



# Electron Localization Function and Maximum Probability Domains analysis of semi-ionic oxides crystals, surfaces and surface defects



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## ARTICLE INFO

### Article history:

Received 12 August 2014

Received in revised form 1 November 2014

Accepted 1 November 2014

Available online 27 November 2014

### Keywords:

Crystalline oxides

Electron Localization Function

Maximum Probability Domains

Surface state

Surface vacancy

F-center

## ABSTRACT

Maximum Probability Domain (MPD) analysis has been recently applied to pure covalent and ionic crystals. The present study is devoted to a first MPD analysis of semi ionic crystals, Silicon Oxide, Aluminum Oxide and Titanium Oxide. These crystals are involved in important catalytic and photo-catalytic processes occurring on their surfaces. For this reason the study has been performed on bulk crystal and on surface slab models. Also surface neutral oxygen vacancy, the F<sup>0</sup> surface defect, has been considered. The Electron Localization Function (ELF) analysis has also been performed, due to its holistic approach to electronic structures.

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## 1. Introduction

In Materials Chemistry and in Surface Sciences often very simple and chemically classical questions are asked: how much ionic is this system? Is the surface more or less ionic than the bulk? What is the oxidation number of the bulk and the surface ions? Is this one a more ionic or covalent compound? These questions are perfectly reasonable within the chemical phenomenological knowledge but are often nonsense within a physical approach: they reside in that territory, up to now partially explored, of the “chemical questions” that need a physical explanation. All these questions have two common conceptual kernels: the recognitions of atoms (or ions) and the recognition of bonds in molecular and crystalline systems, starting from a purely physical description of the systems. The answers can be found following the path indicated by Bader [1]. The present work is devoted to the application of the most promising approaches in searching bonds and “Atoms

in Molecules”: the Electron Localization Function (ELF) [2] and Maximum Probability Domains (MPD) [3]. In the following we will revise the most recent approaches for analyzing chemical bonds starting from physical quantities and observables.

In recent years the traditional discussion of chemical bonding in terms of the canonical orbitals has been challenged [4–6]. In fact, in general SCF theory, the definition of orbitals remains ambiguous [7–9] and several localization procedures have been introduced by suitable unitary transformations of the set of canonical orbitals, in order to provide a more rigorous mathematical meaning to chemical concepts such as bonded atoms, reactants, chemical bonds, electron shells, lone electron-pairs [10–12]. Yet, the realization that theoretical partitioning is not unique “casts a shadow of mistrust over certain definitions” [13].

Alternative approaches to the many-electron problem, working in real space rather than in Hilbert space, and with the electron density playing the major role, are provided by Bader’s “atoms in molecule” [1,14], which partitions the molecular space into basins associated with each atom, and density-functional methods [6,15,16]. Such a localized “Lewis-like” description of bonding and reactivity, which uses a natural bond orbital analysis (associating bonds with localized two-center two electron wave-functions),

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has recently been expanded to bulk materials and/or periodic surface models [17].

Some system cannot be characterized in terms of localized orbitals: an extreme example is provided by the fluxional behavior of  $\text{CH}_5^+$ , where quantum–mechanical fluctuations induce delocalization phenomena and thus fluctuating bonds [18–22].

Most importantly, these systems are amenable to Electron Localization Function (ELF) method [2]. This is a local measure based on the fact that the reduced second-order density matrix, which has pioneered by Lennard-Jones [23], should retain the chemical significance and at the same time reduce the complexity of the information contained in the square of the wave function  $\Psi$ . ELF is defined in terms of the excess of local kinetic energy density due to the Pauli exclusion principle,  $T(r)$ , and the Thomas–Fermi kinetic energy density,  $T_h(r)$ :

$$\text{ELF} = \left[ 1 + \left( \frac{T(r)}{T_h(r)} \right)^2 \right]^{-1} \quad (1)$$

In other words the ELF can be interpreted as the local price that the electronic structure pays in term of kinetic energy for respecting the Pauli Principle.

In the seminal paper of Becke and Edgecombe [2] it was proposed that a topological analysis of the ELF [24–26], permitted a more quantitative analysis of the three-dimensional function. This latter is normalized to the interval between 0 and 1, it is large where the Pauli repulsion is small (two electrons with anti-parallel spin are paired) and it is small in the regions between electron pairs. To identify a region around a maximum (an attractor), which forms a basin, one can consider all the points in space with  $\text{ELF} \geq \zeta$ , which define the  $\zeta$  localization domain and with  $\zeta$  being a positive constant smaller than the value of the maximum. This region in space can be visualized by showing the iso-surface  $\text{ELF} = \zeta$ . All points leading to the same attractor belong to the same basin.

The ELF has been extensively applied to a large number of systems and has also been used to quantify chemical concepts like the strength of the hydrogen bond [27] and aromaticity [28,29]. Moreover, other interesting ELF-like scalar fields have been developed, such as the localized orbital locator (LOL) [30], based on the comparison of the local non-interacting kinetic energy density with that of the uniform electron gas, and the electron localizability indicator (ELI) [31–33], derived directly from the electron pair density without any reference to the uniform electron gas.

In order to get out of the somewhat confusing definition and interpretation of ELF, a more thoroughly investigation of the competition of kinetic terms  $T(r)$  and  $T_h(r)$  of Eq. (1), between regions in which the inhomogeneous or the homogeneous behavior dominates, was carried out by Putz [34,35]. Employing a path integral Markovian pair conditional probability density with the basic concepts of the catastrophe theory, he succeeded in introducing new Markovian ELF classes which generalize the previous Becke–Edgecombe definition. Going beyond the actual interpretation of ELF as the error in electron localization, this new approach provides a quantum step-function indicating where the electrons are trapped rather than where they have peaks of spatial density.

From a computational point of view, it should be stressed that the computational tool of Francisco et al. [36] results in obtaining the electron number probability distribution functions of a  $n$ -electron molecule through an exhaustive partitioning of the real space into arbitrary regions. From the computed probabilities several magnitudes relevant to chemical bonding theory are obtained, such as average electronic populations and localization/delocalization indices.

Recently, Corminboeuf et al. [37] have compared the ELF's of both the canonical wave functions and electron-localized states with those of ELI and LOL, in order to discriminate between

enhanced or reduced electron (de)localization within cyclic  $p$ -conjugated systems. As a result, the authors say, the simplest LOL function gives a more appealing and intuitive picture of the  $p$ -bond, whereas the most popular ELF fails to capture subtle contrasting local electronic properties and suffers from the arbitrariness of the  $\sigma/p$  dissection. Some ELF limitations have been thoroughly discussed in recent years [3] and attempts to search for new tools, capable of providing solutions to still unsolved difficulties in chemical understanding, have been done. A promising methodology has been obtained through a topological analysis by means of Maximum Probability Domains (MPDs) [38–41]. The definition of the probability function is quite simple:

$P(n)$  is the probability of finding exactly  $n$  electron in the space domain  $D$ :

$$P(n, D) = \int_D dr_1 dr_2 \dots dr_n \int_{D'} dr_{n+1} dr_{n+2} \dots dr_N |\Psi|^2$$

where  $\Psi$  is the wave function,  $N$  the number of the electron of the system,  $D$  is the domain,  $D'$  is the complementary space to  $D$  (all the space outside  $D$ ).

The Maximum Probability Domain (MPD) method consists in maximizing  $P(n, D)$  with respect of  $D$ . The implementation of MPD method for molecular and crystalline system is quite complex due to the multiple integrations on limited space domains.

In the definition of MPD the spatial domain appears just in the definition: on the other hand AIM and ELF define the local basins analyzing a scalar field.

An original computational approach has been recently developed for treating and optimizing spatial domains in molecular and periodic systems. This method is now part of a developing version of the computer program CRYSTAL14 [42]: the MPD package will be available to the users in the release version 1.0.4 (spring 2015). Our method conserves and optimizes the domain surface, subdivided in triangles, as it is done in computer graphics and animation [43]. The main points of the MPD program coded in CRYSTAL14 are briefly summarized in the [Supplementary information](#).

## 2. Investigated crystals and computational details

In the present study we considered the following crystalline structures: Silicon (diamond structure), MgO (cubic FCC),  $\text{SiO}_2$  (alpha quartz),  $\text{Al}_2\text{O}_3$  (alpha alumina or corundum) and  $\text{TiO}_2$  (anatase structure). The calculations have been performed at the Hartree–Fock (HF) level because the MPD approach requires the knowledge of the system Wave Function and Density Functional rigorously provides only the one particle Electron Density. On the other hand the DFT approaches provide pseudo one-determinant wave functions and much better energetic data than HF. ELF and MPD are not very sensible to the level of the calculation, so we do not expect any difference in the results of the present analysis if the various DFT methods are applied. We are performing specific studies for assessing the influence of electronic correlation on MPD of crystals [44]. For all the crystals and the surfaces we adopted double  $\zeta$  plus polarization quality basis sets, already adopted in previous crystalline and surface studies [45–49]. We considered the basal plane (001) for all the oxides. We modeled surfaces by means of slab model: a two dimensions periodic slab perpendicular to the surface under study has been cut from the bulk of each oxide and optimized. Our slabs are about 15 Å thick; in our experience this thickness guarantees a reliable model of the up and down surfaces and of the bulk-like sub-layers. In our study the less realistic system under investigation is the (001) surface of alpha quartz since the dangling oxygen (see below) is usually protonated. For homogeneity with the other surfaces we decide to analyze the un-protonated (001) quartz surface, this also because we are more

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