

Oxidation states from wavefunction analysis

Pedro Salvador¹, Eloy Ramos-Cordoba¹

¹ Institut de Química Computacional i Catàlisi, Universitat de Girona, Spain

Campus Montilivi s/n 17071, Girona, Spain, email:pedro.salvador@udg.edu

The concept of oxidation state (OS) is widespread in transition metal chemistry and in the study of redox and catalytic reactions. The reactivity, spin-state, spectroscopic and geometrical features of transition metal complexes are often rationalized on the basis of the oxidation state of the metal center. In coordination chemistry, the OS is typically defined as *the charge left on the metal after all ligands have been removed in their normal, closed shell, configuration*. Thus, formal OS are obtained by assigning integer number of electrons to the atoms/ligands according to some rules. In complicated bonding situations involving non-innocent ligands or in intermediates or transition states of catalytic reactions the formal OS assignment may be rather ambiguous.

Oxidation states are intrinsically related to electronic distribution, but the atomic charge after the formal electron counting is only imaginary; that *an atom would have under certain counterfactual conditions*. [1] Even though electronic populations do change with oxidation/reduction of the metal center, they are only a pointer of the oxidation state. Even spin populations need a previous knowledge of the electronic structure (spin state), [2] and are clearly futile in pure singlet states.

There have been several attempts to derive OS from first principles. [2, 3] In this presentation we will introduce a very simple alternative based upon an a posteriori wavefunction analysis. The method is based on the use of the so-called effective atomic orbitals of Mayer, [4, 5] treating alpha and beta electrons separately and extending the formalism to molecular fragments (if necessary). Moreover, the occupation numbers of the effective atomic orbitals may be used to quantify to which extent a particular wavefunction conforms with the ideal OS assignment. The method is general and it can formally be applied to any molecular system. We will discuss the analysis of the intermediates and active species involved in the C-H catalytic hydroxylation carried out by a Fe(Pytacn) complex, [6] where the presence of high-valent species such as Fe^V-oxo was suggested.

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