

The use of localised orbitals for the bonding and mechanistic analysis of organometallic compounds†

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Through a series of examples we show how, upon orbital localisation, the outcome of an electronic structure calculation reveals features, such as bonding and oxidation states, which are controversial to grasp by alternative methods. The approach can also be applied to the analysis of reaction mechanisms. Because of the insight it provides in a limited execution time, we believe that this approach, known since the early developments of computational quantum chemistry, could find wider applications in the organometallic community than it actually has and facilitate communication between computational and experimental chemists.

Introduction

Is there a bond between atoms X and Y? What is the oxidation state of atom X? Both are central questions in chemistry, to which we can often answer on the basis of the knowledge we built on related systems. However, as chemical research pushes its limits towards the synthesis of compounds with novel properties, new situations arise for which it is difficult to make an assignment. When this occurs, computational quantum chemistry is asked to resolve the issue. Indeed, computational quantum chemistry is capable, within its own limitations, of providing a picture of the system of interest at a resolution which is in general not accessible by experimental means. However, the solution of the quantum chemical problem comes in a form (a set of nuclear coordinates and electronic orbitals) which has to be reconciled with accepted chemical concepts. Concepts such as bonding and oxidation states are deep-rooted in the chemist's way of thinking and are so useful to guide the design of new compounds that we do not want to abandon them. And the problem lies there: *how do we reduce the N-body solution to a set of estimates of chemical concepts*. Many methods have been devised for this purpose. Among these, we recall population analysis (Mulliken¹ and variants^{2,3}), the theory of atoms in molecules,⁴ and molecular orbital analysis (including the natural bonding orbitals⁵). All

these methods are widely used in the theoretical community, each with its own advantages and limitations, such that some researchers may prefer one over the other. In this communication we want to call attention to the use of localised molecular orbitals to perform the analysis. The approach dates back to the work of Boys in the sixties,^{6,7} but is not much used by the organometallic community. In contrast, it is much more employed (in the form of maximally localised Wannier functions^{8,9}) in condensed matter research where it has important applications.¹⁰ Through a few examples drawn from our current research and cases discussed in the literature, we will show how localised molecular orbitals may be conveniently used to answer the opening questions. It is not our intention to criticize previous work, nor to propose that the use of this procedure should substitute other analysis techniques. We just want to share with the reader the clear cut picture of the electronic structure which arises from the application of the localisation procedure.

Methods

Orbital localisation consists of finding the unitary transformation U acting on the Kohn–Sham orbitals φ_i^{KS} ,

$$\varphi_n^{\text{loc}} = \sum_i U_{in} \varphi_i^{\text{KS}}$$

which minimizes the spread functional Ω

$$\Omega = \sum_n [\langle \varphi_n^{\text{loc}} | r^2 | \varphi_n^{\text{loc}} \rangle - \langle \varphi_n^{\text{loc}} | r | \varphi_n^{\text{loc}} \rangle^2]$$

The procedure consists of first performing a standard density functional theory (DFT) calculation within the Kohn–

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