H** and **1-CO<sub>2</sub>Me** are 1.05 and 0.88 eV, respectively.

We also observe a low-lying <sup>4</sup>MLCT state, strongly stabilized by dynamic correlation, that is 1.75 and 0.74 eV for **1-H** and **1-CO<sub>2</sub>Me**, respectively. Heptacoordination with the tren-scaffold and antiferromagnetic coupling with the iminopyridine anionic ligand radical in the doublet ground state geometry should collectively stabilize the doublet configuration by approximately 1.2 eV. These features place the energy of the <sup>2</sup>MLCT excited state below that of the <sup>4</sup>A<sub>2</sub> ground state for **1-CO<sub>2</sub>Me**  which would not be observed in the **1-H** state. Relative to the parent ligand set, we calculate that the 5-CO<sub>2</sub>Me substituent stabilizes the electron affinity of the uncoordinated ligand by -0.58 eV. Rotating the ester substituent so that its  $\pi$ -system is orthogonal to the iminopyridine ligand set diminishes the electron affinity stabilization to -0.18 eV. This suggests that the ester substituent serves as a  $\pi$ -acid that stabilizes the charge transfer state of **1-CO<sub>2</sub>Me**, resulting in its inverted doublet state.

#### 7.5 Conclusions

We have established that the <sup>2</sup>MLCT state is stabilized by a large electron affinity for the methyl ester, strong antiferromagnetic coupling with the anionic ligand radical, and hypervalency with the tren-scaffold. Concurrently, the stability of the ferromagnetic quartet state is lessened due to the delocalization of its metal-centred orbitals, which decreases exchange interactions. Stabilization of the <sup>2</sup>MLCT state is further attributed to the electronic coupling, resonance stabilization, between the doublet metal-centred and charge transfer, <sup>2</sup>MC/<sup>2</sup>MLCT, states. Collectively, these features combine synergistically to invert the ground and excited states for **1-CO<sub>2</sub>Me**, as observed crystallographically, spectroscopically, and magnetically.

States of distinct multiplicities are differentially impacted by resonance. This is foundational to chemistry, the Heitler-London treatment of H<sub>2</sub> assigning resonance, configuration interactions, as the basis of the attractive and dominantly repulsive character of its singlet ( $\alpha\beta$ ) and triplet ( $\alpha\alpha$ ) states, respectively.<sup>122</sup> While intuitive for a covalent bond, resonance in the ground states of paramagnetic coordination complexes are relatively obscured. The stability of the high-spin state for **1-CO<sub>2</sub>Me** predicted from Hund's first rule is complicated by non-degenerate and non-orthogonal orbitals that possess competing magnetic interactions.<sup>123</sup> Herein, we uncover a unique phenomenon where resonance stabilization causes an inversion of the ground (M<sub>S</sub> = 3/2) and excited (M<sub>S</sub> = 1/2) state of a V<sup>2+</sup> (d<sup>3</sup>) transition metal complex.



**Figure 7.10.** The singly occupied orbitals descriptive of the antiferromagnetic coupling of the vanadium complex in **1-CO<sub>2</sub>Me**. This is presented as an orthogonal bonding and anti-bonding orbital combination in the top of the Figure with respect to the CASSCF(3,3) wavefunction. Eq. 7.9 and Eq. 7.10 transforms the orbitals above to non-orthogonal and semi-localized metal-centred ( $\phi_x$ ) and anionic ligand radical ( $\phi_y$ ) orbitals below. The overlap between the two orbitals (S) that is calculated from Eq. 7.11 are provided in parentheses.

The conditions for this inversion to manifest are perfectly satisfied with the ligand environment of **1-CO<sub>2</sub>Me**. Alvarez has previously performed an extensive characterization of the crystallographic structures of heptacoordinate transition metal complexes.<sup>124</sup> Heptacoordinate structures are largely observed in Group 3-6 elements with a d<sup>0</sup>- d<sup>4</sup> electronic population whose conditions are met for V<sup>2+/3+</sup>. While the geometry of heptacoordinate structures is traditionally dynamic, possessing low-barriers of conversion, the  $C_3$  symmetry and multi-dentate chelation of the tren-scaffold enables a capped octahedral coordination environment.<sup>125</sup> Coordination between the V<sup>3+</sup> metal centre and bridgehead nitrogen stabilize the doublet state by approximately 15 kcal mol<sup>-1</sup>.

Lastly, the redox non-innocence of the iminopyridine groups provides  $1-CO_2Me$  a mechanism to access its doublet ground state. The strong electronic coupling between the metal-centred orbitals and anionic ligand radical results in resonance stabilization that assigns the <sup>2</sup>MLCT as the electronic ground state. The ester substituent magnifies this effect which we previously have shown with the emission properties of analogous Cr<sup>3+</sup> complexes that suggest greater metal-ligand covalency.<sup>126,127</sup>

We briefly summarize the advancements that our HDvV-SO method affords the theoretical treatment of open-shell systems. We note that, with select exceptions, <sup>128-131</sup> models for antiferromagnetism have focused on two-electron systems. <sup>112</sup>. Since our HDvV-SO model decomposes the magnetism of a system into its pairwise components, it can be employed to assign competing magnetic interactions in a multi-electron system.<sup>132,133</sup> We establish that metal-ligand covalency will impact the magnitude of electron-electron exchange interactions, thus modulating the strength of the high-spin (ferromagnetic) state. Greater metal-ligand covalency will concurrently stabilize charge transfer states in the molecule. The observance of the  ${}^{4}A_{2}$  and  ${}^{2}MLCT$  ground state for **1-H** and **1-CO<sub>2</sub>Me**, respectively, allude to an attractive design strategy based on established synthetic principles of ligand substituent electronics.<sup>22</sup> The variational approach of our HDvV-SO model can address the avenues for resonance stabilization, magnetic coupling, that are accessible to open-shell systems. This feature also provides the opportunity to transform computationally convenient orthogonal orbitals to nonorthogonal orbitals, orbital overlap being the requirement for antiferromagnetic coupling. From a practical standpoint, the calculation time of the interelectronic terms scales with respect to the volume of an orbital's grid rather than the number of electrons. Since the only required input is the Gaussian cube of a system's singly occupied orbitals, the procedure is agnostic to their originating electronic structure software.

# **7.6 Experimental Procedure**

The following calculations were performed with the Gaussian16 electronic structure software package.<sup>7</sup> We employed the APFD hybrid DFT-functional<sup>8</sup> and a 6-311+g(d) basis set<sup>9</sup> with its parameterized empirical dispersion correction in a PCM acetonitrile continuum solvent.<sup>10</sup> Both the quartet and doublet states of **1-H** and **1-CO<sub>2</sub>Me** were optimized where the V-N<sub>bridge</sub> separation was constrained to 3.15 Å and 2.21 Å, respectively. The structure of **2-H** was optimized with no geometric constraints. TD-DFT was performed under the same conditions for each of the optimized structures.<sup>11</sup> The uncoordinated iminopyridine ligand sets were optimized where the torsion of the bidentate binding group was constrained at 0° for both the neutral and singly reduced, monoanionic, state.

The energy of the  ${}^{2}E$  excited state energy with respect to the quartet geometry of **1-H** and **1-CO<sub>2</sub>Me** was multiplied by a factor of 3/2 to account for the single-determinant character of the DFTbased wavefunction. The foundation of our multideterminant DFT correction has been detailed elsewhere.<sup>12</sup>

The following calculations were performed with the ORCA 4.0 electronic structure software program.<sup>13</sup> We carried out multireference techniques with a CASSCF(3,8) model where the active space was selected to be the five 3d-orbitals and the three lowest-lying  $\pi^*$ -orbitals. The def2-TZVP and def2-TZVPP basis set<sup>14</sup> were used for the non-metal and metal atoms, respectively, with a CPCM acetonitrile continuum solvent. The final energies for the excited states were obtained with the NEVPT2 technique with the same active space and conditions.<sup>15–17</sup>

The HDvV-SO integrals were calculated, and their cubes generated from their corresponding CASSCF(3,8) orbitals. We selected a grid size of  $90 \times 90 \times 90$  for fine resolution. The orbital energies of the magnetic orbitals were approximated from the converged Restricted Open Hartree Fock (ROHF) wavefunction of the quartet state. The coefficients used for the SO-method (A<sub>1</sub>, A<sub>2</sub>, and A<sub>3</sub>) were obtained from the lowest-lying doublet of the corresponding CASSCF(3,3) wavefunction.

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# Chapter 8 Future Direction: Vanadium (II/III) Heptacoordination and Redox Noninnocence as a Molecular Model of the Substrate Binding and Reduction of CO in the Vanadium Nitrogenase Cofactor

#### 8.1 Outlook

The preceding chapters detail the application of electronic structure theory to a diverse set of chemical systems. We argue that the ability to visualize electron-electron interactions as an impact of spin will provide novel insight to longstanding challenges in chemistry. We develop auxiliary quantum chemical codes that allow the visualization and quantification of the following electron-electron interactions: exchange (Pauli) repulsion; medium-range electron correlation (dispersion); coulomb and exchange integrals; non-orthogonal (GVB-SO) orbitals; orbital overlap. Our methods are developed in tandem with experimental chemists that foster scientific literacy and communication between diverse disciplines. I believe that the scope provided from a fundamental approach to chemistry, grounded in electronic spin, is limitless. For our future direction we address the catalytic properties of the vanadium-containing nitrogenase cofactor (FeVco) whose enzymatic class is. routinely classified as the most challenging chemical system to characterize.

## 8.2 Introduction

Bioinorganic complexes and metalloenzymes have long served as muses for elucidating molecularlevel understanding of industrial-scale catalytic processes. Species associated with nitrogenase have been especially important. In addition to the more common molybdenum-based nitrogenase cofactor (FeMoco), responsible for the reduction of atmospheric nitrogen to bioavailable ammonium, a family of vanadium containing cofactors (FeVco) has been discovered.<sup>1–5</sup> FeVco is reported to be adept at the hydrogenation of carbon monoxide (CO), generating hydrocarbons at 800 times the rate of FeMoco.<sup>6–</sup> <sup>11</sup> While identified and isolated in 1986, a structure for FeVco was not reported until 2017.<sup>12–15</sup> Motivated by its direct application to the industrial Haber-Bosh and Fischer-Tropsch processes, there has been significant interest in discerning the chemical properties distinct to FeVco.<sup>16–21</sup>

We have recently reported on the physicochemical properties of a vanadium complex,  $[V(5-CO_2Me-py)_3tren](OTf)_2$  (**1-CO\_2Me**), that features a tren-capped tris(iminopyridine) chelating ligand. Depending on pyridine substituent choice, unusual structural and electronic features are displayed, including a metal-to-ligand charge transfer (MLCT) with an iminopyridine ligand, and a seventh coordinate covalent bond with the tertiary amine of the tren-backbone. The tripodal scaffold of tren- is a pervasive design strategy for molecular models of bioinorganic systems that reproduces the  $C_3$ -symmetry and tridentate chelation of iron-sulfide cubanes.<sup>22</sup> The fluctuation of the pendant tertiary amine (N<sub>bridge</sub>) atom, between the primary and secondary coordination sphere, is dependent on the oxidation and spin state of the transition metal centre.<sup>23-26</sup> This structural feature may illustrate intermediate or transition states of ligand association or dissociation in six- or seven-coordinate species, respectively.<sup>27,28</sup> The coordinative non-innocence of N<sub>bridge</sub> serves as a proxy for the  $\sigma$ -donor properties of CO where hypervalency is a redox-mediated property.

The vanadium complex **1-CO<sub>2</sub>Me** is the first nominally  $3d^3$  octahedral coordination complex that does not have a quartet ( $M_s = 3/2$ ) ground state. The unique electronic structure of our complex arises from the coordinative and redox noninnocence of its tripodal, tren-iminopyridine architecture. Conceptually related to nitrogenase and its models, DeBeer and co-workers have previously reported a doublet, "non-Hund", ground state for the Mo<sup>3+</sup> metal centre ( $4d^3$ ) of FeMoco.<sup>29</sup> Linking these ideas and observations, herein we propose that substrate binding and reduction by FeVco occurs through the concerted heptacoordination and MLCT between V<sup>2+/3+</sup> and CO that is shown in Figure 8.1 and detailed as Results and Discussion.



**Figure 8.1** *(top)* The previously reported iron-based mechanism for the binding of CO by FeVco. *(bottom)*. Our current proposal that the V<sup>3+</sup> metal centre of FeVco binds CO through heptacoordination

# 8.3 Results and Discussion

# 8.3.1 *Coordination of Substrate through Hypervalency in V*<sup>3+</sup> *Ground State*

The iron centers of the FeVco ground state possess tetrahedral coordination environments that consist of bridging sulfides ( $S^{2-}$ ) and a carbonate ( $CO_3^{2-}$ ), and a central carbide ( $C^{4-}$ ).<sup>13,20</sup> The V<sup>3+</sup> heteroatom has an octahedral ligand environment where an iron-sulfur cubane serves as a tridentate ligand with respect to a *C*<sub>3</sub>-symemtric arrangement of S<sup>2-</sup> donor atoms.<sup>13</sup> The remaining coordination sites are occupied with homocitrate, whose adjacent hydroxyl and carboxylate functional groups display bidentate coordination, and the amino acid histidine that coordinates through its imidazole moiety. The iron and heteroatoms of nitrogenase cofactors are classified as coordinatively saturated in their tetrahedral and octahedral ligand environments, respectively.<sup>2</sup> Because of this, a fundamental question is how they bind substrates preceding their electrochemical reduction.<sup>30</sup>

Several crystal structures have been published where CO or N<sub>2</sub> displaces a bridging sulfide-group in FeMoco and coordinates in a  $\mu_2$ -arrangement with its adjacent iron groups.<sup>31,32</sup> This supports an iron-based mechanism for both the binding and reduction of substrates.<sup>33,34</sup> By analogy, the properties of FeVco are treated as an extrapolation of its better studied isostructural nitrogenase cofactor.<sup>35–38</sup> Notwithstanding, a definitive assignment of the active site of FeVco is complicated because it has four distinct substrate binding sites, only one of which is catalytically active.<sup>39</sup>

The vanadium heteroatom is reported to retain its +3-oxidation state throughout its catalytic cycle.<sup>40</sup> Meanwhile, we have shown that a vanadium d<sup>2</sup> transition metal centre is stabilized in a capped octahedral coordination environment, compared to an octahedral geometry. In a related complex,  $[V(py)_3 tren](OTf)_3$  (**2-H**), a bona fide d<sup>3</sup> metal centre is similarly stabilized *from* heptacoordination. that is similarly stabilized with heptacoordination.

Our computational model for the vanadium heteroatom of FeVco is shown in Figure 8.2. We approximate the cubane architecture with a tripodal ligand set of sulfide donors (CHS<sub>3</sub>) and the remaining coordination sites are occupied by dimethyl formamide (DMF).<sup>17,41</sup> We optimize the geometries with the TPSSh, hybrid-DFT functional, that has been benchmarked with FeMoco model complexes.<sup>42,43</sup> Our trivalent structure forms a seventh coordinate covalent bond with CO whose vanadium-carbon bond length is 2.25 Å. The carbon-oxygen bond length of the carbonyl is unperturbed from its equilibrium geometry (1.13 Å) that indicates pure  $\sigma$ -bonding that is shown in Figure 3. We report a small repulsive bond energy of 7.04 kcal mol<sup>-1</sup> where the impact of protein environment requires further consideration.<sup>43,44</sup> Based on our current analysis, the ground (E<sub>0</sub>) state of FeVco can directly bind CO through hypervalency of its V<sup>3+</sup> (d<sup>2</sup>) metal centre.

# 8.3.2 *Reduction of Substrate through Metal-to-Ligand Charge Transfer*

The stabilization provided from  $V^{3+}$  heptacoordination can instigate a metal-to-ligand charge transfer (MLCT) in the  $V^{2+}$  oxidation state. Antiferromagnetic coupling between the  $V^{3+}$  metal centre and anionic ligand radical results in a doublet ground state that we refer to as <sup>2</sup>MLCT. The metal-

centred V<sup>2+</sup> quartet is near-degenerate with the <sup>2</sup>MLCT and will not adopt a heptacoordinate geometry. The vanadium heteroatom of FeVco has EPR signatures consistent with both an  $M_{\rm S} = 1/2$  and 3/2 state.<sup>6,40,45,46</sup> This is consistant with the Sabatier principle where the bond making and breaking steps between the catalyst and substrate are of similar energies.



**Figure 8.2** (*top*) The reaction of our model complex in its trivalent ground state (E<sub>0</sub>) with a CO molecule. (*bottom*) The quasi-restricted orbital (QRO) of the unoccupied  $\sigma^*$ -antibonding orbital between the V<sup>3+</sup> metal centre and CO lone pair of the DFT (TPSSh) optimized complex.

We optimize the doublet state of the reduced model complex that elongates a vanadium-amide bond, consistent with the desymmetrisation and bond length changes observed in **1-CO<sub>2</sub>Me**. In addition, structural data have been used recently to suggest a bi- to monodentate conversion of the molybdenum coordinated citrate ligand of FeMoco under turnover conditions.<sup>47–49</sup> The heptacoordinate geometry in our model complex changes from capped octahedral to pentagonal bipyramidal with substitution of its labile amide with a second molecule of CO. The interconversion between heptacoordinate geometries has been assigned as a dynamic and low-energy process in analogous organometallic complexes.<sup>50</sup>



**Figure 8.3**. Our proposed mechanism for the CO hydrogenation of FeVco, where 'L' refers to the coordination environment detailed in Figure 1. The orange equilibria refer to the ligand substitution between homocitrate and a CO substrate. The red equilibria refer to the respective reduction and oxidation of the E(0) and E(1) mechanistic states.

In Figure 8.3 we illustrate our proposed mechanism for the concerted substrate binding and reduction for the singly reduced (E<sub>1</sub>) state of the hydrogenation of CO by FeVco. Ethylene (C<sub>2</sub>H<sub>4</sub>) is the dominant product of CO hydrogenation in a migratory insertion process. Multireference calculations, NEVPT2(3,8), assigns strong antiferromagnetic coupling ( $J = 1990 \text{ cm}^{-1}$ ) between a local V<sup>3+</sup> metal centre and ethylenedione (C<sub>2</sub>O<sub>2</sub>)<sup>-</sup> anionic ligand radical. The corresponding generalized valence bond-strongly orthogonal (GVB-SO) orbitals that we have previously detailed assign an overlap of 0.52 between the two spin centres that is shown in Figure 8.4. The ligand-centred orbitals exhibit  $\pi$ -bonding between the carbon atoms, their separation being 2.15 Å. The anionic charge and radical are delocalized between the terminal oxygen atoms. The concerted heptacoordination and MLCT between V<sup>2+</sup> and adjacent CO ligands forms a carbon-carbon bond that should template the production of C<sub>2</sub>H<sub>4</sub>.

## **8.4 Conclusions**

We have provided computational methods in the context of literature reports for the following proposals regarding the Fischer-Tropsch type chemistry of FeVco:

(a) the  $V^{3+}$  heteroatom can form a seventh coordinate covalent bond with CO in its ground (E<sub>0</sub>) state

(b) a V<sup>2+</sup> metal centre can coordinate and reduce CO in a concerted process

(c) the one-electron reduction of adjacent CO ligands forms a  $\pi$ -bond between the carbonyl carbons The further development of the reaction mechanism is a current effort of our groups. We are optimistic that our proposal further extends to the catalytic reduction of nitrogen by FeMoco.



**Figure 8.4** The non-orthogonal (GVB-SO) orbitals of the (*left*)  $V^{3+}$ -metal-centred and (*right*) ethylenedione (C<sub>2</sub>O<sub>2</sub>)<sup>-</sup> anionic ligand radical.

#### **8.5 Experimental**

The following calculations were performed with the ORCA 4.0 electronic structure software package.<sup>51</sup> The geometries were optimized with the hybrid-DFT TPSSh functional.<sup>52</sup> The def2-TZVP and def2-TZVPP basis set<sup>53</sup> for the non-metal and metal atoms, respectively, with the corresponding axillary basis set in RIJK approximation<sup>54,55</sup> The DFT-D3 empirical dispersion correction was applied.<sup>56</sup> The calculations were performed in a CPCM water continuum solvent.<sup>57</sup> The Broken-

symmetry solution of the doublet state of the singly reduced complex was found by flipping spins on the vanadium heteroatom.<sup>58</sup>

We carried out multireference techniques with a CASSCF(3,8) procedure where the active space was defined as the five 3d-orbitals and the three lowest-lying  $\pi^*$ -orbitals. The same basis set and solvent conditions described above were applied. The final energies for the excited states were obtained with the NEVPT2 technique with the same active space and conditions.<sup>59–61</sup> The pair coefficients of the CASSCF(3,8) wavefunction were used to transform the orthogonal natural orbitals

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#### **APPENDIX**

### **A1 Three-Electron Formalism**

The quartet state (Q) of a three-electron system is shown with the associated wavefunction and energy expression in Eq. A 1.1 and Eq. A 1.2, respectively. With respect to orthogonal orbitals there are two doublet excited states (D<sub>1</sub> and D<sub>2</sub>) that are descriptive of a spin-flip. The corresponding wavefunction and energy expressions are provided in Eq. A 1.3 and A 1.5 and Eq. A 1.4 and Eq. A 1.6 that detail its energy relative to Q with respect to the loss of favorable exchange interactions (K<sub>ij</sub>).

The one electron terms,  $h_{aa}$ ,  $h_{bb}$ , and  $h_{cc}$  are approximated from the ROHF orbital energies. The terms of interest are the one-electron operators ( $h_{ii}$ ), two-electron coulombic interactions ( $J_{ij}$ ), and two-electron exchange interactions ( $K_{ij}$ ).

$$\frac{4}{Q} \frac{4}{M_{S} = 3/2}$$
(Eq. A 1.1)  $\psi_{Q} = a[(\phi_{a}\phi_{b}\phi_{c})(\alpha\alpha\alpha)]$ 

 $(Eq. \ A \ 1.2) \ E_Q = h_{aa} + h_{bb} + h_{cc} + J_{ab} + J_{ac} + J_{bc}$  -  $K_{ab}$  -  $K_{ac}$  -  $K_{bc}$ 

$$\begin{bmatrix} 4 & 4 & 4 \\ D_1 (M_s = 1/2) \end{bmatrix}$$

$$(Eq. A 1.3) \quad \psi_{D_1} = \frac{1}{\sqrt{2}} a[(\phi_a \phi_b \phi_c)(\alpha \beta \alpha - \beta \alpha \alpha)]$$

$$(\text{Eq. A 1.4}) E_{D_1} = h_{aa} + h_{bb} + h_{cc} + J_{ab} + J_{ac} + J_{bc} + K_{ab} - \frac{1}{2}K_{ac} - \frac{1}{2}K_{bc}$$

$$(Eq. A 1.6) E_{D_2} = h_{aa} + h_{bb} + h_{cc} + J_{ab} + J_{ac} + J_{bc} - K_{ab} + \frac{1}{2}K_{ac} + \frac{1}{2}K_{bc}$$

$$(Eq. A 1.7) h_{aa} = \varepsilon_a - (J_{ab} - K_{ab} + J_{ac} - K_{ac})$$

$$(Eq. A 1.8) h_{bb} = \varepsilon_b - (J_{ab} - K_{ab} + J_{bc} - K_{bc})$$

$$(Eq. A 1.9) h_{cc} = \varepsilon_c - (J_{ac} - K_{ac} + J_{bc} - K_{bc})$$

For degenerate and orthogonal orbitals, the pairwise electron-electron interactions are equivalent so that Q is stabilized by a factor of three exchange interactions.

(Eq. A 1.10)	$h_{aa} = h_{bb} = h_{cc}$
(Eq. A 1.11)	$\mathbf{J}_{ab} = \mathbf{J}_{ac} = \mathbf{J}_{bc}$
(Eq. A 1.12)	$K_{ab} = K_{ac} = K_{bc}$
(Eq. A 1.13)	$E_Q = 3h_{aa} + 3J_{ab} - 3K_{ab}$
(Eq. A 1.14)	$E_{D_1} = E_{D_2} = 3h_{aa} + 3J_{ab}$
(Eq. A 1.15)	$\Delta E_{Q-D} = -3K_{ab}$

The one-electron operators  $(h_{ii})$  are approximated from the orbital energies  $(\varepsilon_i)$  of the restricted open Hartree-Fock (ROHF) wavefunction of the quartet state. The values of the two-electron integrals are obtained from the active space of the corresponding CASSCF(3,3) wavefunction in the format of their Gaussian cubes with our procedure detailed above.

The  $D_1$  and  $D_2$  states are stabilized from a configuration interaction if their energies are inequivalent. This coupling generates a stabilized ( $D_-$ ) and destabilized ( $D_+$ ) doublet state with respect to the average energy of  $D_1$  and  $D_2$ . The electronic coupling term between the two states is provided in Eq. A 1.16 that illustrates the magnitude of the resonance stabilization is dependent on the deviation between the pairwise exchange terms.

(Eq. A 1.16) 
$$E_{D_+,D_-} = \frac{(H_{aa} + H_{bb}) \pm \sqrt{(H_{aa} - H_{bb})^2 + 4H_{ab}^2}}{2}$$

(Eq. A 1.17) 
$$E_{D_+,D_-} = \frac{(H_{aa} + H_{bb}) \pm \sqrt{4K_{ab}^2 + 4K_{ac}^2 + 4K_{bc}^2 - 4K_{ab}K_{ac} - 4K_{ab}K_{bc} - 4K_{ac}K_{bc}}{2}$$

(Eq. A 1.18) 
$$H_{aa} = 2h_{aa} + J_{a} + J_{ac} - \frac{1}{2}K_{ac} + h_{cc} + \frac{1}{2}J_{ac} - \frac{1}{2}K_{ac} + \frac{1}{2}J_{bc} - \frac{1}{2}K_{bc}$$
  
(Eq. A 1.19) 
$$H_{bb} = 2h_{bb} + J_{b} + J_{bc} - \frac{1}{2}K_{bc} + h_{cc} + \frac{1}{2}J_{ac} - \frac{1}{2}K_{ac} + \frac{1}{2}J_{bc} - \frac{1}{2}K_{bc}$$

The Strongly Orthogonal (SO) method assigns multielectron systems into non-orthogonal pairs preceding the optimization of their spin-coupling.<sup>18,19</sup> The SO-GVB wavefunction is provided in Eq. A 1.20 in terms of their spin-pair coefficients (A<sub>1</sub>, A<sub>2</sub>, and A<sub>3</sub>) that are obtained from the state coefficients of the doublet ground state of the corresponding CASSCF(3,3) wavefunction. We note that the spin-pair coefficients are provided as  $A_1^2$ ,  $A_2^2$ , and  $A_3^2$  with respect to the ORCA 4.1 electronic structure software. The distinct spin ( $\varepsilon_1$  and  $\varepsilon_2$ ) and pair-( $c_1$  and  $c_2$ ) coefficients are provided in Eq. A 1.21 and their relation to the cumulative spin-pair coefficients in Eq. A 1.22-A 1.26. The natural orbitals of the CASSCF(3,3) wavefunction are related to their non-orthogonal general valence bond (GVB) orbitals with respect to their pair-coefficients in Eq. A 1.29-Eq. A 1.32. The corresponding energy expression is detailed in Eq. A 1.33-Eq. A 1.47.

$$\begin{aligned} (\text{Eq. A 1.20}) \qquad & \psi = \begin{bmatrix} A_1 \phi_1 \phi_1 \phi_3 - A_2 \phi_2 \phi_2 \phi_3 \end{bmatrix} (\alpha \beta \alpha - \beta \alpha \alpha) + A_3 [(\phi_1 \phi_2 - \phi_2 \phi_1) \phi_3] (2 \alpha \alpha \beta - \alpha \beta \alpha - \beta \alpha \alpha) \\ (\text{Eq. A 1.21}) \qquad & \psi = \varepsilon_1 [c_1 \phi_1 \phi_1 \phi_3 - c_2 \phi_2 \phi_2 \phi_3] (\alpha \beta \alpha - \beta \alpha \alpha) + \varepsilon_2 [(\phi_1 \phi_2 - \phi_2 \phi_1) \phi_3] (2 \alpha \alpha \beta - \alpha \beta \alpha - \beta \alpha \alpha) \\ & (\text{Eq. A 1.22}) \qquad A_1 = c_1 \varepsilon_1 \\ & (\text{Eq. A 1.23}) \qquad A_2 = -c_2 \varepsilon_1 \\ & (\text{Eq. A 1.24}) \qquad A_3 = \varepsilon_2 \\ & (\text{Eq. A 1.25}) \qquad \varepsilon_1 = \sqrt{1 - A_3^2} \\ & (\text{Eq. A 1.26}) \qquad c_1 = \frac{A_1}{\sqrt{1 - A_3^2}} \\ & (\text{Eq. A 1.27}) \qquad \varepsilon_1^2 + \varepsilon_2^2 = 1 \end{aligned}$$

(Eq. A 1.28)  

$$c_1^2 + c_2^2 = 1$$
  
(Eq. A 1.29)  
 $\phi_a = \frac{\sqrt{c_1}\phi_1 + \sqrt{c_2}\phi_2}{\sqrt{c_1 + c_2}}$   
(Eq. A 1.30)  
 $\phi_b = \frac{\sqrt{c_1}\phi_1 - \sqrt{c_2}\phi_2}{\sqrt{c_1 + c_2}}$   
(Eq. A 1.31)  
 $S_{ab} = \langle \phi_a | \phi_b \rangle \neq 0$   
(Eq. A 1.32)  
 $S_{ab} = \frac{c_1 - c_2}{c_1 + c_2}$ 

 $\psi = \varepsilon_1 \Big[ \Big( \phi_a \phi_b + \phi_b \phi_a \Big) \phi_3 \Big] (\alpha \beta \alpha - \beta \alpha \alpha) + \varepsilon_2 [ \Big( \phi_1 \phi_2 - \phi_2 \phi_1 \Big) \phi_3 ] (2 \alpha \alpha \beta - \alpha \beta \alpha - \beta \alpha \alpha) \Big]$ (Eq. A 1.33)  $E = 2\sum_{i}^{n} f_{i}h_{ii} + \sum_{i,j}^{N} \left[ a_{ij}J_{ij} + b_{ij}K_{ij} \right] + \sum_{m}^{np} \sum_{i \neq m_{1},m_{2}}^{n} c_{mi} < \phi_{m_{1}} |M_{i}|\phi_{m_{2}} >$ (Eq. A 1.34) (Eq. A 1.35)  $f_1 = A_1^2 + \frac{1}{2}(A_3^2)$ (Eq. A 1.36)  $f_2 = A_2^2 + \frac{1}{2}(A_3^2)$ (Eq. A 1.37)  $f_3 = \frac{1}{2}$ (Eq. A 1.38)  $a_{11} = A_1^2$ (Eq. A 1.39)  $a_{22} = A_2^2$ (Eq. A 1.40)  $a_{12} = \frac{1}{2}(A_3^2)$ (Eq. A 1.41)  $a_{13} = f_1$ (Eq. A 1.42)  $a_{23} = f_2$  $b_{12} = A_1 A_2 - \frac{1}{2} (A_3^2)$ (Eq. A 1.43) (Eq. A 1.44)  $b_{13} = \frac{1}{4} (A_3^2 - 2A_1^2)$ (Eq. A 1.45)  $b_{23} = \frac{1}{4} (A_3^2 - 2A_2^2)$ (Eq. A 1.46)  $c_{13} = \sqrt{6}A_3(A_1 - A_2)$ 

$$(Eq. A 1.47) \quad E = A_1^2 (2h_{aa} + h_{cc} + J_{aa} + 2J_{ac} - K_{ac}) + A_2^2 (2h_{bb} + h_{cc} + J_{bb} + 2J_{bc} - K_{bc}) + A_3^2 (h_{aa} + h_{bb} + h_{cc} + J_{ab} - K_{ab} + J_{ac} + \frac{1}{2}K_{ac} + J_{bc} + \frac{1}{2}K_{bc}) + 2A_1A_2K_{ab} + \sqrt{6}A_3(A_1 - A_2)M_3$$