The Quantum Theory of Atoms in Molecules in Condensed Charge Density Space

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Abstract

We map the gradient field of the electron charge density ($\rho$) onto a 2D space. This produces the condensed charge density ($P$) that encompasses the full volumetric behavior of $\rho$ in a set of atomic charts called a molecular atlas. The observable bond is defined as the image in $\rho$ of the basin of attraction in $P$, analogous to the Bader atom, which is the basin of attraction in $\rho$.

Keywords: QTAIM, bond bundle, gradient bundle, charge density analysis, condensed charge density, atomic chart, molecular atlas

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1 Introduction

Richard Bader’s Quantum Theory of Atoms in Molecules (QTAIM) \cite{1} has been recognized as the only fully quantum mechanics-based theory that enables the use of traditional chemical concepts in an unambiguous manner \cite{22}. This singular achievement stems from the decomposition of a molecule or solid’s electron charge density ($\rho$) into non-overlapping proper open subsystems, each characterized by a well-defined energy and a set of properties that depend on energy. The sole condition constraining a proper open subsystem is that the net flux of the gradient ($\nabla\rho$) across its boundary must vanish \cite{17}.

While there are an infinite number of regions over which this zero flux condition is satisfied—regions now referred to as quantum divided basin \cite{8}—Bader realized that every nucleus is bounded by a unique surface over which the flux of $\nabla\rho$ is everywhere zero, denoted as a zero flux surface (ZFS). These regions Bader recognized as the atoms in molecules, which he called atomic basins, though they are also referred to as Bader atoms. Each of these atoms is diffeomorphic to a polyhedron, and is characterized by a nonarbitrary boundary, a well defined energy, and an unambiguous electron count. With a single insight Bader transformed fuzzy chemical concepts, such as atomic size and atomic energy, into quantum observables. Bader became the leading advocate for the school of thought seeking to reframe all of chemistry in terms of measurable quantities and his belief was that QTAIM would be the central framework from which this new chemical perspective would evolve.

The Bader atom is easily represented in terms of $\nabla\rho$ and its corresponding critical points (CPs)—the maxima, minima and saddle points where $\nabla\rho$ vanishes. An arbitrary gradient path (GP) originates from a minimum, called a cage CP, which may be located at infinity, and terminates at a maximum called a nuclear CP because it is typically coincident with an atomic nucleus. Equivalent to the ZFS-based definition, a Bader atom is the union of all GPs terminating at a specific nuclear CP. Bader noted that when two atoms share a polyhedral face, their nuclei must, as a topological necessity, be connected by a unique GP he called a bond path; a ridge along which $\rho$ is a maximum with respect to all neighboring paths. Such a path also necessitates the existence of a saddle point of index $-1$ located between bound nuclei and called a bond CP.

Perhaps due to the word “bond” in their designations, an unwarranted amount of attention has been focused on bond paths and bond CPs as researchers have repeatedly discovered bond CPs between atoms whose interactions are assumed to be destabilizing \cite{19,6,7,13}. These researchers have argued that such points cannot reflect bonding, and recently it has been proposed that “bond” should be stricken from their discussion \cite{21}. However, these arguments are antithetical to the premise of QTAIM, because neither a bond CP nor a bond path is bounded by a ZFS and hence do not have well defined energies and by themselves are not required to provide stability information. Still, the shear number and often extensive analyses of CPs, particularly bond CPs and bond paths, serves to obscure the main focus and strength of QTAIM; the partitioning of a molecule into proper open subsystems.

The Bader atom was recognized as the sole proper subsystem of a molecule until the introduction of the repulsive basin of Pendas et al. in 1997 \cite{14} (and later Popelier’s cage in 2000 \cite{20}). They argued that just as there are nuclear CP centered polyhedra there must be cage CP centered polyhedra satisfying the local zero flux condition. Repulsive basins were defined as the union of gradient paths that originate at a common cage CP. The ZFSs bounding repulsive basins must contain a number of nuclear CPs. Bader had originally discounted the significance of such ZFSs due
to the cusp in \( \rho \) at nuclear CPs resulting in undefined points in \( \nabla \rho \). However, the nuclear cusp is not real but rather a manifestation of the coulomb approximation to the Schrödinger equation.

The absence of a nuclear cusp opened the door to an infinity of ZFS-bounded volumes. Eberhart [4] and later Jones and Eberhart [11, 12], introduced one such volume they called the irreducible bundle (IB), a tetrahedral volume that is the simplex of \( \rho \), incorporating all four types of CPs—bond, cage, nuclear and ring (a saddle point of index +1). The vertices, edges, and faces of an IB are respectively the four types of CPs, the six shortest-length GPs connecting them pairwise, and the four least-area ZFSs with triplets of CPs as their corners. Like Bader atoms, IBs share vertices, edges and faces so as to fill space. The union of IBs sharing a common nuclear CP gives rise to the Bader atom. The union of IBs sharing a common cage CP gives rise to the repulsive basin. And the union of IBs sharing a common bond CP gives rise to the bond bundle (BB)—a partitioning of the charge density into unique ZFS-bounded volumes, each of which contains a single bond path and bond CP. BBs recover traditional bond properties like bond order [12, 5], and address issues like spurious bond CPs which have been shown to have tiny bond orders [15].

However, unlike Bader atoms and repulsive basins, which are readily apparent from an inspection of \( \nabla \rho \), all the boundaries of IBs are not obvious and are often difficult to locate. In correspondence with Eberhart [R. Bader, personal communication, 2004], Bader expressed concern that his theory with only one ZFS and a bond path was becoming less elegant, and with the boundaries of the IB defined as least area surfaces, QTAIM was becoming ad hoc, with the definition arising as but a means to specify a unique boundary between bonds. His point was, at least philosophically, well taken. And though Bader has passed away, we posthumously answer his question; an answer that points to a possible future research emphasis for QTAIM.

2 Condensed Charge Density Space

Developing a more satisfying means of identifying the special boundaries of QTAIM involves constructing the space of all volumes bounded by ZFSs, what we call the condensed charge density \( P \). Specifically, we will map GPs of \( \rho \) to points in \( P \) and show that the bond bundle is the topological analogue in \( P \) of the Bader atom in \( \rho \).

Recall that every GP in \( \rho \) originates from a cage CP and terminates at a nuclear CP. Sufficiently close to its terminus, GPs are radial, making it conceptually convenient to imagine every nuclear CP as the center of a sphere \( S_i \) of radius \( dr \). Passing through every point on the surface of these spheres is a GP. The points on such a sphere may be specified by a polar and an azimuthal angle, so each of the molecule’s GPs may be specified by a pair of coordinates and the index of the nuclear CP at it terminus, i.e. \( GP_i(\theta, \phi) \). Imagine covering each \( S_i \) with a set of nonintersecting differential elements of area \( dA = d\theta d\phi \) (Fig. 1a). The GPs passing through the points interior to each of these area elements gives rise to a family of differential volume elements each of which is bounded by a local ZFS. These differential gradient bundles, \( dGB_i(\theta, \phi) \) (Fig. 1b), are the smallest structures bounded by ZFSs and accordingly possess well-defined energies. The union of all \( dGB_i \) is equivalent to the union of all GPs terminating at nuclear CP \( i \) and hence recovers Bader’s atomic basin.

We define the condensed charge density, \( P_i(\theta, \phi) \), as the electron density contained in each \( dGB_i(\theta, \phi) \), such that \( P_i(\theta, \phi) = \int_{dGB_i(\theta, \phi)} \rho \). \( P \) is a scalar field with units of electrons per unit area, and maps \( \rho \) within a Bader atom onto a two-dimensional closed surface. As a visualization
tool, this allows one to view the intricate geometric behavior of $\rho$ at a glance, as in Fig. 2a, for a carbon atom in an ethene molecule.

Borrowing terminology from differential geometry, each $P_i$ is referred to as an atomic chart and the set of all atomic charts comprising a molecule is termed its molecular atlas. As an alternative to representing atomic charts as spheres, they may be projected onto a flat space as shown in Fig. 2b where a stereographic projection of the atomic chart in Fig. 2a is depicted. Every point in $P$ maps to a GP in $\rho$, every trajectory through $P$ maps to a ZFS in $\rho$, and any closed loop in $P$ maps to a volume in $\rho$ bounded by a ZFS and hence characterized by a well-defined energy. Such volumes are called gradient bundles (GBs) [16], and they describe all previously noted ZFS-bounded volumes, e.g. the atomic basin and the bond bundle.

3 Computational methods

All chemical simulations were performed with the Amsterdam Density Functional [23,3] ab initio software using the Perdew-Burke-Ernzerhof (PBE) functional [18] and a triple-zeta with polarization (TZP) all-electron basis set. Calculation of $P$ was performed using the gradient bundle analysis tool of the in house Bondalyzer package by the Molecular Theory Group at Colorado School of Mines.
Figure 2: Condensed charge density, $P$, of a carbon atom in ethene. Contour levels are those of a heat map throughout this paper, where red and blue indicate high and low values respectively.

a) Spherical mapping. Inset: Black, white, and red spheres respectively indicate carbon nuclear, hydrogen nuclear, and bond CPs (same scheme used when appropriate in remaining figures).

b) Stereographic projection with C-C bond path at the origin. Axes are in units of radians, corresponding to rotation around the sphere in (a). See electronic version of this text for color images.
Figure 3: Left) Three stereographic projections of \( P \) for a carbon in ethene, centered at the \( C = C \) bond path (center) and at each of the \( C - H \) bond paths (left and right). The three projections are overlapped and truncated on the left and right so as to avoid the largest regions of overlap, but overlap persists—the three upper (and lower) minima correspond to the same point on the sphere. GPs through \( P \) are shown, defining the three basins of attraction. The \( C = C \) and the two \( C - H \) basins are demarcated by a dashed green path, and the two \( C - H \) basins by a dot-dashed orange path. The right side of the figure shows these paths without the duplicate portions shown here.

Right) Multiple views of the same \( P \) mapped onto a sphere. The middle left view is centered at the \( C = C \) bond path, top/bottom show the same region from above/below, and the right shows the opposite side of the sphere. The dashed green and dot-dashed orange paths are the same as those in the left side of the figure. See electronic version of this text for color images.

4 The Topology of the Condensed Charge Density

Maxima in \( P \) typically map to bond paths in \( \rho \), as demonstrated in Fig. 2a where the three maxima on the carbon atomic chart coincide with the intersections of the carbon-carbon and two carbon-hydrogen bond paths (black paths) with the sphere. Just as all GPs terminating at the same maxima in \( \rho \) define the atomic basin as a unique volume, all the GPs in \( P \) terminating at a the same maxima define a similarly unique GB, and hence a unique ZFS-bounded volume in \( \rho \).

As an example, shown in Fig. 3 are stereographic projections for the carbon atomic chart in ethene centered on each of its three maxima. Also shown are three sets of GPs (black paths with arrows) each delineating a basin of attraction in \( P \). These basins are bounded by zero flux paths in \( P \) (dashed and dot-dashed paths) that map to ZFSs in \( \rho \). The union of such ZFSs for a molecular atlas partitions \( \rho \) into space-filling regions, each of which contains a single bond path. The energy of these regions is well defined and the sum of these energies gives the molecular energy. Additionally, they appear to be identical with the previously defined bond bundle delineated by special gradient surfaces [12].
An atomic chart maps to a Bader atom, so a basin in $P$ does not itself correspond to a BB, but rather to a bond wedge, the intersection of a BB and a Bader atom—i.e. a single atom’s contribution to a BB. The term “bond wedge” was suggested by Blanco [M. Blanco, personal communication at the 5th European Charge Density Meeting, 2008].

We offer the following definition of a BB: the image in $\rho$ of GPs in $P$ terminating at a common maximum. As the Bader atom is the union of GPs in $\rho$ terminating at a common nuclear CP, the Bader atom and the BB are conceptually equivalent, one is a basin in $\rho$, and the other is a basin in $P$.

For the vast majority of cases, the BB definition provided here recovers the same regions as those resulting from the earlier definition [11, 12]. This is demonstrated in Fig. 4 where the BB surface coincides with the zero flux path (the green dashed line in Fig. 3).

There are some noteworthy exceptions, however, as in the case of dibenzene where conventional QTAIM analysis reveals a bond CP between hydrogen atoms. The presence of this bond CP has sparked controversy within the QTAIM community because the H–H bond path is not accompanied by any of the telltale energetic or spectroscopic properties associated with a “bond” [19]. We have previously analyzed this system using the earlier criteria for a BB [15] and discovered that the H–H BB contains 0.6 ± 0.3 electrons and has a shape indicative of instability [9, 10]. We suggested at the time that a BB’s electron count and shape serve as measures of its “strength” and that the existence of a bond CP alone should not be taken as an indicator of “bonding.”

To our delight, the issue becomes moot when analyzed within the new bond bundle perspective, as the H–H bond path of dibenzene (Fig. 5) does not map to a maximum in $P$ (within the accuracy of our calculations). Obviously the existence of a bond CP and its corresponding bond path is not a sufficient condition for the formation of a BB. A maximum in $P$ requires, in addition to a bond

Figure 4: $P$ for carbon atom in ethene (sphere) shown with $C = C$ bond bundle surfaces (blue) that were identified according to the previously defined special gradient surface criteria. Contours on BB surfaces are only shown to enhance perspective. See electronic version of this text for color images.
Figure 5: Stereographic projections of $P$ for the terminal (left) and H-bonded (right) hydrogen nuclear CPs in dibenzene. Red arrows indicate the respective origins of the projections. See electronic version of this text for color images.

path in $\rho$, constraints on the relative eigenvalues of the Hessian along and near the bond path and interatomic surface.

The nature of these constraints can be illustrated by considering a bond path’s two nearest neighboring $d$GBs, one of which ($d$GB$_1$) contains the bond path, thus coinciding with the interatomic surface, as shown in Fig. 6. If $d$GB$_1$ is to map to a maximum in $P$, it must contain a greater charge density than $d$GB$_2$, which in turn will be mediated by the relative charge densities in these $d$GBs over two regions. First, the region (I) along the bond path where the curvature perpendicular to the bond path is negative. Over this region the density contained in $d$GB$_1$ is always greater than the density in $d$GB$_2$—the greater the negative curvature the more pronounced will be this difference. In the second region (II), which runs along the interatomic surface, the curvature of the charge density perpendicular to the interatomic surface is positive. So, in this region the density contained in $d$GB$_2$ will be greater than that in $d$GB$_1$. This difference is minimized by a less curved charge density perpendicular to the interatomic surface. Combining the two constraints, bond paths will map to maxima in $P$ when the curvature perpendicular to the bond path is large and negative and that perpendicular to the interatomic surface is small and positive.

To the extent that the Hessian at the bond CP captures the behavior of $\rho$ over a wider region, a BB will form when the curvature of $\rho$ at the bond CP is flatter parallel to the bond path and steeper (negatively) perpendicular. Such behavior will be indicated by a large negative value of the laplacian ($\nabla^2 \rho$) at the bond CP. Bader, arguing from a totally different perspective, came to this conclusion years ago [2] when he asserted that bond energy—or the degree of covalence—was given by $\nabla^2 \rho$ at a bond CP.
Figure 6: Simple representation of the two closest dGBs to a bond path and a line separating the bond path and interatomic surface regions.

5 Summary

It is an established consequence of density functional theory that chemical phenomena are dictated by $\rho$ and its redistribution through a physical or chemical process. And though the ability to recover and predict chemical behavior directly from $\rho$ would be transformative, this goal is as yet unrealized.

QTAIM, as originally formulated, made some progress toward a full charge density representation of chemical phenomena by providing a framework through which to quantify charge redistribution between atoms and to describe the topological changes associated with bond breaking and rearrangement. However, moving from a qualitative topological picture of charge redistribution to a precise quantitative description framed within traditional chemical concepts has proved tenuous, leading some to suggest that Bader’s original aspirations for QTAIM are unachievable.

Here we have rejected this prognosis for QTAIM. It seems to us that as we seek the energy mediated traces of chemical behavior, the natural place to look is within a space over which energy is well-defined. The condensed charge density ($P$) is one such space, and consequently, images in $P$ reflect the energetically constrained behavior of $\rho$ by the full, and only, region to which it corresponds.

The condensed charge density space also allows for a QTAIM-appropriate definition of the bond bundle by revealing the observable bond as the analog of the observable (Bader) atom. For where the Bader atom is an attractor in $\nabla\rho$, the bond bundle is an attractor in $\nabla P$. Together these observations imply that $P$ is an appropriate space in which to describe the energetics of bond breaking and rearrangement.

Investigation to explore the evolution of $P$ accompanying physical and chemical processes, across all classes of materials and molecules, will open the door to explanations of chemical phenomena as the manifestation of charge density redistribution within and among observable bonds and atoms.
6 Conflicts of Interest

There are no conflicts of interest to declare.

7 Acknowledgments

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