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Covalent interactions in oxides

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ABSTRACT

The covalent character of ionic metal compounds, in particular oxides, may lead to substantial departures from nominal oxidation states. Since this covalent character changes the effective charge of the cation, it contributes to the chemical and physical properties of these compounds. A novel method of determining the degree of the covalent mixing by projection is presented. In this method, cation and ligand orbitals determined for the isolated species are projected on the total wavefunctions for clusters used to model the electronic structure of these compounds. An important advantage of this method is that it can be used to obtain estimates of the uncertainties in the assignments of effective charges to the cations and anions. Such estimates of the uncertainty directly reflect the overlap of cation and anion orbitals and, hence, their potential for chemical bonding. These kinds of estimates are not generally given when assignments of charge are made. The core-hole states created in X-ray photoemission spectroscopy, XPS, have a very different covalent character than the initial states where the core shells are filled. It is shown that the increase of the covalent character in the core-hole configurations provides insight into a major aspect of the core-hole screening.

1. Introduction

The occupations of atoms or fragments in a system and the related matter of the covalent mixing to form bonding and anti-bonding orbitals are key to understand the chemistry and properties of molecules and of condensed phase compounds [1–3]. In particular, the covalent properties of oxides are an important problem with possibly important consequences for their properties. For a study of the covalent mixing in a transition metal oxide, MnO, see Ref. [4] where the different covalent mixing in the ground state and in the core-hole states probed by X-ray photoelectron spectroscopy, XPS, was examined. For a review of the covalent mixing in lanthanide and actinide complexes, see Ref. [5] where the covalency is examined using experimental data and theoretical wavefunctions. An early theoretical analysis to determine atomic occupations was the method of population analysis introduced by Mulliken [6–9] in 1955. It is known that there are limitations to the quantitative accuracy of the atomic occupations obtained from Mullen population analyses; see, for example, Refs. [10,11]. Because of the limitations of the Mulliken method of population analysis, alternatives and generalizations have been developed over the years. In the 1960s, Davidson introduced a method based on the projection of atomic orbitals on molecular orbitals [12]. Modifications of Davidson's projection method have been proposed by Nelin et al. [13] and by Faegri and Saue [14]. There have also been alternative approaches based on the curvature of the molecular charge densities to define regions of space to be associated with each atom or fragment [15] and on a population analysis based the use of special sets of orbitals for the atoms and the molecule described as "natural orbitals" [16].

Despite the known limitations of the Mulliken population analysis, it is commonly used, even at present, to obtain qualitative information about the occupations and the covalent mixings of atomic orbitals because it is a straightforward and direct way to analyze orbital character. It has been used, quite recently, in the analysis of the covalent character of DFT Kohn-Sham orbitals for actinide compounds [5,17,18]. The objective of the present work is to extend our previous application of projections [13] to the analysis of the covalent character of a series of oxides. In particular, the analysis has been extended to allow us to estimate the uncertainties in the occupations that we obtain by projections. Further, we show that this uncertainty is significant for the occupations of the frontier d orbitals in lanthanide and actinide oxides. Specifically, we report the covalency for oxides with 3d transition metals, for a representative lanthanide oxide, CeO_2, and for two representative actinide oxides, UO_2 and UO_3, We examine the covalent character in the ground states of these oxides and in states where there is a core-hole for the final states of transitions where the core electron binding energies, BE's, are measured in XPS. For the lanthanide and actinide oxides, we examine the relative importance of the

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covalent character for the frontier d and f orbitals of the cation for both the ground and core-hole states. For the ground states, we analyze why the covalent character is different for the different oxides considered and relate the differences to such features of the compound as the nominal oxidation state and the bond distances. The distinction of the covalent character of the core-hole states from that of the initial ground states is useful for the analysis of the XPS in terms of the materials properties of the oxides [19]. In particular, the increase in the covalent character of orbitals in the core-hole states can be viewed as a closed shell screening of the core hole [4]. In the present work, we show that this closed shell screening is common to all the oxides considered but that its magnitude is different among the different oxides and, for a given oxide, different for different core-levels.

The organization of the paper is as follows. In Section 2, rigorous definitions of the projection of the occupations of the cation and anion orbitals are given and we describe the cation and anion fragments whose orbitals are projected on the oxides. We indicate how comparing the cation and anion projections can be used to estimate the uncertainties of the occupations obtained with the projections. We also indicate that the projections are for the occupations of a particular configuration, more precisely for the average of configurations. However, it is possible to obtain occupations for specific states that take into account the angular momentum coupling of the open shell electrons and other many-body effects as well [19]. In Section 3, the clusters that are used to model the oxides as well as the cation and anion fragments are described. The Hartree–Fock, HF, wavefunctions and orbitals that are determined for these clusters are also described. In addition, other technical details about the calculations are briefly described. In Section 4, the covalent character of the cluster models of MnO, NiO, Cr_2O_3, CeO_2, and UO_x are compared and contrasted. This is done for both the ground state, GS, configuration as well as for core hole configurations. Finally, in Section 5, the conclusions about the covalent character of the oxides are summarized.

2. Method of projection

An early paper by Davidson [12] used the projection of atomic orbitals, AO's, onto Self-consistent Field, SCF, Hartree–Fock, HF, wavefunctions for molecules in order to obtain a population analysis that would provide reliable atomic compositions, or populations, for the molecules. In this section, we describe our implementation of the ideas that Davidson presented and discuss our extensions, which permit us to assign an uncertainty to the assignments of atomic population based on the projection. One of our major concerns is to examine the character of individual orbitals as well as to have a population for the system as a whole. Our representations for the oxides are clusters that contain metal cations, oxygen anions and an embedding to represent the condensed phase environment [19]. The wavefunctions for these clusters are used to describe the electronic structure of the oxide; they are SCF HF wavefunctions [1] and are usually relativistic but non-relativistic wavefunctions are also used. However, wavefunctions that include many-electron effects through configuration mixing, configuration interaction [1], CI, wavefunctions can also be analyzed with the projection method. The choice of clusters and the wavefunctions for the clusters is described in more detail in the following section. In this section, we consider a generic cluster model of the oxide with a central metal cation, denoted M, and n neighboring O anions, denoted O_n to form the cluster MO_n. Wavefunctions are computed for the MO_n cluster and for the fragments M and O_n. The charges of the MO_n and fragment clusters, in terms of the numbers of electrons explicitly included in the wavefunction, are usually taken from the nominal cation and anion ionicities for a given oxidation state.

Projection involves projecting the fragment orbitals, denoted φ^F, on the total wavefunction of the MO_n cluster. The cluster wavefunctions are denoted by $\Psi[MO_n]$ and their orbitals by φ, where the absence of the superscript F indicates that these orbitals have been optimized for the cluster while the fragment orbitals are optimized for the particular fragment. We consider first HF wavefunctions for both the cluster and the fragments. These wavefunctions may be either a single determinant or some suitable linear combination of determinants to represent the angular momentum coupling chosen to describe an open shell system. The essence is that the wavefunction is for a single configuration which is described by orbitals and occupation numbers of these orbitals: φ_i^F and n_i^F for the fragments and φ_i and n_i for the cluster. The orbitals φ^F and φ may represent either a single spin-orbital or they may be a shorthand to represent groups of orbitals where the grouping is normally made over degenerate orbitals in a particular shell. As we note in the next section, these orbitals are normally optimized for the HF wavefunctions for the average of configurations of the coupling of open shell electrons [20].

The electron density of the cluster wavefunction, $\Psi[MO_n]$, is given by

$$\rho[MO_n] = \sum_i n_i \times [\varphi_i{}^\dagger \varphi_i] \tag{1}$$

The projection operator for a fragment orbital φ_α^F is $[\varphi_\alpha^F] \times [\varphi_\alpha^F]^\dagger$ and the projection of φ_α^F on $\Psi[MO_n]$, denoted $N_P[\varphi_\alpha^F]$ is [13,21]

$$N_P[\varphi_\alpha{}^F] = \langle \Psi[MO_n] | [\varphi_\alpha^F] \times [\varphi_\alpha^F]^\dagger | \Psi[MO_n] \rangle \tag{2a}$$

$$N_P[\varphi_\alpha{}^F] = \sum_i n_i \times |\langle \varphi_\alpha{}^F | \varphi_i \rangle|^2 \tag{2b}$$

where the notation N_P indicates that the quantity is an estimate, obtained by projection, of the occupation of the fragment orbital φ_α^F in the wavefunction $\Psi[MO_n]$. It is very important to note that a non-zero occupation does not mean that the fragment orbital appears in the configuration for $\Psi[MO_n]$. For some orbitals, especially core orbitals, it is possible that a cluster orbital φ_j is essentially the same as the fragment orbital φ_α^F and $|\langle \varphi_\alpha{}^F | \varphi_j \rangle| \approx 1$. However, for the higher lying orbitals the value of $N_P[\varphi_\alpha^F]$ normally arises because the orbitals of the complex are covalent linear combinations of cation and anion orbitals rather than being pure orbitals of either cation or anion. This is precisely the reason that projection provides direct information about the covalent character of interactions in oxides and other ionic compounds. In order to examine the covalent character of particular orbitals or groups of orbitals, the summation in Eq. (2b) can be, and often is, restricted to groups of orbitals. Thus, the open shell orbitals of the cluster are a set where we will wish to examine departures from pure cation d or f orbitals. Alternatively, one could project the high lying, frontier, metal d and or f orbitals from the closed shell orbitals of the cluster where, using the logic of formal oxidation states, the nominal metal d and or f occupations should be zero.

As we mentioned above, one of the sets of fragment orbitals that it is of interest to project is the metal open shell or unoccupied d and or f orbitals. Thus for the first row transition metals, one would want to project the 10 3d spin orbitals to obtain a total value of $N_P(3d)$ by summing the projections for each individual spin orbital [4]. For the lanthanides, the metal cation orbitals to be projected are the 4f and 5d, while for actinides, the metal cation 5f and 6d would be projected on the cluster wavefunctions. The other fragment of interest is the isolated O_n fragment. It is easy to separate the orbitals of the O_n fragment into groups that are dominantly O(1s), O(2s), and O(2p). Further groupings into additional sets of orbitals based on the point group symmetry of the O_n fragment may also be possible and such groupings will be discussed in later sections. The formal oxidation states are obtained assuming

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