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Rendering of quantum topological atoms and bonds

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Abstract

In this article, we describe and apply an algorithm that visualizes atoms and bonds in molecules and van der Waals complexes, based on the topology of the electron density. The theory of quantum chemical topology defines both atoms and bonds via a single consistent procedure, and enables the association of an atomic shape with an atomic property (charge, dipole moment, volume, . . .). Special attention is paid to the bridging of gaps arising in interatomic surfaces, in the presence of ring critical points or high ellipticity. This algorithm, in conjunction with the graphical user interface of the computer program MORPHY enables robust and efficient rendering of complicated interatomic surfaces, as found in larger systems.

Keywords: Electron density; Quantum chemical topology; Atoms; Bonds; Graphical user interface; Interatomic surface; Atoms in molecules

1. Introduction

Visual representations of atoms and bonds are important tools in chemical research and scientific progress in general. Three-dimensional ball-and-stick models, used alongside flexible graphical user interfaces, provide insight in complex molecules and crystalline materials. Molecular simulations benefit too from images that enable the rapid analysis of intricate structural details. Of course, prior to any such visualization one must first decide what atoms and bonds really are. Although this question seems innocuous, and its answer taken for granted by many, it is still under debate (e.g. [1] and references therein and particularly [2–4]).

Atomic properties can be obtained [5] via three classes of methods: partitioning of orbital space, partitioning of the Hamiltonian and partitioning of the electron density. The first class encompasses popular population analyses such as Mulliken's and Natural Population Analysis. Although these methods supply atomic charges they do not provide a concomitant picture of the atom's shape. In other words, the atomic property is severed from the atom's visual representation. Similarly, distributed multipole analysis (DMA), which also belongs to the first class of methods, allocates high-order multipole moments to atomic sites, again without providing a visual representation of the atom. The second class of methods poses the even more fundamental, if not impossible, challenge of wedding an atom's (physical) property to its picture. *Only the third class, which involves the electron density, provides a natural path to achieve this aim.* Moreover, the electron density, performing a central role in density functional theory, acts as a convenient information "platform" where experiment meets theory. A variety of computational schemes all yield the electron density at some point, regardless of the type of basis function (if present) or the way they tackle electron correlation, for example. It is therefore desirable that one's definition of an atom and a bond depends directly on the electron density itself, rather than on the features of the scheme by which the electron density was obtained. To give a simple example, the concept of a Mulliken charge ceases to exist when using plane-wave basis functions because such basis functions are not centered on nuclear positions.

We propose the topology of the electron density as a starting point to define an atom and a bond. Not only do they both follow from the same topological analysis, in a computable manner, but they also associate pictures of atomic shapes with atomic properties. Indeed, one can associate the well-defined bounded region in three-dimensional space occupied by a topological atom with its

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multipole moments. In addition, the quantum chemical topology (QCT) [6–11] approach is rooted [12] in quantum mechanics via Schwinger's quantum action principle, which was taken as a natural starting point to generalize quantum mechanics to subspace quantum mechanics.

In summary, *QCT enjoys the benefit of visual representation going hand in hand with physical property*, and the benefit that it is based on the electron density itself, rather than on the way it was obtained. However, this accomplishment is overshadowed by the computational time and intricacy posed by the algorithms that generate topological atoms and bonds. Nevertheless, substantial progress has been made by various groups. The program EVolVis [13], for example, enables the user to interactively explore a molecule's electron density for topological features. The popular electron localization function (ELF) [14] is also regularly subject to a visual analysis [15–18], while high-resolution X-ray electron density can be analyzed via the program TOPXD [19] and crystalline materials via TESSEL [20].

That there is a need to visualize molecules is clearly demonstrated by the popularity of molecular surfaces, such as the Corey–Pauling–Koltun (CPK) [21] surfaces and solvent accessible surfaces [22]. The method presented here is able to carve a molecule out of a supermolecular cluster, since according to QCT a molecule is simply a union of non-overlapping and space-exhausting atoms. The need for visualization is straightforwardly extended from molecules to atoms. For example, the small volume of sp^3 carbons [23] can be understood in terms of a simple picture, and so is the formation of spikes in the Li^+ cation in the rock-salt phase of the LiF crystal [24]. The curvature of the boundaries of topological atoms (i.e. interatomic surfaces) has also been related to atomic hardness by an in-depth study [25] based on work [26] pioneering the use of differential geometry in QCT. Communicating the meaning of topological atoms via pictures instead of mathematical descriptions is very direct. On the ''technical'' front, being able to visualize atoms is simply vital in the design of correct and robust algorithms for integration over topological subspaces or basins.

Perhaps contrary to some readers' expectations we do *not* investigate the issue of transferability in this paper. In fact, we believe it to be imprudent, if not wrong, to assess transferability on the basis of visual information alone. To make this point more acute, one should visually compare the actual molecular electron density and the corresponding promolecular electron density. The latter is a simple superposition of spherically averaged and unhybridized atomic electron densities. Visually, the promolecular density is virtually identical to the real one, which leaves one with the false impression that the physical properties (e.g. energy, dipole moments) associated with both densities would also be virtually identical. If this were true, then there would be no need to keep developing faster and more accurate ab initio quantum chemistry algorithms and packages. The MEDLA approach [27] is an example of a visual assessment of transferability.

In this article, we present a new algorithm that generates smooth interatomic surfaces (or zero-flux surfaces), without gaps and in complex topological situations. This accomplishment required much careful thought and development. The applications shown are subject to the illustration of the algorithm although they have interest in their own right. We also aim at handling larger systems than typically published so far. When combined with the current power of Java-based graphical user interface (GUI) tools (including the non-standard Java3D extension to enable 3D graphics), we hope to have furthered the frontier of topological visualization.

2. The algorithm

2.1. Problem description

An interatomic surface (IAS) is a bundle of gradient paths (GPs) originating at infinity and attracted to a bond critical point (BCP). A GP is a path of steepest ascent through the electron density and a BCP is a type of saddle point marking the boundary between two atoms, together with the IAS. The IAS constitutes a sharp boundary between two topological atoms.

The first step in the representation of IASs is obtaining sample points on the whole surface. This is easily achieved by tracing GPs *backwards* (i.e. in the direction of steepest descent), starting from a small circle centered at the BCP and proceeding towards infinity. This small circle contains a number of equidistant points from which the GPs start their journey. Sample points (yellow points in Fig. 1) are then collected at regular intervals on the GPs. However, these points often do not represent the complete IAS, because two originally adjacent GPs may wander off in increasingly different directions, leaving a gap in the IAS. One of the main challenges of a robust surface representation algorithm is to bridge such gaps efficiently. These gaps can have two origins.

One possibility is that the gap is caused by a high ellipticity at the BCP. The ellipticity essentially measures the ratio of two local curvatures in the electron density, each one in a direction orthogonal to the other, and both describing the orientation of a plane tangent to the IAS. A high ellipticity means that a GP advances much faster in one direction than in the other, as shown in Fig. 1. Here, the vertical direction dominates the horizontal one; as the GPs take off from their initial points, equidistantly spaced on a small circle, they are immediately pulled in the vertical direction. This effect creates two enormous gaps at the left-hand side of the picture.

The other possible cause for the appearance of a gap is the presence of a ring critical point (RCP) inside the IAS. An RCP is the other possible type of saddle point, so called because it emerges inside a ring of topologically connected nuclei. An RCP suddenly alters the direction of certain GPs of the IAS as they approach the RCP. This is shown in Fig. 1