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Simple, Unambiguous Theoretical Approach to Oxidation State Determination via First-Principles Calculations

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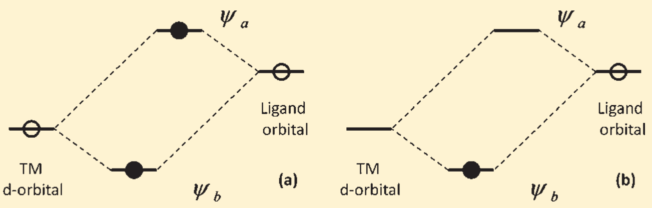
S *Supporting Information*

ABSTRACT: We introduce a novel theoretical approach for determining oxidation states (OS) from quantum-mechanical calculations. For a transition-metal ion, for example, the metal−ligand orbital mixing contribution to the charge allocated to the ion is separated from that due to the actual occupation of the d-orbitals from which OS can then be inferred. We report the application of this approach to different transition-metal systems: molecular complexes, ruthenium-dye molecules, ruthenium complexes with noninnocent ligands, and bulk semiconductors. The computations were carried out using density-functional theory with a Hubbard U correction. The oxidation states were determined without ambiguity.



1. INTRODUCTION

Transition-metal (TM) ions are ubiquitous in enzymatic[1−5] and electro-catalytic[6−8] redox chemistry because of their ability to accommodate a variable number of electrons. The oxidation-state(s) (OS) concept[9,10] formalizes such electron-number variations by assigning an integer number of electrons to each oxidation state of an ion and has often been used to study redox reactions and to identify their intermediates. It allows us to track electron movement during reactions. It facilitates the interpretation of many experimental observations, for example, redox potentials, X-ray absorption and photoemission spectra, bond lengths, spin-states, and Jahn−Teller effects.[9,11−18] Its widespread successful utilization provides it a sound empirical basis. It is important to provide a comparably sound fundamental theoretical basis for the OS concept through its determination by quantum-mechanical calculations, particularly for TM ions.

Numerous methods have been proposed to determine OS theoretically or empirically. Molecular geometry often provides information for characterizing the OS of TM ions in molecular complexes. The Bond-Valence-Sum method,[19−22] for example, relies heavily on empirically determined distance parameters extracted from systems with various bonding environments and known OS of the TM ions. However, problems arise when applying this method to systems with uncommon bonding environments. Since an OS of an ion is a direct consequence of the electronic structure of the system of which it is a part, one would expect that OS can be determined from electronic structure calculations alone. This has led to a deeper question: is the OS a physical observable? In other words, is there a quantum-mechanical operator for the OS? Although such a rigorous quantum-mechanical definition of OS is lacking, there have been many electronic-structure based techniques proposed for OS determination. Such methods often infer the OS of ions from schemes for allocating charges to the ions. Those schemes fall roughly into several distinct categories: among them partition of space with integration of the total charge density within the space allocated to each atom or ion, for example, Bader[23] or Voronoi[24] charges; projection techniques, for example, Mulliken charges,[25] Löwdin charges,[26] or natural bond orbitals (NBO);[27] and matching techniques aimed at allocating charges to reproduce a computed property of the system, for example, electrostatic potential (ESP)[28] or restrained electrostatic potential (RESP).[29] In the partition schemes, all orbitals contribute in principle to the charge within the allocated volume, thereby losing the connection to the OS of individual ions. In projection schemes, there is basis-set dependence, dependence on the projection techniques, and dependence on cutoffs used in some methods. In the matching schemes, there is no clear connection between the property matched and the oxidation state, for example, the electrostatic potential surfaces. While these calculated electronic populations can sometimes give an indication of the OS, the noninteger values for allocated charges and their changes are usually significantly smaller than the proposed formal integer OS and their changes during redox reactions.[9,30] Assigning OS using these approaches often faces ambiguity even after careful calibration and can sometimes lead to wrong results.[30,31]

Raebiger et al.[30] argued that this diminished change in the allocated charge when the OS changes is a consequence of a 'negative feedback' mechanism in the metal−ligand orbital mixing between orbitals of the TM ion and those of the surrounding

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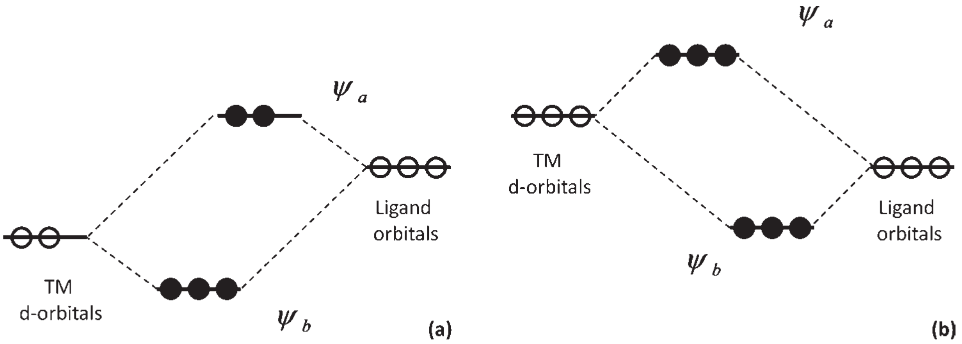

Figure 1. TM orbitals mixing with ligand orbitals. The outer levels are those before orbital mixing, and their occupancy is indicated by open circles. The inner levels are those after orbital mixing, and their occupancy is indicated by solid circles. **a.** (left, *n* electrons initially on the TM ion) When the energy of the TM level is lower than that of the ligand level, the bonding orbital (ψ_b) has a strong TM character, and the antibonding orbital (ψ_a) forms mostly from the ligand orbitals. **b.** (right, *n* + 1 electrons initially on the TM ion) Charge doping causes the TM levels and, consequently, the bonding and antibonding levels to shift upward in energy. The atomic TM level rises relative to the ligand level, and the relative weight of the bonding orbitals shifts toward the ligands (see also ref 30).

atoms. They suggested that any gain in local electron density when a TM ion is reduced is compensated by the decrease in electron donation from neighboring atoms to the TM ion, and vice versa. It has also been shown[31] that the allocated charges depend greatly on the natures of the surrounding ligands and have less to do with the formal oxidation states of the TM ions. This leads to the conclusion that the allocated charge is a poor measure of the oxidation state of TM ions.[31]

Recently, Thom et al.[32] introduced the localized-orbital bonding analysis (LOBA) method for OS determination. In this method, optimally localized orbitals are projected onto the atomic basis functions of a TM ion. The electron corresponding to a localized orbital is allocated to the ion when the projection exceeds a certain percentage. The percentage is determined by sampling a series of transition-metal complexes with known OS. This method provides a pragmatic way to determine OS and has been shown to work in a series of transition-metal complexes and a Mn-based oxygen-evolving catalyst.[32] However, there is no rigorous theory to support the choice of the cutoff percentage.

The absence of a rigorous quantum-mechanical theory of OS has opened to questioning the status of OS as a physical quantity.[30] OS could be merely a 'bookkeeping tool'[30] for a set of experimental properties and could have no physical meaning itself.[30] In view of this controversy, we propose here a novel theory of OS. An unambiguous computational method is derived from the theory for determining the OS of TM ions. The method allows us to separate the contribution from metal−ligand orbital mixing to the charge allocated to an ion from that due to the actual occupation of its d-orbitals, as only the latter determines the OS. The paper is organized as follows. In section 2, we discuss in detail the novel theory of OS and the computational method for determining OS. In section 3, we apply the method to several TM systems: molecular complexes, bulk semiconductors, ruthenium-dye molecules and ruthenium complexes with noninnocent ligand(s) (NIL). In section 4, we investigate some discrepancies found by our method and their possible causes. We offer further observations and present our conclusions in section 5.

2. THEORETICAL ANALYSIS OF OS

2.1. Negative Feedback Mechanism. Charges allocated to TM ions calculated by projection approaches like the Mulliken and Löwdin population analysis are known to exhibit small changes in redox processes.[5,33−36] Raebiger et al.[30] attributed this tendency to maintain constant local charges under external perturbation to a negative feedback mechanism in the mixing between the TM d-orbitals and the ligand orbitals. They illustrate this idea by considering a TM ion impurity embedded in a host crystal. The TM d-orbitals originally occupied by *n* electrons split into crystal field levels of different irreducible representations (for cubic symmetry the orbitals of the levels have the representations t_{2g} (triply degenerate) and e_g (doubly degenerate)). The irreducible orbitals of the TM mix with the irreducible ligand orbitals of the same representation and spin to produce bonding (ψ_b) and antibonding (ψ_a) orbitals (Figure 1a). When the energy of the TM level is lower than that of the ligand level, the bonding orbitals have a strong TM character, and the antibonding orbitals form mostly from the ligand orbitals. The reverse occurs when the energy of the TM level is higher than that of the ligand level. Population analysis performed on the TM ion will inevitably give an allocated charge that contains contributions from both the fully occupied d-orbitals and the mixed ligand orbitals.

When the TM ion of Figure 1a is doped with an extra electron, the level occupancy of the TM-induced mixed states increases (Figure 1b). Such charge doping causes the TM levels and, consequently, the bonding and antibonding levels to shift up in energy. The atomic TM level rises relative to the ligand level, and so the relative weight of the bonding orbitals shifts toward the ligands. This negative feedback causes a depopulation of TM charge in the bonding states, counter-balancing the increase due to the doping charge. As a result of this self-regulated response, the net local charge at the TM site remains approximately constant.[30]

Raebiger et al.[30] presented first-principles calculations to support their argument quantitatively and thereby explained the decoupling between local charges and OS. The authors concluded that the OS concept is merely a "bookkeeping tool", a claim that has stirred significant controversy.[9,31,37] We introduce here a novel method for determining the OS of TM ions from first-principles calculations. Backed by a sound theoretical framework for defining OS, this method allows us to determine OS in TM systems in a clear and simple way, contributing to the resolution of the controversy.

2.2. A Novel Approach. In the special case of an isolated TM ion, the OS is unambiguously defined as the nuclear charge minus the number of electrons in the ion. When ligands are

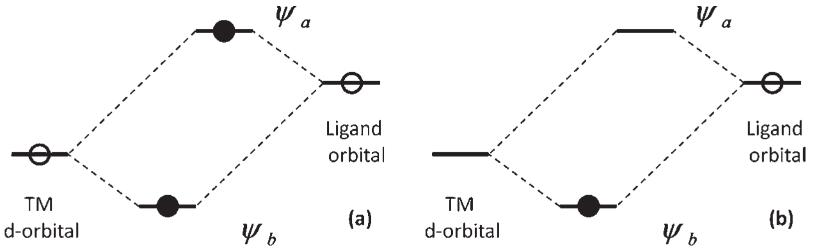

Figure 2. **a.** (left) Fully occupied bonding and antibonding orbitals formed from occupied TM d- and ligand orbitals. **b.** (right) A fully occupied bonding orbital and an empty antibonding orbital formed from an empty TM d-orbital and an occupied ligand orbital. Open circles on the outer levels indicate occupancy before orbital mixing, solid circles on the inner levels after orbital mixing.

brought close to this ion, mixing between the ligand orbital and the TM orbitals makes it difficult to assign the correct number of electrons to the ion. Moreover, as explained above, mixing with the ligand orbitals tends to keep the charge allocated to the ion nearly constant even when there is an integer change in OS. Just as for the isolated ion, it is the actual d-orbital occupation of the ion in the complex from which its OS is to be inferred and not from its allocated charge. Our proposed method aims to separate out the contribution to the allocated charge due to metal−ligand orbital mixing, leaving the desired d-orbital occupancy. This is achieved by establishing a connection between the isolated ion and the same ion surrounded by ligands. Since the OS is known in the isolated ion case, we can unambiguously determine the OS of TM ions in various chemical environments through this connection.

Consider a relatively weakly bound TM−ligand complex in which bonding ψ_b and antibonding ψ_a orbitals can be accurately represented as the linear combinations of an atomic d-orbital ϕ_d and an isolated ligand orbital ϕ_l, which has been orthogonalized to ϕ_d via the Gram-Schmidt procedure[38]

$$\psi_b = \alpha\phi_d + \beta\phi_l \tag{1}$$

$$\psi_a = \beta^*\phi_d - \alpha^*\phi_l \tag{2}$$

The coefficients α and β satisfy the normalization criterion, $|\alpha|^2 + |\beta|^2 = 1$. The magnitudes of α and β depend on the relative energies of the TM and ligand levels. If the TM d-orbital is lower in energy than the ligand orbital, the bonding orbital, ψ_b, will have a larger contribution from ϕ_d and a smaller contribution from ϕ_l, and vice versa.

When an originally occupied d-orbital mixes with a ligand orbital (which is also occupied), as in Figure 2a, both bonding (ψ_b) and antibonding (ψ_a) states are occupied, irrespective of whether the occupied d level lies above or below the ligand level. The occupation number of a d-orbital is the projection of all occupied orbitals onto the atomic d-orbital of the TM. In the simple case that involves one d-orbital and one ligand orbital, the occupation number is the sum of the projection of the bonding and antibonding states on the d-orbital. This number is always 1 (eq 3) when both bonding and antibonding states are occupied (Figure 2a), robust against any degree of mixing. As the occupation number is 1, the d-orbital retains the full occupancy it had before the orbital mixing:

$$\begin{aligned}\text{occupation number for full occupancy}\\ &= \langle\psi_b|\phi_d\rangle\langle\phi_d|\psi_b\rangle + \langle\psi_a|\phi_d\rangle\langle\phi_d|\psi_a\rangle\\ &= |\alpha|^2 + |\beta|^2 = 1\end{aligned} \tag{3}$$

One electron should then be included in the electron count from which the OS of the ion is determined.

On the other hand, when an originally unoccupied d-orbital mixes with a ligand orbital (Figure 2b), only the bonding state is occupied, irrespective of whether the unoccupied d level lies above or below the ligand level. The same projection procedure on the d-orbital gives an occupation number smaller than 1 (eq 4) which originates entirely from orbital mixing. Consequently, this partial occupancy does not contribute to the electron count for the OS, for which purpose we say that this d-orbital is unoccupied.

$$\begin{aligned}\text{occupation number for partial occupancy}\\ &= \langle\psi_b|\phi_d\rangle\langle\phi_d|\psi_b\rangle = |\alpha|^2 < 1\end{aligned} \tag{4}$$

Thus, from the occupation numbers calculated, we are able to distinguish full occupancy of d-orbitals from the contribution to the local charges from orbital mixing giving rise to partial occupancy. Counting the number of d-electrons in the ion in this way allows us to determine the OS of the ion. This conclusion holds as well when more than one ligand orbital can mix with a d-orbital only when all ligand orbitals are empty or full. The intermediate case is discussed in section 4 in connection with the effect of pi back-donation.

We now generalize the above argument to apply to all d-orbitals of the ion. We define a 5 × 5 occupation matrix ($n^\sigma_{mm'}$) by projecting the first-principles eigenfunctions (ψ^σ_v) of the system onto the 5 atomic d-orbitals (ϕ_m) of the TM ion (eq 5)

$$n^\sigma_{mm'} = \sum_\nu \langle\psi^\sigma_\nu|\phi_{m'}\rangle\langle\phi_m|\psi^\sigma_\nu\rangle \tag{5}$$

where m,m′ label the 5 orthonormal orbitals of the d-manifold. Only in spin-polarized situations does the occupation matrix depend on the spin index σ. Parallel to eqs 3 and 4, occupation numbers can be defined as the eigenvalues of the 5 × 5 occupation matrix. In the same manner, assignment of an electron to the TM ion is based on the value of the occupation number. If an occupation number equals 1, one d-orbital is said to be fully occupied, and we assign one d-electron to the TM ion. If the occupancy is less than 1, one d-orbital is partially occupied which partial occupancy comes from an originally empty d-orbital mixed with ligand orbitals. Therefore, no electron pertaining to that occupation number is assigned to the TM ion. By counting the number of d-orbitals with full occupancy, we are able to determine the actual number of d-electrons to be assigned to the ion and to determine the OS unambiguously. This definition of the occupation matrix and of the occupation numbers as its eigenvalues means that the method is insensitive to the choice of the orthonormal d-orbitals.

The procedure for determining the OS is

(1) Calculate the wave functions of the TM system by the first-principles technique of choice.

Table 1. Computed Hubbard *U* Values[43] Used, the Spin-up and Spin-down d-Orbital Occupation Numbers, the OS of the Fe Ions, and the d-Orbital Löwdin Populations for Fe Complexes in Two Different Charge States with H_2O, Cl^-, CO, and CN^- as Ligands[a]

	U value (eV)	spin	occupation numbers (d-orbitals)					OS	Löwdin
$[Fe(H_2O)_6]^{2+}$	5.6	up	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	Fe(II)	6.09
		down	0.02	0.02	0.08	0.09	**0.98**		
$[Fe(H_2O)_6]^{3+}$	5.6	up	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	Fe(III)	5.54
		down	0.07	0.07	0.08	0.24	0.24		
$[FeCl_6]^{4-}$	6.8	up	**0.99**	**0.99**	**1.00**	**1.00**	**1.00**	Fe(II)	6.12
		down	0.02	0.03	0.10	0.12	**0.96**		
$[FeCl_6]^{3-}$	5.3	up	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	Fe(III)	5.80
		down	0.05	0.05	0.05	0.39	0.39		
$[Fe(CO)_6]^{2+}$	9.7	up	0.27	0.27	**0.96**	**0.96**	**0.96**	Fe(II)	6.47
		down	0.27	0.27	**0.96**	**0.96**	**0.96**		
$[Fe(CO)_6]^{3+}$	8.6	up	0.60	0.61	**0.97**	**0.97**	**0.98**	Fe(III)	6.36
		down	0.01	0.35	0.35	**0.96**	**0.96**		
$[Fe(CN)_6]^{4-}$	9.7	up	0.22	0.22	**0.97**	**0.97**	**0.97**	Fe(II)	6.41
		down	0.22	0.22	**0.97**	**0.97**	**0.97**		
$[Fe(CN)_6]^{3-}$	8.5	up	0.62	0.62	**0.96**	**0.96**	**0.97**	Fe(III)	6.47
		down	0.02	0.42	0.42	**0.95**	**0.95**		

[a] The occupation numbers for full occupancy are shown in bold.

(2) Obtain a 5 × 5 occupation matrix ($n^{\sigma}_{mm'}$) for each spin by projecting the wave functions onto the atomic d-orbitals of the TM ion.
(3) Calculate the occupation numbers as the eigenvalues of the occupation matrix.
(4) Set the number of d-orbitals with full occupancy (i.e., occupation number =1) as the number of d electrons assigned to the ion.
(5) Determine the OS of the TM ion from the number of d-electrons assigned to it in step 4.

This theoretical approach for OS determination also provides a foundation for the use of an occupation matrix eigenvalue as an order parameter in computing diabatic free-energy surfaces for electron-transfer reactions as in a previous work[39] by one of the authors.

We show in the next section the results of applying the method to different TM systems using DFT as the first-principles computation method. The method is available in the PW code of the Quantum-ESPRESSO package.[40] However, the applicability of this method does not depend on the choice of first-principles techniques, and the method can be implemented in any electronic-structure code by following the above 5 steps.

3. EXAMPLES

The systems we studied include transition-metal molecular complexes, crystalline transition-metal semiconductors, and ruthenium-dye, and ruthenium-NIL molecules. Calculations were performed with the PW code of the Quantum-ESPRESSO package[40] within the framework of density-functional theory at the GGA-PBE level of theory. For the calculations on molecular complexes, ruthenium dyes, ruthenium-NIL molecules, and pyrite, we employed ultrasoft pseudopotentials[41] with plane-wave expansions of the soft part of the Kohn−Sham wave functions and of the charge density up to a kinetic-energy cutoffs of 25 and 200 Ry, respectively. We also employed ultrasoft pseudopotentials in TiO_2 calculations, but higher kinetic-energy cutoffs of 40 and 400 Ry were used. Norm-conserving pseudopotentials were used in Co_3O_4 calculations with cutoffs of 120 and 480 Ry. A Hubbard-U correction[42,43] was adopted to provide an improved description of the strongly correlated electron charge around the transition-metal center. The Hubbard U values were calculated by the first-principles linear-response procedure.[43] The calculations for TM molecular complexes, ruthenium dyes and ruthenium complexes with NIL were performed in cubic unit cells of edge 10.6, 15.9, and 15.9 Å, respectively, with Γ-point sampling. The calculations for bulk semiconductors were done in their respective primitive unit cells with the experimental cell sizes. A *k*-point sampling mesh of 8 × 8 × 8 was used in these calculations. The atomic d-orbitals were computed for the isolated ions at the GGA-PBE level.

For Fe complexes in two different charge states with H_2O, Cl^-, CO, and CN^- as ligands, Table 1 shows the spin-up and spin-down d-orbital occupation numbers and the OS of the Fe ions obtained from the approach described above, as well as the Hubbard U values used. The corresponding Löwdin populations are also shown. The Fe OS were found to agree in all cases with the formal OS obtained according to the rules set in the IUPAC gold book.[10] Take the $[Fe(H_2O)_6]^{2+}$cluster as an illustrative example. All five spin-up d-orbitals have full occupancy; we therefore assign all five spin-up electrons to the Fe ion. For the spin-down orbitals, one occupation number is close to 1 (0.98), and the other four are significantly smaller and due to orbital mixing. We therefore assign one spin-down d-electron to the ion. Such small deviations of the occupation numbers from 1 are due mainly to the distortion of the atomic d-orbitals in the presence of the ligand fields, the measure of which we take as the extent to which the 5-fold degeneracy of the atomic d-level is lifted. We discuss this in detail in section 4. With this counting procedure, we find that there are five spin-up d-orbitals and one spin-down d-orbital with full occupancy. There are, therefore, six d-electrons assigned to the ion, giving an OS of II which is the formal OS for this cluster. Our approach gives the correct spin state ($S = 2$) of the complex as well. With CO and CN^- ligands, the occupation numbers of the fully occupied d-orbitals deviate more from 1. This likely arises from their stronger ligand fields and larger orbital mixing which induce low spin and larger distortions in the atomic d-orbitals. The presence of pi back-donation in these complexes can also be a contributing factor. However, such discrepancies do not introduce any ambiguity in the OS assignments in the cases studied since there are sufficiently distinct differences between occupation numbers for full and partial occupancy.

The Löwdin populations are reported only for the d-orbitals. Since the Löwdin populations contain significant contributions from ligand orbitals mixed with empty d-orbitals, the numbers are not indicative of the actual number of d-electrons the Fe ions have. Our results agree with the recent suggestion that populations calculated with projection methods are highly dependent on the ligands involved; the values obtained are consequently related less to the OS of the ion.[31]

The Hubbard U values of 8.5−9.7 eV calculated for the low-spin $[Fe(CO)_6]$ and $[Fe(CN)_6]$ complexes are considerably larger than the range of U values for Fe complexes typically reported in the literature.[5,44−47] This is consistent with our experience with some low-spin complexes.[48] Consequently, we examined the effect of the Hubbard U correction on the results by performing PBE calculations without a Hubbard U present on the $[Fe(H_2O)_6]$, $[Fe(CO)_6]$, and $[Fe(CN)_6]$ complexes. The results are shown in Table 2. In the $[Fe(H_2O)_6]$ cases, the occupation numbers for full occupancy show no significant change from the PBE+U calculations. However, the occupation numbers counted as full occupancy in the cases of $[Fe(CO)_6]$ and $[Fe(CN)_6]$ drop to as low as 0.85. This larger departure from 1 is due to a lack of self-interaction correction in PBE calculations which leads to excess delocalization of the d-electron wave functions. The consequences of this delocalization are discussed further in section 4. Nevertheless, despite these larger discrepancies, the differences between occupation numbers assigned to full occupation and those to partial occupation numbers are at least 0.31 in all the cases shown. More important, the difference from unity in all cases in which full occupancy is assigned is much smaller than all cases in which partial occupancy is assigned, and there is no need to assign an arbitrary cutoff. Our approach therefore introduces no ambiguity to OS determination.

Table 2. Spin-up and Spin-down d-Orbital Occupation Numbers and the OS of the Fe Ions, and the d-Orbital Löwdin Populations for Fe Complexes in Two Different Charge States with H_2O, Cl^-, CO, and CN^- as Ligands from Standard PBE Calculations[a]

	spin	occupation numbers (d-orbitals)					OS	Löwdin
$[Fe(H_2O)_6]^{2+}$	up	**0.99**	**0.99**	**0.99**	**1.00**	**1.00**	Fe(II)	6.18
	down	0.04	0.04	0.13	0.15	**0.97**		
$[Fe(H_2O)_6]^{3+}$	up	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	Fe(III)	5.75
	down	0.13	0.14	0.14	0.26	0.26		
$[Fe(CO)_6]^{2+}$	up	0.54	0.54	**0.85**	**0.85**	**0.85**	Fe(II)	6.70
	down	0.54	0.54	**0.85**	**0.85**	**0.85**		
$[Fe(CO)_6]^{3+}$	up	0.59	0.59	**0.93**	**0.93**	**0.95**	Fe(III)	6.43
	down	0.07	0.53	0.53	**0.90**	**0.90**		
$[Fe(CN)_6]^{4-}$	up	0.53	0.53	**0.85**	**0.85**	**0.85**	Fe(II)	6.70
	down	0.53	0.53	**0.85**	**0.85**	**0.85**		
$[Fe(CN)_6]^{3-}$	up	0.61	0.61	**0.92**	**0.92**	**0.94**	Fe(III)	6.50
	down	0.13	0.55	0.55	**0.89**	**0.89**		

[a] The occupation numbers for full occupancy are shown in bold.

Table 3 shows for [MnCl], [MnCO], and [MnCN] complexes in two different charge states the occupation numbers, the OS of Mn ions, the Hubbard U values, and the d-orbital Löwdin populations. As for the Fe cases, the calculations for the [MnCl] complex give occupation numbers for full occupancy very close to 1. The deviation from unity of the computed eigenvalue (0.79) of the fifth spin-up orbital, 0.21, for $[MnCl_5]^{2-}$ is so much larger than those of the other, fully occupied spin-up orbitals that we can treat it with confidence as partially occupied, and omit it from the electron count. The Hubbard U values obtained in these calculations are in the moderate range. On the other hand, the calculations for the [MnCO] and [MnCN] complexes show larger deviations from one of the occupation numbers for full occupancy, as in the corresponding Fe cases. Nevertheless, our approach to OS determination unequivocally yields OS which agree with the formal OS of Mn in these complexes, as shown by Table 3.

Table 4 shows the results of applying our approach to the crystalline transition-metal semiconductors pyrite (FeS_2), TiO_2 (anatase and rutile), and Co_3O_4. In pyrite, it is known that the two S ions in each unit are covalently bonded to each other forming an S_2^{2-} ion.[49] The formal OS of Fe is therefore II. Löwdin population analysis shows that there are 7.04 d-electrons

Table 3. Computed Hubbard *U* Values[43] Used, the Spin-up and Spin-down d-Orbital Occupation Numbers, the OS of the Mn Ions, and the d-Orbital Löwdin Populations for Mn Complexes in Two Different Charge States with Cl^-, CO, and CN^- as Ligands[a]

	U value (eV)	spin	occupation numbers (d-orbitals)					OS	Löwdin
$[MnCl_4]^{2-}$	4.7	up	**0.99**	**0.99**	**0.99**	**0.99**	**0.99**	Mn(II)	5.12
		down	0.03	0.03	0.07	0.07	0.07		
$[MnCl_5]^{2-}$	5.4	up	0.79	**0.99**	**0.99**	**1.00**	**1.00**	Mn(III)	5.06
		down	0.05	0.05	0.06	0.11	0.22		
$[Mn(CO)_6]^{2+}$	8.2	up	0.27	0.28	**0.95**	**0.96**	**0.97**	Mn(II)	5.37
		down	0.01	0.22	0.23	**0.94**	**0.94**		
$[Mn(CO)_6]^{3+}$	7.4	up	0.55	0.60	**0.97**	**0.98**	**0.98**	Mn(III)	5.20
		down	0.01	0.01	0.27	0.27	**0.94**		
$[Mn(CN)_6]^{4-}$	7.5	up	0.29	0.29	**0.95**	**0.95**	**0.97**	Mn(II)	5.42
		down	0.01	0.23	0.23	**0.93**	**0.93**		
$[Mn(CN)_6]^{3-}$	7.5	up	0.58	0.63	**0.97**	**0.98**	**0.98**	Mn(III)	5.32
		down	0.02	0.02	0.32	0.34	**0.93**		

[a] The occupation numbers for full occupancy are shown in bold. Note that Mn^{2+} and Mn^{3+} are, respectively, four- and five-fold coordinated by Cl^- in the optimized configurations.

Table 4. Computed Hubbard *U* Values[43] Used, the Spin-up and Spin-down d-Orbital Occupation Numbers, the OS of the TM Ions, and the d-Orbital Löwdin Populations for Several Crystalline Transition-Metal Semiconductors[a]

	U values (eV)	spin	occupation numbers (d-orbitals)					OS	Löwdin
FeS_2	6.9	up	0.45	0.45	**0.95**	**0.95**	**0.96**	Fe(II)	7.04
		down	0.45	0.45	**0.95**	**0.95**	**0.96**		
TiO_2 (anatase)	0.0	up	0.31	0.31	0.32	0.48	0.48	Ti(IV)	2.28
		down	0.31	0.31	0.32	0.48	0.48		
TiO_2 (rutile)	0.0	up	0.28	0.30	0.31	0.48	0.50	Ti(IV)	2.25
		down	0.28	0.30	0.31	0.48	0.50		
high spin Co in Co_3O_4	4.4	up	**0.99**	**0.99**	**0.99**	**0.99**	**0.99**	Co(II)	7.29
		down	0.22	0.22	0.22	**0.99**	**0.99**		
low spin Co in Co_3O_4	6.7	up	0.51	0.51	**0.99**	**0.99**	**0.99**	Co(III)	7.51
		down	0.51	0.51	**0.99**	**0.99**	**0.99**		

[a] The occupation numbers for full occupancy are shown in bold.

Table 5. Computed Hubbard *U* Values[43] Used, the Spin-up and Spin-down d-Orbital Occupation Numbers, the OS of the Ru Ions, and the d-Orbital Löwdin Populations for Four Ruthenium-Dye Molecules[a]

	U values (eV)	spin	occupation numbers (d-orbitals)					OS	Löwdin
$[Ru(2bpy\text{-}2NCS)]^0$	5.1	up	0.57	0.58	**0.91**	**0.96**	**0.97**	Ru(II)	7.04
		down	0.57	0.58	**0.91**	**0.96**	**0.97**		
$[Ru(2bpy\text{-}2NCS)]^{1+}$	4.7	up	0.59	0.60	**0.95**	**0.97**	**0.98**	Ru(III)	6.96
		down	0.58	0.60	0.72	**0.96**	**0.97**		
$[Ru(3bpy)]^{2+}$	4.8	up	0.57	0.57	**0.94**	**0.94**	**0.97**	Ru(II)	7.10
		down	0.57	0.57	**0.94**	**0.94**	**0.97**		
$[Ru(3bpy)]^{3+}$	4.1	up	0.66	0.66	**0.98**	**0.98**	**0.99**	Ru(III)	6.73
		down	0.11	0.62	0.63	**0.97**	**0.97**		

[a] The occupation numbers for full occupancy are shown in bold.

on each Fe ion. We cannot infer unambiguously from this number the OS of Fe. However, our counting approach shows that there are three spin-up and three spin-down d-electrons on Fe so that the OS of Fe is II. It also shows that there is no net spin on Fe, which agrees with the experiment.[50] Applying our approach to TiO_2 shows that there is no full d-orbital occupancy in Ti in both the anatase and rutile structures. The OS of Ti is therefore IV in both cases. Note that no Hubbard U correction was applied to the TiO_2 calculations since the Ti ions are believed to have no d-electrons. Our results confirm this.

The Co ions in Co_3O_4 are expected to have two different OS, II and III.[51] The Co(II) ions are in a high-spin state ($S = 3/2$) in an antiferromagnetic arrangement, while the Co(III) ions are nonmagnetic. The Co(II)/Co(III) ratio is 1:2, yielding charge neutrality with oxygen in the O^{2-} state. Our DFT calculations show that there are indeed two sets of Co ions, one magnetic and the other nonmagnetic. By counting d-orbitals with full occupancy, the high-spin Co ions have five spin-up and two spin-down d-electrons, indicative of an OS of II. The nonmagnetic species have three spin-up and three spin-down d-electrons, leading to an OS of III. The Löwdin population analysis wrongly suggests that the Co(III) species has more d-electrons than the Co(II) counterpart. There is an unexpectedly larger Löwdin population on the Co(III) ions because they are coordinated by six O ions, whereas the Co(II) ions are 4-fold coordinated. The reduction of the d-electron population assigned to the Co(III) ions by the OS of III is overcompensated by the gain from mixing with orbitals of more O ions.

Ruthenium-dye molecules have been extensively studied[52−56] in recent years because of their promising use in solar cells where they form part of an electron-transfer system. OS changes are key to the understanding of such electron-transfer systems. We examine here two of the most extensively studied dye molecules, Ru(2bpy-2NCS) and Ru(3bpy) in different charge states. We find, Table 5, that in $[Ru(2bpy\text{-}2NCS)]^0$, Ru has three spin-up and three spin-down d-orbitals with full occupancy and an OS of II. For $[Ru(2bpy\text{-}2NCS)]^{1+}$ molecule, we find five fully occupied d-orbitals and an OS of III. For $[Ru(3bpy)]^{2+}$, our results show that there are six fully occupied d-orbitals and an OS of II. For $[Ru(3bpy)]^{3+}$, there are five d-electrons and an OS of III. These results all agree with the formal OS of Ru in these molecules.

Noninnocent ligands (NIL) are redox-active ligands that can attain different charge states. One well-known example is a bidentate ligand comprised of 1,2-disubstituted phenylene subunits (Figure 3). This type of ligand can have three possible charge states (NIL^{Red}, $NIL^{\bullet}$, and NIL^{Ox}) related by one-electron redox transformations. Many studies have been performed on NIL due to their intriguing electronic properties.[57−63] In particular, Boyer et al.[64] have recently conducted an extensive review of a wide variety of ruthenium-NIL complexes. These Ru-NIL complexes can exhibit OS configurations related by the intramolecular transfer of electrons between the NIL and the Ru ion. Which is the ground-state OS configuration among them is sensitive to substituent effects on the NIL and the choice of ancillary ligands.

We examine here three examples of Ru−NIL complexes, $[Ru(C_6H_4O_2)(PMe_3)_4]^0$ $[Ru(Br_4C_6O_2)(PPh_3)_2(CO)_2]^0$ and $[Ru(Br_4C_6O_2)(PPh_3)_2(CO)_2]^{1+}$. In $[Ru(C_6H_4O_2)(PMe_3)_4]^0$, the Ru ion is 6-fold coordinated by the bidentate NIL and the four ancillary ligands of trimethylphosphine (PMe_3). Three OS configurations, Ru(II)-NIL^{Red}, Ru(I)-NIL$^{•}$, and Ru(0)-NIL^{Ox}, are possible in this neutral complex. We found, Table 6, that the Ru ion has three spin-up and three spin-down d-orbitals with full occupancy, the OS is therefore II. This OS assignment also agrees with previous assignments based on the C−O bond lengths of the NIL.[64,65] In $[Ru(Br_4C_6O_2)(PPh_3)_2(CO)_2]^0$, four hydrogen atoms in the previous NIL are substituted by bromine atoms. The four ancillary ligands are two triphenylphosphine (PPh_3) molecules and two CO. Our results show that the Ru ion is in the low-spin state with six fully occupied d-orbitals and an OS of II. Interestingly, one-electron oxidation of this complex also yields the Ru OS of II as shown in Table 6. There is essentially no change in the d-orbital occupation numbers when $[Ru(Br_4C_6O_2)(PPh_3)_2(CO)_2]^0$ is oxidized to $[Ru(Br_4C_6O_2)(PPh_3)_2(CO)_2]^{1+}$. It can be concluded that the electron is removed from the redox-active NIL ligand during oxidation instead of from the Ru ion. This Ru(II)-NIL^{Red} to Ru(II)-NIL• oxidation has also been observed experimentally,[66] confirming our theoretical OS assignments.

4. REASONS FOR DEVIATION FROM UNITY OF OCCUPATION NUMBERS FOR FULL OCCUPANCY

In the examples shown above, occupation numbers for full occupancy are often smaller than 1. We discuss here several possible causes for this discrepancy. First, the assumption should be questioned that the atomic d-orbitals and the isolated ligand orbitals orthogonalized to them constitute an adequate basis for the bonding and the antibonding orbitals in eqs 1 and 2. Weaker validity of this assumption is expected in systems with larger ligand fields and orbital mixing, and therefore a larger lifting of the 5-fold degeneracy of the atomic d-levels. The spin state depends on how that splitting compares with the less sensitive exchange and direct Coulomb interactions. When the splitting due to ligand-field and orbital mixing exceeds those interactions, a low-spin state is favored. The reverse favors a high-spin state. Therefore, there should be a correlation between the spin state and the deviations from unity: low spin implies higher deviations; high spin implies lower deviations. That correlation is precisely what is found in Tables 1 and 3. The occupation numbers for full occupancy deviate more from unity for CO and CN^- as ligands, the low-spin cases, than for H_2O or Cl^- as ligands, the high-spin cases.

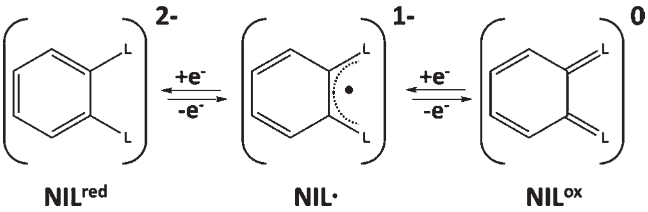

Figure 3. Redox transformation of a bidentate 1,2-disubstituted phenylene NIL ligand, where L = O in this work.

After projection of the atomic d-orbital from the corresponding Kohn−Sham bonding and antibonding orbitals, the normalized residual functions would be the orthogonalized unperturbed ligand function in both cases only if the assumption holds that the unperturbed orbitals form an adequate basis. However, the orbital mixing itself distorts the Kohn−Sham orbitals away from the simple linear combinations of eqs 1 and 2 because of the shifts of the Kohn−Sham eigenenergies from the unperturbed levels. We show in section SI1 of the Supporting Information (SI) that this effect reduces the fully occupied eigenvalues below unity, the larger the orbital mixing the larger the deviation in agreement with the findings summarized in the previous paragraph. Nevertheless, it is possible to determine a set of optimal, d-like orbitals from the atomic d-orbitals and the KS bonding and antibonding orbitals corresponding to each, as shown in section SI2 of the SI. When those distorted d-like orbitals are used to construct the occupation matrix, the fully occupied eigenvalues become unity. Because this discrepancy is well understood, our counting procedure gives no ambiguity to the OS assignments. For all the chemical environments studied, the atomic orbitals of isolated atoms are adequate to use as basis functions in our method.

Another possible cause, although less important, is that 3d antibonding orbitals can come close in energy to the atomic 4s and 4p orbitals and mix with them in the presence of a Jahn−Teller effect. Hybridization among them could lead to electrons leaking to the 4s and 4p states. To eliminate this possible source of errors, one could include the 4s and 4p orbitals in constructing the occupation matrix. Occupation numbers can then be obtained from the eigenvalues of this 9 × 9 occupation matrix including the 4s and 4p states. We took as an example the $[Mn(CN)_6]^{4-}$ complex to investigate the magnitude of this error. The two spin-down occupation numbers for full occupancy in the $[Mn(CN)_6]^{4-}$ complex are 0.93 and 0.93 which show the largest deviation from one among all Mn molecular complexes. With the inclusion of the 4s and 4p states, the two spin-down occupation numbers for full occupancy remain 0.93 and 0.93. These negligible changes show that the effects from the hybridization between 3d and higher orbitals of the ion are insignificant in the $[Mn(CN)_6]^{4-}$ complex. However, in cases when such an effect is significant, occupation numbers can be obtained from an occupation matrix by including more atomic orbitals of the ion.

When the d-ligand mixing is relatively large or an empty ligand orbital lies relatively low in energy, pi back-donation can occur for a d-orbital of relevant symmetry. In that case, the occupied

Table 6. Computed Hubbard *U* Values[43] Used, the Spin-up and Spin-down d-Orbital Occupation Numbers, the OS of the Ru Ions, and the d-Orbital Löwdin Populations for Three Ruthenium−NIL Complexes[a]

	U values (eV)	spin	occupation numbers (d-orbitals)					OS	Löwdin
$[Ru(C_6H_4O_2)(PMe_3)_4]^0$	6.0	up	0.65	0.73	**0.95**	**0.95**	**0.96**	Ru(II)	7.57
		down	0.65	0.73	**0.95**	**0.95**	**0.96**		
$[Ru(Br_4C_6O_2)(PPh_3)_2(CO)_2]^0$	6.3	up	0.67	0.76	**0.91**	**0.94**	**0.94**	Ru(II)	7.32
		down	0.67	0.76	**0.91**	**0.94**	**0.94**		
$[Ru(Br_4C_6O_2)(PPh_3)_2(CO)_2]^{1+}$	6.3	up	0.65	0.76	**0.92**	**0.94**	**0.94**	Ru(II)	7.34
		down	0.66	0.77	**0.92**	**0.93**	**0.94**		

[a] The occupation numbers for full occupancy are shown in bold.

bonding and antibonding orbitals are admixtures of three orbitals, one occupied d-orbital, one occupied ligand orbital, and one unoccupied ligand orbital. Our procedure can then yield occupation numbers less than unity. Pi back-donation can thus be a contributing factor to the reduction below unity in those cases where mixing is expected to be stronger. Nevertheless, the occupation numbers of the optimal d-type orbitals described in Supporting Information section SI2 remain unity. At issue then is whether the orbital mixing is not so strong that the optimal d-type orbital resembles the atomic d-orbital closely enough for the oxidation state concept to be meaningful.

Spurious self-interactions in DFT can also contribute to the discrepancy. Self-interactions are more significant for the strongly localized d-electrons on which they have two effects. First, they artificially delocalize the d-electrons to reduce the magnitude of the self-interaction energy, increasing the orbital mixing with the ligands and the ligand-field effects already discussed. Second, they induce mixing in of the unoccupied atomic d-orbitals to reduce the self-interaction energy by replacing it in part by the smaller $m-m'$ Coulomb interaction. Both effects lead to systematically smaller occupation numbers for the fully occupied states and systematically larger numbers for the partially occupied states. The results in the Tables show that the use of Hubbard U corrections, which partially correct for self-interaction, gives us occupation numbers for full occupancy closer to 1 and numbers for partially occupied states closer to zero, as expected. It should be stressed that our proposed procedure can be applied to other electronic structure methods, like HF and post-HF techniques,[67] which are self-interaction-free.

5. CONCLUSIONS

The oxidation state concept has been used extensively in the study of transition-metal compounds and their reactions. In particular, this formally defined concept is used to interpret many experimental results, but a fundamental theoretical basis for the OS concept through determination by quantum-mechanical calculations has been lacking. By extracting the information needed to determine the OS from an approximate d-electron occupation matrix, we have implicitly introduced the one-electron occupation matrix as the quantum-mechanical operator underlying the oxidation state concept and have to some extent mitigated that lack. Moreover, by relating OS to the occupation matrix, we have provided a fundamental connection between the OS and the wide range of physical and chemical properties known empirically to be sensitive to it.

In this work, a theory for OS is introduced. A simple procedure is developed from the theory to determine OS using quantum mechanical calculations. This theoretical approach allows the separation of the orbital mixing contribution to the allocated charge from that due to the actual occupation of d-orbitals, from which OS can be inferred. This is applied to a range of TM systems from molecular complexes and ruthenium-dye and ruthenium–NIL molecules to bulk semiconductors and is shown to work without ambiguity. This new theory for OS also provides the theoretical basis for the choice of the occupation number as the order parameter to compute electron-transfer diabatic free-energy surface in a previous work by one of the authors.[39] Several possible causes for computational discrepancies when occupation numbers for fully occupied d-orbitals are smaller than 1 are examined and improvements on the approach are suggested. As expected, the eigenvalues of the occupation matrix corresponding to the unoccupied d-orbitals are nonzero but always significantly smaller than those corresponding to the occupied d-orbitals. Moreover, the deviations from unity of the eigenvalues corresponding to the fully occupied d-orbitals are much smaller than those of the eigenvalues corresponding to the unoccupied d-orbitals. There is consequently no ambiguity or arbitrariness in the assignment of OS. The essence of the method is that it distinguishes the occupancy of the d-orbitals from the total charge allocated to the TM ion by, e.g. projection methods. It is the d-orbital occupancy and thus the formal OS which is relevant to the special chemical and optical properties of embedded TM ions as revealed in redox and X-ray absorption experiments[12] among many others.

The focus here has been on systems in which there are no significant metal–metal bonds, which can introduce ambiguity in OS assignments. Generalization of the theory to include such cases would be worthwhile.

In conclusion, this new theory provides a sound and fundamental basis for the use of OS in quantum-mechanic calculations. Its simple and unambiguous approach to OS determination can be used independently of the choice of first-principles methods.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Detailed calculations and discussions on the reduction of occupation number from unity due to metal–ligand orbital mixing and ligand fields, and on the optimal d-type orbital. This material is available free of charge via the Internet at http://pubs.acs.org.

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