RhoRi: An Interface Between the Theories of Quantum Chemical Topology and the 3D Graphics Program Blender.

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**Abstract**

The analytical methods collected under the umbrella of Quantum Chemical Topology (QCT) provide a means for obtaining understanding of chemical problems directly from underlying quantum mechanical principles. The theory imposes no parameters, and chemical insight falls freely from scalar functions computed from the wavefunction. Understanding of chemistry is routinely assisted by creation of visual representations of chemical concepts, and QCT is rich in potential for such images. However, visual representation of the topological elements of QCT has traditionally lagged behind what is possible with the best free tools of the day. Towards a remedy for this problem, a general abstraction of the topology (and concrete corresponding file format) is provided into which the output of existing, mature QCT codes can be converted. This abstraction permits the definition of mappings between topological objects and their 3D representations. An attempt at a canonical mapping is provided and implemented as a Python ‘Add-On’ for the state-of-the-art free 3D modeling program Blender. This allows chemists to access modern drawing tools, and artists to access QCT data within a familiar program. The full flexibility of Blender can be utilized in creation of rendered topological figures.

**Introduction**

Human understanding of chemistry has been advanced since its beginnings by visual representations of chemical concepts. Probably the most famous is the ‘ball & stick’ model of chemical structure, both in its real world implementation as building kits and in its virtual implementation in computer graphics.

Despite the wealth of examples littering the literature, 3D representations of chemistry are often based on information that does not have a sound basis in theory, i.e. properties that cannot be computed directly from quantum mechanics. To give an example, the sticks of the ball & stick methods depict bonds, but bonding still lacks a rigorous and unambiguous quantum mechanical definition. In practice, empirical estimates of the ‘size’ of atoms (another ill-defined quantity) are used to determine whether a pair of atoms is close enough to warrant depiction of a bond between them. A second example is the van der Waals representation, wherein each nucleus centers a sphere large enough to contain practically all of an atom. This representation neglects the fact that the wavefunction extends to infinity, and that atoms are, by no good approximation, overlapping spherical objects. The list of representations and their connection to fuzzily-defined chemical concepts continues, but the preceding is hopefully sufficient to make our point. To provide the precise understanding of chemistry necessary for exacting reasoning, the visual representation must map to well-defined, quantitative concepts.

It is well understood that chemical systems are described by quantum mechanics, although for chemical systems of significant size that the solution of the Schrodinger equation is intractable. Despite this restriction, much can be learned from studying systems with sizes for which computation of the wavefunction is possible. Hardware improvements continue to increase the size of systems that can be treated, just as better approximation schemes allow accurate results to be obtained more cheaply. As such the future is bright for quantum chemistry, and difficulties should not be seen as disheartening.

Quantum chemistry provides the source of well-defined concepts that mirror the favoured concepts of experimental chemists, for example chemical bonding, isomerism, resonance, etc. The traditional view of chemistry in terms of the wavefunction however is hampered by the massive dimensionality of the wavefunction. One possible redrawing of the problem is to attempt to define chemistry in terms of the electron density. A much more familiar concept is the scalar field defined in 3-dimensional real vector space, with which humans are certainly comfortable. Quantum Chemical Topology (QCT) is an umbrella term encompassing all methods of analysis that involve scalar functions derived from the wavefunction. The canonical example is perhaps the set of methods termed ‘Atoms in Molecules’ by its creator, although the field has certainly expanded since. This communication takes the topology of the electron density as its central scalar function, although all scalar fields have a topology and the abstractions described apply to each.

**Topology of a Scalar Function**

A scalar function can be written , where . It maps each vector to a single real value. In the following, these vectors are points in a real, 3-dimensional space in which the chemical system (of nuclei and electrons) resides. We will abstract the vector as an object with the following Python class definition:

The scalar functions of QCT are determined from the wavefunction, which is usually computed under the Born-Oppenheimer approximation using the LCAO-MO method with either gaussian or plane-wave basis sets. The scalar functions are agnostic as to how the wavefunction was computed or is represented.

The electron density is denoted . From here on we will focus on this particular function, as it provides us with a computable concept of the atom within a molecule, as well as with a quantifiable concept of bonding and of structure. Representations of the topology of the electron density reveal information about each of these concepts.

The first topological element to discuss is the critical point (CP). A CP has position and is defined by the property that the gradient, . Critical points appear in various chemical contexts, particularly a CP practically coincides with every nucleus of a system, and a CP exists between pairs of atoms that would normally be considered bonded to each other. This suggests that the CPs should be categorisable, and it is natural to use the second derivative matrix, to characterize them. This symmetric matrix can be diagonalised to yield 3 eigenvalues, . Two properties serve to represent the character of a CP. The first is its *rank*, , which is simply the number of non-zero eigenvalues (i.e. ). The second is the sum of the signs of the eigenvalues, , the *signature* of the CP. These are often written as the ordered pair . In most chemical situations, only CPs of rank 3 appear in the topology of .

A CP is a maximum of the electron density, and all nuclei of the system have a nearly-coincident CP. The CP is usually termed a bond critical point (BCP) due to its appearance between pairs of atoms that would be considered by normal chemical intuition to be bonded to each other. The CP is the ring critical point (RCP), and the CP is a minimum, termed a cage critical point (CCP).

In order to abstract this object, we define a critical point as the union of vector, rank and signature objects. The corresponding Python class definition is:

The next important topological element is the gradient path. Several objects that correspond to chemical concepts are made concrete by gradient paths (or sets thereof). All gradient paths begin and end either at critical points or at .

Topological objects consisting of single gradient paths typically connect CPs.

Topological objects consist of multiple gradient paths. These connect CPs to infinity. The electron density naturally falls into atomic basins separated by non-trivial surfaces termed interatomic surfaces (IAS). An IAS is a set of gradient paths connecting to a particular BCP.

A gradient vector field is the complete set of gradient paths of a system. Studies using QCT often require atomic properties to be evaluated, and the gradient vector field inside an atom is then needed. This is the set of gradient paths that connect a specific NCP to other CPs and to points where . Those GPs that connect the NCP to are often truncated once is below a specified threshold treated as a practical zero.

Whilst all chemical systems extend to infinity in all directions, we can define an isosurface, which is the set of points with a single value of and use such a surface to cap the atoms of the system. The choice of capping value is a parameter introduced in the visualization and is usually chosen such that roughly of the electron density of the chemical system is enclosed.

Having discussed scalar functions and their topology (and in particular how the topology of the electron density, is connected to chemical concepts, we can now discuss the visualization of quantum chemical topologies.

The structure of a topology (as describe above) can be defined using a markup language. Here we use XML, and the allowed tags, their hierarchy and the type of their contents are defined with a schema written in XSD. The UML diagram corresponding to the schema is shown in a figure.

**Visualization of Topology**

The visualization of the topology requires that each topological object, as defined above, be mapped to a 3D object.

Critical points of the scalar function are typically represented as spheres. This choice allows the CPs to be clearly located, and provides two additional variables for further delineation between CPs, radius and colour. Nuclear critical points can be coloured according to the element of the nucleus they represent, and we give them all equal size. The remainder of rank 3 critical points (BCP, RCP and CCP) are given their own colours and a equal radius, small enough for these critical points to be told apart from NCPs. Rigorously we could set the radius by relative values of electron density at CPs. Nuclear critical points swamp the remainder, justifying the used of smaller radii for the non-nuclear CPs but resulting in practically zero radii for them, such that they are not visible.

All GPs are represented by smooth lines connecting their known points. As lines, we are able to inject further information using colour, radius and design.

For AILs, colours have typically been equal and dark, although visualizations from AIMAll exist that incorporate the colour of the connected CPs into the AILs. The radius is also usually left equal and is set as to create an aesthetically pleasing result to the artist. In order to improve on this, noting that AILs exist between atoms that are widely considered to be interacting, we can use a computed measure at the connected BCP to set the thickness of lines. This will result in thicker AILs for bonds and thinner AILs for ‘non-bonded’ interactions. Design is more tricky to use without invoking an ill-defined measure or introducing an arbitrary cut-off value.

The remaining line types (RCP lines, CCP lines etc.) are treated similarly, although in many plots of the topology they are left out entirely as it is hard to connect them to any common chemical concept.

Surfaces are represented either as a set of points or (via triangulation) as a set of quadrilaterals or triangles. As these objects contain points belonging to neither of the atoms that they separate, colouring them is difficult. When interested in atom A, for example, it seems sensible to colour the surface according to the element of A. However, that surface also belongs equally to B, so in rendering the AB system in either colour is inappropriate.