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4 **Oxidation states “naturally”: A Natural Bond Orbital method for**
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6
7 **determining transition metal oxidation states.** ¹

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14 **1. Introduction.**

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16 The oxidation state (OS) concept is arguably one of the most useful formalisms in
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18 chemistry. OSs are used to explain catalytic behavior at a variety of transition metal (TM)
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20 centers.[1] They are also used to interpret a wide variety of spectroscopic results, such as
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22 the structure of electron paramagnetic resonance, UV-visible, and Mössbauer spectra.[2,
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24 3] More broadly, the OS concept aids in categorizing the behavior of TMs in a general
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26 way, enabling its use as both a predictive and postdictive tool in chemical reactions.
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28 Indeed, inorganic chemists still use the masterfully organized—often by OS— tome,
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30 *Advanced Inorganic Chemistry*, as a way of rationalizing the chemistry of TM
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32 complexes.[4]

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35 However, while tremendously useful from a categorization perspective, the OS
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37 concept continues to inspire debate within the chemical community.[5-10] Recent
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39 exchanges show just how far the debate has gone: two competing points of view
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48 ¹ Supporting Information: Crystal structure and optimized geometry coordinates, Perl
49 scripts for NBO calculations, isosurface plots of NBOs, NBO perturbation theory
50 analyses, and electronic structure programs supporting NBO can be found in the
51 Supporting Information.

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eloquently arguing, on the one hand, that OS has nothing to do with electronic charges of the components in TM complexes, while others argue that they do! This controversy highlights the crux of the problem with the OS concept: associating the behavior of an isolated TM ion with its behavior in a complex, where it is surrounded by various ligands which may behave very differently than when isolated in a vacuum. Indeed, Linus Pauling famously stated he doubted "whether the ferrous ion and ferric ion, and similar ions of the transition elements, exist in chemical substances. I think instead that the atoms of iron in all ferrous and ferric compounds form covalent bonds in such a way as to remain essentially neutral." [11]

In order to fully appreciate and apply the OS concept we need to consider the range of OS definitions and interpretations from the chemical community and how that impacts OS determination for TM in complexes. A recent IUPAC Reference Report, "Toward a comprehensive definition of oxidation state", discusses both the history of OS and the arguments surrounding it. [10] The report formulates a very generic definition of OS: "The OS of a bonded atom equals its charge after ionic approximation". The idea is simple—the atom contributing most to a bonding molecular orbital becomes negative. The idea, however, becomes complicated if the atom in question is bonded to a Lewis acid.

The IUPAC report uses various electronegativity scales in its ionicity discussion, ultimately advocating for the Allen scale. [12] But the report also discusses the use of direct quantum chemical methods for calculating oxidation states, many of them using so-called population analyses. Another method cited in the IUPAC report was by one of

the coauthors, which ultimately simulates an ionic model.[13] This method is described herein.

The theoretical approach advocated by Sit and coworkers allowed the separation of the ligand-metal mixing contributions to the allocated charge from that due to the actual *d*-orbital occupations, from which OSs were inferred. It was applied to several TM systems including simple molecular complexes, to the study of the oxidation states in bulk semiconductors, Ru-dye molecules and non-innocent ligand complexes, and to the study of the oxidation mechanism of a pyrite surface resulting in OS assignments.[14] In this approach, a 5×5 *d*-orbital occupation matrix of the TM ion was constructed for each electronic spin. The matrix $n_{mm'}^\sigma$ consisted of a projection of the first-principles eigenfunctions of the system (ψ_v^σ) onto the 5 atomic *d*-orbitals of the transition metal ion (ϕ_m), according to the following equation:

$$n_{mm'}^\sigma = \sum_v \langle \psi_v^\sigma | \phi_{m'} \rangle \langle \phi_m | \psi_v^\sigma \rangle$$

The occupation numbers were then computed as the eigenvalues of this occupation matrix. The number of *d*-electrons assigned to the TM ion was the number of *d*-orbitals with full occupancy, i.e. occupation number=1 under ideal circumstances, and the OS was therefore inferred.

The occupied Kohn-Sham orbitals were obtained from a calculation on the complex being studied, while the atomic *d*-orbitals were computed from a separate calculation on the isolated ion. In some calculations, however, the occupation numbers corresponding to ‘full’ occupancy were less than unity. Several causes for this discrepancy were discussed in detail in the previous work. One potential issue was with the use of the atomic *d*-orbitals (the very foundation of the work!) as the basis for

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4 projection. This choice was based on the assumption that the atomic *d*-orbitals exhibit
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6 insignificant perturbation by the ligand fields, which is not true (*vide infra*). The use of
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8 the atomic *d*-orbitals also introduced an extra complication by requiring a separate
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10 calculation on an isolated ion, which lacks any ligand field perturbation and certainly not
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12 an accurate representation of a metal in a complex, as pointed out by Knizia.[15]
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16 In order to address the aforementioned problems the authors of the current work
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18 propose a broader formulation for OS determination. The occupation matrix can be
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20 constructed by projecting the occupied Kohn-Sham orbitals onto the natural atomic
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22 orbitals (NAOs) of the TM atom—within its chemical environment—in place of the
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24 atomic *d*-orbitals. The NAOs of the atom are its *localized* orbitals, which can be taken as
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26 the effective natural orbitals in the molecular environment.[16] The NAOs coincide with
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28 the atomic orbitals in the case of an isolated atom and are perturbed according to the
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30 chemical environment. The use of NAOs in place of the atomic *d*-orbitals has two
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32 advantages: 1) NAOs take into account orbital perturbations due to surrounding ligands,
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34 and 2) NAOs avoid the need to calculate the atomic orbitals of isolated TM ions.
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41 We wish to note that the present work is *not* an attempt at investigating the OSs of
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43 TMs in controversial complexes (see the **Conclusions** section); this work is a proof of
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45 concept. We demonstrate below that our method, herein referred to as the Natural
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47 Oxidation State (NOS) method, can make theoretical OS investigations more general and
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49 more easily accessible to even the practicing synthetic chemist; the calculations are not
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51 confined to one particular electronic structure software package. Rather, we have used
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53 our method to determine the OS of TM atoms in several representative examples.
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58 **2. Experimental.**

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Geometry optimizations, single point energy calculations, and vibrational frequency analyses were performed using spin-unrestricted density functional theory as implemented in the Gaussian09 suite of programs[17] using default convergence criteria and the nosymm keyword. The B3LYP[18-20] exchange-correlation functional was used for each complex. The Los Alamos National Labs double-zeta (LanL2DZ) basis set / effective core potential (ECP) was used on all metal atoms.[21-23] The Pople-style 6-31G(d,p) basis set was used on all non-metal atoms.[24]

Crystal structure coordinates for $[\text{Fe}(\text{C}_5\text{H}_5)_2]$,[25] $[\text{Ru}(\text{C}_5\text{H}_5)_2]$,[26] $[\text{Os}(\text{C}_5\text{H}_5)_2]$,[27] $[\text{Cr}(\text{CO})_6]$,[28] $[\text{Mo}(\text{CO})_6]$,[29] $[\text{W}(\text{CO})_6]$,[30] $[\text{CrCl}_6]^{3-}$,[31] $[\text{MoCl}_6]^{3-}$,[32] $[\text{WCl}_6]^{3-}$,[33] $[\text{Ni}(\text{C}_6\text{F}_5)_4]^{2-}$,[34] and $[\text{Ni}(\text{C}_6\text{F}_5)_4]^-$ [34] were obtained from the Cambridge Crystallographic Database[35, 36]. Both single point energy calculations and geometry optimizations were performed on each complex (Cartesian coordinates can be found in **Supporting Information SI1 and SI2**). Crystal structure coordinates for $[\text{Fe}(\text{H}_2\text{O})_6]^{2+/3+}$,[37] $[\text{Fe}(\text{CO})_6]^{2+/3+}$,[38] $[\text{Fe}(\text{CN})_6]^{3-/2-}$,[39] $[\text{MnCl}_4]^{2-}$,[40] $[\text{MnCl}_5]^{2-}$,[41] $[\text{Mn}(\text{CO})_6]^{2+/3+}$,[42] and $[\text{Mn}(\text{CN})_6]^{4-/3-}$,[43] (from the work of Sit and coworkers), were also obtained from the Cambridge Crystallographic Database. Both single point energy calculations and geometry optimizations were performed on each complex (Cartesian coordinates can be found in **Supporting Information SI1 and SI2**). The single point calculations on different charged species, i.e. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+/3+}$, were run by simply varying the input charges for the same set of crystal structure coordinates. All optimized structures were verified as local minima on their respective potential energy surfaces through vibrational frequency analyses.

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4 Natural Bond Orbital (NBO) analyses on were performed on all single point
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6 energy and geometry optimized structures using the NBO 5.G suite of programs.[44] The
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8 NBO partitioning scheme does not suffer from many of the nonphysical drawbacks of the
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10 commonly used Mulliken population analysis.[16] Another benefit of NBO theory is that
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12 the partitioning scheme is relatively insensitive to the level of theory utilized,[16]
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14 whether using wavefunction-based methods such as Hartree-Fock theory, or density
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16 functional theory. As such, the same basis set/density functional was employed
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18 throughout the study.
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23 The NBO analysis of each complex was performed using the DMNAO keyword
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25 (using a Perl script, section **Supporting Information SI3**, operating on a .47 NBO file).
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27 The *d*-orbital occupation matrices were then extracted from the complete DMNAO
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29 matrices (using a Perl script, section **Supporting Information SI4**, operating on a .nbo
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31 output file). The resulting *d*-orbital occupation matrices were diagonalized using GNU
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33 Octave[45] to obtain the eigenvalues corresponding to *d*-orbital occupancy. All natural
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35 orbitals were visualized using the Chemcraft[46] software package. Natural occupations
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37 were compared to Mulliken[47] and Löwdin[48] populations on metals in each complex,
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39 calculated using the QMForge[49] program. The occupations were calculated by adding
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41 the electron populations from each d-orbital basis function under each population
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43 scheme.
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50 In order to gauge the extent of metal-to-ligand backdonation in complexes with
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52 occupations less than unity we performed a second-order perturbation theory analysis of
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54 the Fock matrix in the NBO basis. The analysis considers the donor-acceptor energy
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56 interaction, $\Delta E_{i \rightarrow j^*}$, between a donor NBO ϕ_i , and an acceptor NBO ϕ_{j^*} .
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3. Results and Discussion.

3.1. NOS assignments: What really works

Our assignments of natural oxidation states are based on *d*-orbital occupations generated from the 5×5 occupation matrix. We count a *d*-orbital as “occupied” if it has an electron count greater than 0.9 (that is, close to unity, although there are exceptions, *vide infra*). **Table 1** lists the natural, Mulliken, and Löwdin occupations from geometry optimizations of all the complexes in this study, including some originally studied by Sit and coworkers.[13]. We note that single-point energy calculations—performed on the same crystal structure coordinates for the complexes in **Table 1**—were also performed, and are included at the end of the **Supporting Information** as **Table SI1**. No appreciable difference was found between the geometry-optimized or single-point results.

It is readily apparent that NOSs assigned to the halides $[\text{MnCl}_4]^{2-}$, $[\text{MnCl}_5]^{2-}$, $[\text{CrCl}_6]^{3-}$, $[\text{MoCl}_6]^{3-}$, and $[\text{WCl}_6]^{3-}$, are almost precisely what we would ascribe to them with pen and paper. We can say that $[\text{MnCl}_4]^{2-}$ contains a Mn^{2+} (4.99, or 5 *d*-electrons), and $[\text{MnCl}_5]^{2-}$ contains a Mn^{3+} (3.99, or 4 *d*-electrons). The unoccupied *d*-orbitals contain essentially 0 electrons (more specifically, on the order of between 0.02-0.39 electrons). The halides $[\text{CrCl}_6]^{3-}$, $[\text{MoCl}_6]^{3-}$, and $[\text{WCl}_6]^{3-}$ also have almost “perfect” NOSs of +3. For all the halides the Mulliken and Löwdin *d*-orbital occupations are greater than the natural *d*-orbital occupations, in some cases by ca. 2 electrons.

Another set of complexes with near integer NOSs are the hexaaqua complexes $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$. The complexes contain iron centers in the +2 and +3 NOSs, respectively. The most conspicuous feature of the aforementioned complexes is they all contain classic σ -donor ligands. But what happens when we incorporate π -

acceptor ligands into the complexes, such as carbonyls or cyanides, or even cyclopentadienyls? The inorganic chemist would expect back donation from the metal to the ligand according to the Dewar-Chatt-Duncanson model,[50, 51] perhaps giving us *d*-orbital occupations that are not quite unity. This is, in fact, precisely what is observed, and described in section 3.2.

3.2 More complicated cases: the effect of π^* acceptor orbitals

Metallocenes such as $(C_5H_5)_2M$ ($M=Fe, Ru, Os$) are amongst the most ubiquitous organometallic complexes. The occupation numbers for each complex indicate an assignment of the $M(II)$ oxidation state (**Table 1**). In ferrocene, for example, three of the spin-up electrons have values of 0.93, 0.93, and 0.99, while there are three spin-down electrons with values of 0.93, 0.93, and 0.99. The values are close enough to unity to assign six *d*-electrons to iron, with the same argument being made for ruthenocene and osmocene. The situation changes dramatically, however, when we consider some classic organometallic complexes containing carbonyl (CO) and cyanide (CN^-) ligands.

The most conspicuous electron counts come from the $M(CO)_6$ complexes of the chromium triad ($M=Cr, Mo, W$). The numbers being ascribed to “occupied” are six occupations of 0.79 electrons for $Cr(CO)_6$; six occupations of 0.77 electrons for $Mo(CO)_6$; and six occupations of 0.72 electrons for $W(CO)_6$. How can such small numbers—0.72 electrons!—be attributed to an occupation? The answer can be found in the extent of metal-to-ligand π -backdonation in the aforementioned complexes.

One of the strengths of NBO theory is its ability to partition localized electronic interactions in terms of an electron-pair donor, NBO $\phi_i^{(0)}$, and an electron-pair acceptor, NBO $\phi_j^{(0)}$. A pictorial representation of this interaction can be found in **Figure 1**, which

represents the effects of a second-order perturbation theory interaction between $\phi_i^{(0)}$ and $\phi_{j*}^{(0)}$ given by the following equation:

$$\Delta E_{i \rightarrow j*}^{(2)} = -n_i^{(0)} \frac{\langle \phi_i^{(0)} | \hat{F} | \phi_{j*}^{(0)} \rangle^2}{\epsilon_{j*}^{(0)} - \epsilon_i^{(0)}}$$

The full details of the derivation of the aforementioned equation can be found elsewhere,[16] but a general explanation follows. The magnitude of the energy lowering, $\Delta E_{i \rightarrow j*}^{(2)}$, indicates the relative importance of a donor-acceptor interaction. The larger the value, the more we can view the interaction as being an appreciable one. This donor-acceptor description of bonding helps to paint a more quantitative picture of the classic, so-called Dewar-Chatt-Duncanson (DCD) model often used to describe the bonding of transition metals to olefins (and, more generally, to π -acceptors).[50, 51] The donor orbital in the DCD model is a metal d -orbital, while the acceptor is an empty π^* orbital on a ligand; this interaction is illustrated, for a CO ligand, in **Figure 2**. The utility of this approach has been illustrated elsewhere.[52]

The three neutral $M(\text{CO})_6$ complexes (*vide supra*, $M=\text{Cr}$, Mo , and W) have unusually low occupation numbers, and they also contain classically strong π -acceptor ligands. This poses two questions: first, can we easily locate $\phi_i^{(0)}$ (a metal d -orbital-based NBO) and $\phi_{j*}^{(0)}$ (a ligand π^* NBO), and second, are the energy lowerings ($\Delta E_{i \rightarrow j*}^{(2)}$) for those interactions appreciably large compared to other complexes containing strong π^* -acceptors, but with occupations close to unity? The answer to both questions is yes.

An NBO analysis will, by default, produce the results of a second-order perturbation theory analysis of donor-acceptor interactions, with one of the parameters being $\Delta E_{i \rightarrow j*}^{(2)}$. For our purposes, we identified interactions whose $\phi_i^{(0)} \rightarrow \phi_{j*}^{(0)}$ donor-

acceptor character was primarily metal d -orbital on $\phi_i^{(0)}$, and C-O π^* in nature (BD* in NBO parlance) on $\phi_{j*}^{(0)}$. We then proceeded to visualize those results (see **Supporting Information SI5** for pictorial representations of the key NBOs of $M(\text{CO})_6$, $M=\text{Cr}, \text{Mo}, \text{W}$) and considered only BD* interactions that were π^* in character (some BD* interactions were σ^* in nature and were not part of our analysis). The results were quite revealing.

The sum of all $\Delta E_{i \rightarrow j*}^{(2)}$ (for $\phi_i^{(0)} \rightarrow \phi_{j*}^{(0)}$, based on the criteria previously described) in each complex gave a total of 106.44 kcal mol⁻¹ for $\text{Cr}(\text{CO})_6$, 161.33 kcal mol⁻¹ for $\text{Mo}(\text{CO})_6$; and 231.21 kcal mol⁻¹ for $\text{W}(\text{CO})_6$ (see **Supporting Information SI2** for a list of the individual donor-acceptor energies contributing to these complexes). As a comparison consider the analogous $\phi_i^{(0)} \rightarrow \phi_{j*}^{(0)}$, $\Delta E_{i \rightarrow j*}^{(2)}$ interactions in the other transition metal carbonyl and cyanide complexes of this study. The $\Delta E_{i \rightarrow j*}^{(2)}$ for all of the other carbonyl and cyanide complexes are roughly an order of magnitude smaller than for the Cr, Mo, and W carbonyl complexes. This observation, coupled with the strong occupation deviations from unity for $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ as opposed to $[\text{Mn}(\text{CO})_6]^{2+}$, $[\text{Mn}(\text{CO})_6]^{3+}$, $[\text{Fe}(\text{CO})_6]^{2+}$, $[\text{Fe}(\text{CO})_6]^{3+}$, $[\text{Mn}(\text{CN})_6]^{4-}$, $[\text{Mn}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$ (whose occupations are all close to unity), leads us to conclude that larger $\Delta E_{i \rightarrow j*}^{(2)}$ values for backdonation interactions significantly decrease the occupations of the metal d -orbitals. This phenomena will be the subject of future investigations.

4. Conclusions.

A natural bond orbital theory method for determining the oxidation states of transition metals in a variety of complexes has been presented. There are several

important points that need to be made with respect to this method. (1) This method is a very general one, in that any electronic structure program incorporating NBO analyses can be used. A list of several programs that make use of NBO theory can be found in the **Supporting Information SI7**. (2) One cannot expect occupation numbers that are always unity or zero. There is a subtle range to consider, and that range is influenced by the nature of the ligands attached to the metal center. The biggest factor contributing to large deviations from unity (ca. 0.75 electrons for the $M(CO)_6$ complexes, $M=Cr, Mo, W$) is the presence of strong π^* -acceptor ligands. This phenomena will be explored in future investigations. (3) The method described in this paper (*vida supra*) suggests that if the OS of a TM center can be determined, then the OS of the ligands surrounding the metal can also be determined. We anticipate testing nitrosyl complexes, which are controversial for their ambiguous electron counts in complexes.[53] From there, nuanced arguments may be made to connect the ideas of charge and OS to each other. (4) The OS method described here can also, in theory, be applied to main-group complexes. One example is the fascinating μ^3 -Cu cluster with a bridging S_2 unit.[6, 54, 55] Several heated debates have ensued as to the nature of the S-S bond in this complex, and the NOS method could logically be extended here as a means of clarifying metal and ligand oxidation states.

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Tables

Table 1. NOS, Mulliken, and Löwdin d-orbital occupations from geometry-optimized structures.

spin		occupation numbers (d-orbitals)						OS	Natural Total	Mulliken	Lowdin
[Fe(H ₂ O) ₆] ²⁺	up	0.99	0.99	1.00	1.00	1.00	1.00	Fe(II)	5.97	6.31	6.82
	down	0.02	0.03	0.08	0.09	1.00					
[Fe(H ₂ O) ₆] ³⁺	up	1.00	1.00	1.00	1.00	1.00	1.00	Fe(III)	4.98	5.99	6.44
	down	0.13	0.13	0.13	0.22	0.22					
[Fe(CO) ₆] ²⁺	up	0.53	0.53	0.95	0.95	0.95	0.95	Fe(II)	5.72	7.18	7.49
	down	0.53	0.53	0.95	0.95	0.95	0.95				
[Fe(CO) ₆] ³⁺	up	0.57	0.57	0.98	0.98	0.99	0.99	Fe(III)	4.91	6.83	7.02
	down	0.03	0.50	0.50	0.98	0.98	0.98				
[Fe(CN) ₆] ⁴⁻	up	0.45	0.45	0.96	0.96	0.96	0.96	Fe(II)	5.75	7.14	8.12
	down	0.45	0.45	0.96	0.96	0.96	0.96				
[Fe(CN) ₆] ³⁻	up	0.59	0.59	0.98	0.98	0.98	0.98	Fe(III)	4.88	6.90	7.10
	down	0.06	0.53	0.53	0.97	0.97	0.97				
[MnCl ₄] ²⁻	up	1.00	1.00	1.00	1.00	1.00	1.00	Mn(II)	4.99	5.41	5.66
	down	0.03	0.03	0.07	0.07	0.07					
[MnCl ₅] ²⁻	up	0.68	1.00	1.00	1.00	1.00	1.00	Mn(III)	3.99	5.44	5.71
	down	0.07	0.07	0.11	0.12	0.27					
[Mn(CO) ₆] ²⁺	up	0.48	0.49	0.95	0.95	0.97	0.97	Mn(II)	4.72	6.08	6.37
	down	0.03	0.45	0.46	0.93	0.93	0.93				
[Mn(CO) ₆] ³⁺	up	0.53	0.54	0.98	0.99	0.99	0.99	Mn(III)	3.92	5.72	5.94
	down	0.03	0.03	0.44	0.45	0.97	0.97				
[Mn(CN) ₆] ⁴⁻	up	0.42	0.43	0.95	0.95	0.97	0.97	Mn(II)	4.72	6.02	6.32
	down	0.03	0.38	0.41	0.92	0.92	0.92				
[Mn(CN) ₆] ³⁻	up	0.56	0.57	0.97	0.98	0.98	0.98	Mn(III)	3.89	5.78	6.03

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6		down	0.05	0.05	0.46	0.49	0.95				
7	[Fe(C ₅ H ₅) ₂]	up	0.47	0.47	0.93	0.93	0.99	Fe(II)	5.70	7.23	7.49
8		down	0.47	0.47	0.93	0.93	0.99				
9											
10	[Ru(C ₅ H ₅) ₂]	up	0.50	0.50	0.91	0.91	0.98	Ru(II)	5.59	7.2	7.53
11		down	0.50	0.50	0.91	0.91	0.98				
12											
13	[Os(C ₅ H ₅) ₂]	up	0.49	0.49	0.87	0.87	0.96	Os(II)	5.39	6.91	7.22
14		down	0.49	0.49	0.87	0.87	0.96				
15											
16	[Cr(CO) ₆]	up	0.56	0.56	0.79	0.79	0.79	Cr(0)	4.75	5.56	5.99
17		down	0.56	0.56	0.79	0.79	0.79				
18											
19	[Mo(CO) ₆]	up	0.51	0.51	0.77	0.77	0.77	Mo(0)	4.61	5.49	5.91
20		down	0.51	0.51	0.77	0.77	0.77				
21											
22	[W(CO) ₆]	up	0.50	0.50	0.72	0.72	0.72	W(0)	4.33	5.32	5.65
23		down	0.50	0.50	0.72	0.72	0.72				
24	[CrCl ₆] ³⁻	up	0.43	0.43	0.99	0.99	0.99	Cr(III)	2.98	4.52	4.90
25		down	0.06	0.06	0.06	0.24	0.24				
26											
27	[MoCl ₆] ³⁻	up	0.38	0.39	0.99	0.99	0.99	Mo(III)	2.97	4.53	5.18
28		down	0.13	0.13	0.13	0.31	0.31				
29											
30	[WCl ₆] ³⁻	up	0.35	0.35	0.99	0.99	0.99	W(III)	2.96	4.37	5.16
31		down	0.13	0.13	0.13	0.29	0.29				
32											
33	[Ni(C ₆ F ₅) ₄] ²⁻	up	0.56	0.97	0.98	0.99	0.99	Ni(II)	7.86	8.87	8.99
34		down	0.56	0.97	0.98	0.99	0.99				
35											
36	[Ni(C ₆ F ₅) ₄] ⁻	up	0.77	0.99	0.99	1.00	1.00	Ni(III)	6.95	8.49	8.56
37		down	0.08	0.66	0.98	1.00	1.00				