

Chemical bonds in minerals: topological analysis of the electron localization function

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Introduction

The characterization of the chemical bonds in minerals and particularly in silicates is a puzzling problem which is related to the criteria used to classify them. As discussed by Tossell and Vaughan (1992), the availability of an absolute description of covalency versus ionicity in terms of observable properties is questionable. From the experimental point of view, the relevant information is provided by the analysis of the electron density. However, different schemes can be applied to partition the crystal into atomic domains which yield slightly different atomic charges. Moreover, the nature of chemical bond is not only a matter of electron distribution, but above all, of distribution of electron pairs. Theoretically most analyses of the bonding rely either on the valence bond (VB) or molecular orbital (MO) schemes, in which the VB and MO functions are themselves expressed in terms of atomic basis functions. Therefore, the guidelines used to characterize the bonding depend upon the level of approximation, they cannot be applied with exact wavefunctions.

The characterization of chemical bond is qualitative, not quantitative. The topological analysis of the gradient field of local functions is the mathematically founded approach to go from quantitative to qualitative. This method has been pioneered by Bader (1990) who emphasized the role of the electron density. It allows to define bond paths and atomic basins and therefore rationalizes the concept of bonded atoms, provides an objective partitioning scheme and gives a theoretical foundation to structural chemistry. However, as already mentioned, with the electron density alone it is not easy to reveal the formation of electron pairs which are the consequences of the Pauli exclusion principle. In this communication, we apply such a topological analysis to the gradient field of local functions, named hereafter localization functions, which measure the Pauli repulsion. This enables us to propose a new set of criteria to classify chemical bonds which are applied to silica and related materials.

A sketch of the topological theory of chemical bonds.

The electron localization function, ELF, has been recently introduced by Becke and Edgecombe (1990) in order to provide local information on the curvature of the Fermi hole. Formally, it is written as:

$$ELF(\mathbf{r}) = \frac{1}{1 + \left(\frac{D_{\sigma}(\mathbf{r})}{D_{\sigma}^{\circ}(\mathbf{r})}\right)^2}$$

in which D_{σ} and D_{σ}° represent the curvature of the electron pair density for electron of identical spins (the Fermi hole) for respectively the actual system and a homogenous electron gas with the same density. An alternative interpretation has been proposed by Savin and coworkers (1992) who considered the excess local kinetic energy due to the Pauli repulsion. The local kinetic energy $K(\mathbf{r})$ is:

$$K(\mathbf{r}) = \int \Psi^* \hat{T} \Psi d\tau'$$

In which Ψ is the wave function of the system, \hat{T} the kinetic energy operator and the prime indicates that the integration is performed over the space and spin coordinates of all particles but one. The ground state kinetic energy of a non interacting system of bosons with identical density is given by:

$$K^B(\mathbf{r}) = \frac{1}{8} \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})}$$

in which $\rho(\mathbf{r})$ denotes the electron density, is a lower bound to $K(\mathbf{r})$. The excess local kinetic energy is simply the difference of these two quantities:

$$D_{\sigma}(\mathbf{r}) = K(\mathbf{r}) - K^B(\mathbf{r})$$

Though $D_{\sigma}(\mathbf{r})$ provides the useful information, the actual analytical form of the ELF function allows to build a comprehensive scale. ELF is therefore a measure of the bosonic behaviour of the electron-density. In the regions of space where are located anti parallel spin electron pairs or single electrons

ELF is close to 1 because D_σ tends to zero, whereas ELF tending to zero indicates a strong Pauli repulsion due to parallel spin electrons. Of course, ELF is not the unique choice for an electron localization function, nevertheless it fulfills the requirements of being scalar, defined for any point of the direct space and its definition does not rely upon the approximation used to calculate the actual wavefunctions.

For this kind of functions, the gradient X defines a vector field. The theory of gradient vector fields has been developed as a part of the Dynamical System theory (see Abraham and Shaw (1992) for a comprehensive introduction). It is possible to build trajectories (the field lines) by introducing a fictitious time coordinate. The points corresponding to $t \rightarrow -\infty$ and $t \rightarrow \infty$ are respectively the $\alpha(p)$ and $\omega(p)$ limits of the trajectories. The set of ω -limits is the set of the attractors of the dynamical system. The basin of an attractor is the set of points for which this attractor is the ω -limit. For gradient-type dynamical systems, the property to have 0-dimensional attractors is generic [Palis and Smale, 1970]. Nevertheless, for the examples that need to be investigated in chemistry, the system could belong to a continuous symmetry group (e.g. $C_{\infty v}$, $SO(3)$) which in turn implies that the attractor could be no longer 0-dimensional. In the most general case, without symmetry, the attractors are point attractors and the Pauli principle implies that the electron density integrated over one basin $q(A)$ is bounded by 2. An attractor for which $q(A)$ is less than 2 will be called hereafter an unsaturated attractor. The formation of a molecule or a crystal from atoms breaks the $SO(3)$ symmetry and therefore leads to the competition between the attractors which are reorganized accordingly. From a chemical point of view there are three types of attractors: core, bonding (located between the core attractors of different atoms) and non-bonding. Following Bader [Bader, 1990], there are basically two kinds of bonding interactions which are the shared-electron interaction and the closed-shell interaction. Covalent, dative, and metallic bonds are subclasses of the shared-electron interaction whereas ionic, hydrogen, electrostatic and van der Waals bonds belong to the other class. For electron-shared interaction there is always at least one bond attractor between the core attractors of the atoms involved in the bond.

Results and discussion

The method previously described has been applied to silica polymorphs, namely quartz, cristobalite

and stishovite and to the modifications of Mg_2SiO_4 in order to have a picture of the Si-O bonds. The approximate wave functions have been calculated with the periodic Hartree-Fock software CRYSTAL92 [Dovesi et al., 1992], a detailed description of these calculations have been previously published elsewhere [Silvi et al., 1990, 1992, 1993]. For every cases, bonding attractors lie on the bond paths between the silicon and oxygen nuclei giving support to a description of the bonding in terms of shared-electron interaction. The averaged distance between the oxygen centre and bonding attractors and nonbonding attractors are respectively 0.75 and 0.55 Å. The main difference between, hexacoordinated and tetra-coordinated silicons is that there are five attractors around the oxygen instead of four in the latter case. Therefore, in stishovite the bonding attractors are less saturated than in the other polymorphs which explains why the bonds are larger.

Most discussion of the covalency of the SiO bond are made in terms of hybridization of the silicon atom. The localization of attractors, on the contrary, indicates that most of the covalent character comes from the oxygen side. This picture is consistent with basis set effects which indicates that d -polarization functions on oxygen are necessary. Unpolarized split valence basis set predict the β -phase of quartz and cristobalite to be stable, d functions on oxygen have been shown to correct this artefact. The polarization of the oxygen atoms has been recently emphasized by Lacks and Gordon (1993). The criterium we use to classify interactions is independent of the density distribution and characterizing the SiO bond as a shared electron interaction does not mean that the atomic charges calculated within Bader's partition are small.

References

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