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Revisiting the Foundations of the Quantum Theory of Atoms in Molecules: Toward a Rigorous Definition of Topological Atoms

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ABSTRACT: An explicit classification of consistent variational constraints within the context of the "quantum theory of proper open subsystems" as well as the "quantum theory of atoms in molecules" (QTAIM) it presented. It is demonstrated that the general variational procedure is not sensitive enough to discriminate between different mathematically consistent variational conditions. The uniqueness of the regional kinetic energy is employed to derive the net zero-flux condition and the regions satisfying this condition are named as *quantum divided basins*. A modified form of the local zero-flux is proposed in order to define topological atoms within the context of the orthodox QTAIM.   © 2008 Wiley Periodicals, Inc. Int J Quantum Chem 109: 726–732, 2009

Key words: quantum theory of atoms in molecules; zero-flux conditions; topological atom; variational procedure; quantum divided basins; homotopy groups

1. Introduction

The quantum theory of atoms in molecules (QTAIM) is now routinely used for identification and computational consideration of atoms within molecules [1–5]. The recent applications of this approach go far beyond the theoretical community and penetrate even into experimental crystallography [6]. In contrast to these vast applications (see [7] as a comprehensive compendium), less attention has been paid to the mathematical foundations of this approach. This is particularly true for the basic quantum mechanical formalism behind QTAIM namely, the "quantum theory of proper open subsystems" (QTPOS); QTPOS is the general framework for a local description of quantum observables within 3D space (see [1] for details).

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In this regard, the controversial exchanges [8–14] some years ago clearly demonstrate the need for a through analysis of the mathematical foundations of QTAIM. In a recent article, we have reinvestigated the variational procedure of this theory in some detail [15]. The outcome of our analysis demonstrates that it is possible to employ a consistent variational procedure (without the previously mentioned mathematical flaws) within the context of QTAIM. On the other hand, the same analysis came to the conclusion that the local zero-flux condition (as the basic equation describing the topological atoms, TAs [1]) is not directly extractable from the variational procedure (see Section 4 of [15]). Accordingly, the relevant mathematical elaborations demonstrate vividly that the local zero-flux condition is not the only consistent variational constraint and the net zero-flux condition is equivalently acceptable. Although based on Gauss's theorem it is possible to derive the net zero-flux condition from the local zero-flux equation, but the reverse is not true [15]. This casts doubt whether usual TAs that are derived from the local zero-flux equation are the only 3D regions satisfying the net zero-flux condition.

On the other hand, employing finite nucleus models instead of the usual point charge model of the nucleus it demonstrated that each TA could be divided into tighter basins [8]. Figure 1 depicts a 2D view of a typical example. These 3D regions fulfill both the net and local zero-flux conditions, consequently all the regional theorems of QTPOS that were derived for TAs may be also applied to these regions. In this article, we have to go further and introduce 3D regions that satisfy the net but not the local zero-flux equation irrespective of the nucleus model. To verify this possibility, we will employ the hydrogen atom in its ground state. Accordingly, it will be demonstrated that the hydrogen atom is *dividable* into 3D regions each of which satisfies the net but not the local zero-flux condition. The approach described in this article could be extended easily to more complex atoms and molecules revealing a general but less recognized feature of the difference between these two zero-flux conditions. Although one may discard such 3D regions from QTAIM-based on current chemical or physical intuition (since they are different from TAs), mathematically, there is no reason to dismiss them from the general framework of QTPOS. We name collectively all these 3D regions (that are different from TAs) as quantum divided basins (QDBs). Because the main theorems of QTPOS, e.g., the local virial
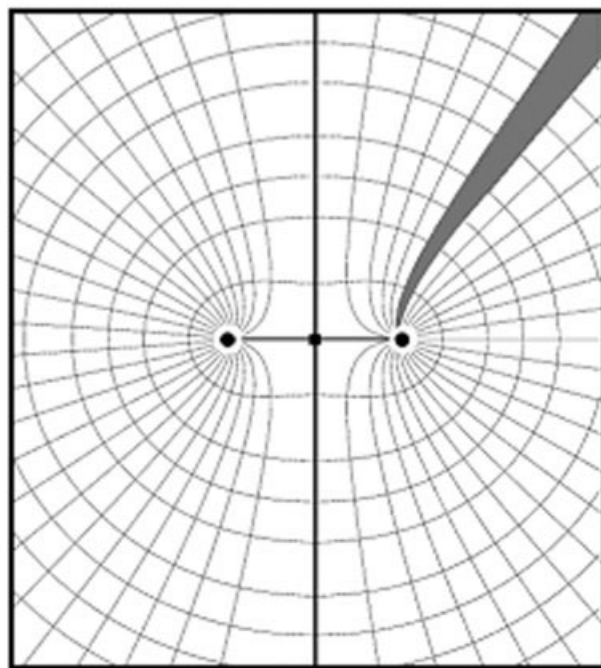

FIGURE 1. A 2D view of a typical example of a QDB (the shadowed part) in a homopolar diatomic molecule assuming finite nuclei (the black dots are nuclei whereas the black square is the bond critical point). The line in the middle of picture is the border of atoms (interatomic surface) within the plane. Note that the contours of the charge density are superimposed on the gradient vector field of the charge density in a plane containing both nuclei.

theorem [1–5], may equivalently be applied to both TAs and QDBs, the question may arise that how it is possible to classify and distinguish TAs from QDBs. This account is a primary quest to touch this problem.

2. The Variational Procedure and the Primary Classification of Proper Subsystems

The net and local zero-flux conditions are both introduced as variational constraints within framework of the variational procedure [1, 15]. The general variational constraint is $\delta_\Psi L(\Psi,\Omega) = (-\hbar^2/4mN)\delta_\Psi \int_\Omega dr \nabla^2 \rho_\Psi = 0$ where, ρ_Ψ is the one-electron charge density and Ψ is the statefunction of molecular system (see 5.88b in [1]). This variational constraint could be derived equally from the following independent conditions (as prototype examples):

$$\vec{\nabla}\rho_{\Psi}(r) \cdot \vec{n}(r) = 0 \text{ (local zero-flux)} \qquad (1a)$$

$$\int_{\Omega} \nabla^2 \rho_{\Psi}(r) = 0 \text{ (net zero-flux)} \qquad (1b)$$

$$\int_{\Omega} \nabla^2 \rho_{\Psi}(r) = c(c \neq 0, c \in R) \text{ (net constant-flux)}$$

$$(1c)$$

All these equations are consistent with the general variational constraint. In other words, the variational procedure is *not* sensitive enough to distinguish the 3D regions Ω that satisfy each of these equations. More importantly, each of these conditions could yield unique and disparate 3D regions. Thus, one needs *external guides* in order to introduce the *proper subsystems*. An explicit example may highlight this obstacle.

In the orthodox QTAIM, the outcome of application of the local zero-flux equation to a hydrogen atom (assuming the point charge nucleus model) is the trivial borderline at infinity [1]. So, the regional theorems of QTPOS must be applied to the whole system as a single atomic basin. This is not the case if one assumes the net zero-flux condition. Taking into account the ground state eigenfunction $\Psi(r) = 1/\sqrt{\pi}e^{-r}$, the corresponding Laplacian of the charge density is:

$$\nabla^2 \rho(r) = 4\pi^{-1}\left(1 - \frac{1}{r}\right)e^{-2r} \qquad (2)$$

Then, the result of integration of the Laplacian on a 3D region assuming $r \geq 1/2$ is:

$$\int_{\phi_0}^{\phi_1} \int_{0_0}^{0_1} \int_{\frac{1}{2}}^{\xi} \nabla^2 \rho(r) r^2 Sin(\theta) dr d\theta d\phi$$

$$= \lambda[\xi^2 e^{-2\xi} - (4e)^{-1}] \qquad (3)$$

where $\lambda = 2\pi^{-1}(\phi_1 - \phi_0)(Cos\theta_1 - Cos\theta_0)$ and, ϕ_i and $\theta_i (i = 0,1)$ are arbitrary angular boundaries. The continuous function $g(\xi) = \xi^2 e^{-2\xi}$ with absolute maximum $g(1) = e^{-2}$ satisfies the condition $g(0) = \lim_{\xi \to \infty} g(\xi) = 0$. Taking into account that $e^{-2} > (4e)^{-1}$, the equation $\xi^2 e^{-2\xi} - (4e)^{-1} = 0$ has a solution ξ_0 greater than 1 ($\xi_0 \approx 1.7564$). Accord-
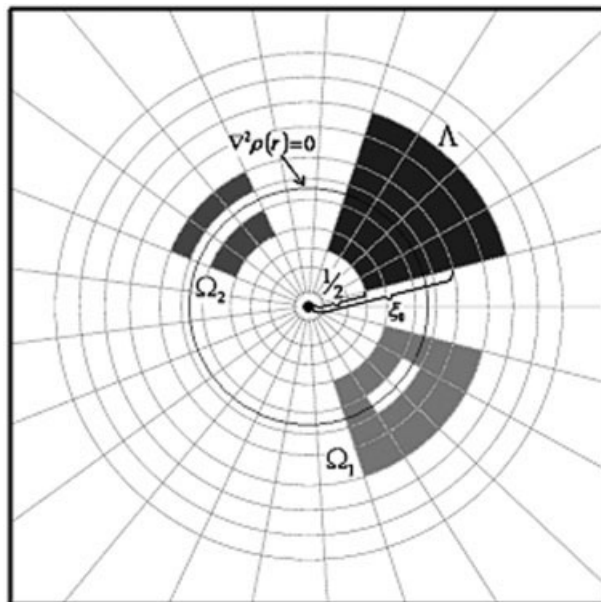

FIGURE 2. A 2D view of three typical examples of QDBs in hydrogen atom. See text for details.

ingly, for a simple connected region Λ described in spherical coordinates by $\phi_0 \leq \phi \leq \phi_1, \theta_0 \leq \theta \leq \theta_1$ (ϕ_i and $\theta_i (i = 0,1)$ are arbitrary) and $1/2 \leq r \leq \xi_0$ one obtains:

$$\int_{\Lambda} \nabla^2 \rho(r) d\Lambda = 0 \qquad (4)$$

On the other hand, for each $(r,\theta,\phi) \in \partial\Lambda$ subject to $r = \xi_0$ or $r = 1/2$ we arrive at the following result:

$$\vec{\nabla}\rho(r) \cdot \vec{n}(r) \neq 0 \qquad (5)$$

In this accord, the region Λ does not satisfy the local zero-flux condition. Figure 2 depicts a 2D view of this connected region Λ and two other typical regions satisfying the net zero-flux condition. As stated previously, we name these regions as well as those like Figure 1 collectively as "QDBs" to emphasize their unique nature namely, satisfaction of the net zero-flux condition and their difference with TAs. Figure 2 demonstrates that a QDB is not necessarily a connected region. For instance, it could be a non-simply connected Ω_1 or a completely disconnected Ω_2. Irrespective of these geometrical differences, due to satisfaction of the net zero-flux con-

dition, the regional kinetic energy is a well-defined quantity in all these QDBs (see the Appendix for details). This directly results from the net zero-flux condition because:

$$T(\Omega) = \int_{\Omega} K(r)dr = \int_{\Omega} G(r)dr \Rightarrow -\frac{\hbar^2}{4m}\int_{\Omega} dr\nabla^2\rho_{\Psi}(r) = 0$$

(6)

where K and G are the local kinetic energy densities of the operators P^2 and $P^T \cdot P$, respectively [1, 16]. So, there is *no* intrinsic difference between QDBs and TAs within the general framework of QTPOS. It is possible even to conceive a condition that is consistent with the general variational constraint but does not yield 3D regions with well-defined regional kinetic energies. The net constant-flux condition (1c) is a prototype example. It is easy to verify that $\int_{\Omega} K(r)dr - \int_{\Omega} G(r)dr = -\hbar^2 c/4mN \neq 0$. Therefore, the regional kinetic energy is not unique for a 3D region that satisfies the net constant-flux condition.

Because QTAIM deals solely with the TAs, one must somehow distinguish them from QDBs. This could be done in a two-step procedure. First, the local zero-flux condition must be used as the variational constraint [1, 15]. This removes all other regions that satisfy the net but not the local zero-flux condition. Then, in the second step, the 3D regions that are constructed from surfaces that satisfy the local zero-flux equation must be classified. In this latter step, we must somehow distinguish the usual interatomic surfaces from those that cross the finite nuclei. The relevant mathematical procedure is discussed in following section.

3. Homotopy Groups and the Rigorous Definition of TAs

As was mentioned earlier, selection of the local zero-flux condition as a variational constraint cannot rid us from the atomic surfaces that cross finite nuclei. Therefore, we need a secondary mathematical tool (the so-called external guide) to discard these extra solutions. To do so, we appeal to an algebraic method that allows us to produce a forthright definition of proper subsystems.

Let M be a molecular system in the stationary state Ψ. Also, consider Δ_ρ to be the set of (3, −3) critical points (topological attractors [1]) of the ρ_{Ψ}.

Suppose that T_M is a "transformation" from the molecular system M into itself defined by:

$$T_M:M \rightarrow M - \Delta_\rho$$

(7)

In other words, the transformation T_M eliminates all (3, −3) critical points of the molecular system and M − Δ_ρ is nothing other than M with some "holes" instead of (3, −3) critical points. It is essential to note that these holes are *only* mathematical artifacts to allow us to recognize the (3, −3) critical points via *algebraic topology*, a theory that discriminates between connected regions with and without holes [17]. Moreover, we emphasize that these holes yield no *real singularities* within the charge density distribution. In a certain sense, the charge density is not aware of the presence of these holes. In this way, in what follows we will replace the molecular system M by $\dot{M} \equiv M - \Delta_\rho$, without loss of generality. Suppose that S is a surface that satisfies the local zero-flux condition. i.e.,

$$r \in S \Rightarrow \nabla\rho_{\Psi}(r) \cdot n(r) = 0$$

(8)

It is important to realize that this surface is not unique. In fact one may represent S via a function F as follows:

$$S = S_F = \{r \in R^3 : F(r) = 0\}$$

(9)

where the function F satisfies Bader's equation [18]:

$$\partial_x\rho_{\Psi}\partial_x F + \partial_y\rho_{\Psi}\partial_y F + \partial_z\rho_{\Psi}\partial_z F = 0$$

(10)

In other words, the gradient of ρ_{Ψ} is tangent to the surface S_F (i.e., S_F is a "separatrix surface" of the vector field $\nabla\rho_{\Psi}$). Generally, without any initial or boundary conditions, a partial differential equation like (10) has a class of solutions $\{F\}$. Therefore, according to relation (9), one can attribute a class of surfaces $\{S_F\}$ to a molecular system that is in the specific state Ψ. On the other hand, for each member $F \in \{F\}$ the corresponding surface S_F partitions the molecular system (the electron density in real space) into nonoverlapping connected regions, each of which is bounded by zero-flux surfaces (*not* necessarily Bader's interatomic surfaces). So, each connected component is a QDB. We represent this union of the nonoverlapping connected regions by $\dot{M} - S_F$ and call the corresponding partitioning an *F*-partitioning. In this way, we have a "rule" that relates a family of partitioning to a molecular sys-
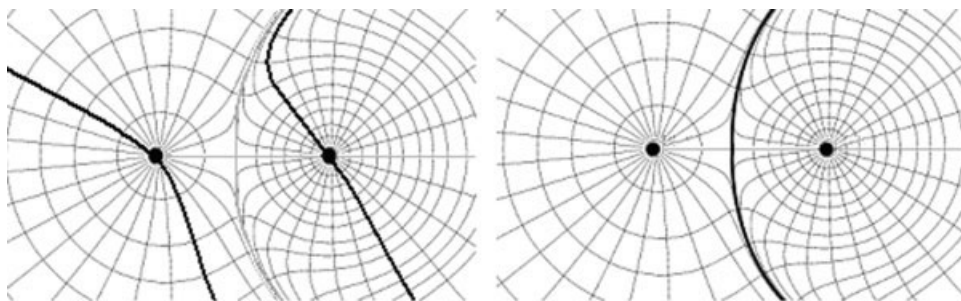
FIGURE 3. The shape at the left side represents one of infinite number of non-proper solutions of Baderâ's equation while the shape at the right side represents the unique proper solution.

tem in the specific state Ψ by means of Bader's equation. i.e.,

$$\Psi \rightarrow Bader's\ equation \rightarrow$$
$$\{F\} \rightarrow family\ of\ partitionings \quad (11)$$

Figure 3 shows two different partitionings for a typical heteropolar diatomic molecule. At this stage of development, the fundamental issue is the discrimination of proper *F*-partitioning. Because within QTAIM Eq. (10) is not linked to any initial condition, one *cannot* attribute a unique proper solution to this equation. Thus, we appeal to the celebrated algebraic method, algebraic topology [17], to achieve this goal.

To do so, we assign a group so-called the *second homotopy group* [17] to each QBD. The second homotopy group of the region Ω is denoted by $\pi_2(\Omega)$. Accordingly, it is possible to discriminate between QDBs containing a $(3, -3)$ critical point (a hole as an interior point) and those without one. For every QDB containing a $(3, -3)$ critical point (hole) the second homotopy group is the set of integer numbers "Z", while if the $(3, -3)$ critical point is in the exterior of a QDB, then, the associated homotopy group will be "trivial" (note that because QDBs are open regions so each critical point on the boundary, by definition, is assumed as an exterior point). One may introduce the *characteristic map* $\chi:\{F\} \rightarrow N$ from the class of solutions of Bader's equation into the set of natural numbers, N:

$\chi[F] =$ The number of *QDB*s of F-partitioning

in which their second homotopy groups is $\pi_2 = Z$

$$(12)$$

In practice, the characteristic map counts the number of connected components (QDBs) of *F*-partitioning that contains $(3, -3)$ critical points. Thus, the proper solution of Bader's equation may be defined as follows:

The solution P of Bader's equation is called proper if and only if $\chi[P] = |\Delta_\rho|$, where $|\Delta_\rho|$ denotes the cardinality number of Δ_ρ.

Thus, Bader's equation can be reexpressed in a new "analytic-algebraic" form:

$$\begin{cases} \nabla F \cdot \nabla \rho_\psi = 0 \\ \chi[F] - |\Delta_\rho| = 0 \end{cases} \quad (13)$$

The first analytical equation is what traditionally employed within the orthodox QTAIM, while the second algebraic one is a mathematical expression of what Bader conceives about proper partitioning of molecular systems. Accordingly, Eq. (13) has a unique solution P such that each nonoverlapping connected regions of $\dot{M} - S_P$ is called a TA. According to this definition, the number of pseudo-atoms (regions containing nonnuclear attractors [1]) is the difference between $\chi[P]$ and the number of nuclei.

4. Conclusion

In this article, a detailed analysis was done of the mathematically acceptable variational constraints. The analysis demonstrates that one may conceive 3D regions (QDBs) with well-defined regional kinetic energies that are not similar to TAs. Nothing inherent in the mathematical foundations of QTPOS distinguishes QDBs from TAs but this was done by an ad hoc selection [19]. This is understandably based on current chemical intuition. The

analytic-algebraic form of the local zero-flux equation is a mathematically rigorous alternative definition of TAs. One may assume this definition as an axiom (the so-called external guide) that must be added to QTPOS to reach to the orthodox QTAIM. In this point of view, QTAIM is a possible variant of QTPOS. Possible applications of QDBs in molecular systems are another problem that is under consideration by the authors and will be discussed in a separate publication.

Appendix: A General Consideration of the Regional Kinetic Energy and the Local Virial Theorem for QDBs

The regional kinetic energy is a well-defined quantity in all QDBs. This could be demonstrated for a general family of kinetic energy densities [20, 21] namely:

$$T_\alpha(r) = (2\pi)^{-6} \int \exp(-i\tau \cdot p + i\eta \cdot (u - r))\alpha(\eta,\tau)\frac{p^2}{2m}$$

$$\Psi^*\left(u - \frac{1}{2}\tau\hbar\right)\Psi\left(u + \frac{1}{2}\tau\hbar\right)d\eta d\tau du dp \quad (A1)$$

where α is any function confined to the constraint $\alpha(\eta,\tau) = \alpha(\eta \cdot \tau)$. Integrating over a QDB, Λ, leads to the following result:

$$T_\gamma(\Lambda) \equiv \int_\Lambda T_\gamma(r)d\Lambda = \int_\Lambda T_\beta(r)d\Lambda \equiv T_\beta(\Lambda)$$

$$(A2)$$

The relation (2) indicates that the regional kinetic energies that are introduced by the relation (1) are well-defined for all QDBs. Especially, assuming $\gamma = Cos(\hbar/2(\eta \cdot \tau))$ and $\beta = \exp(\hbar^2/8(\eta \cdot \tau)^2)$ in the relation (1), one obtains [20, 21]:

$$T_\gamma(\Lambda) \equiv K(\Lambda) = \int_\Lambda d\tau \frac{-\hbar^2}{4m}\{\Psi*\nabla^2\Psi + \Psi\nabla^2\Psi^*\}$$

$$(A3)$$

$$T_\beta(\Lambda) \equiv G(\Lambda) = \int_\Lambda d\tau \frac{\hbar^2}{2m}|\nabla\Psi|^2 \quad (A4)$$

These are the usual forms of the regional kinetic energies that are considered in the orthodox QTAIM. According to relation (2), one obtains:

$$K(\Lambda) = G(\Lambda) = T_\alpha(\Lambda) \quad (A5)$$

where $T_\alpha(\Lambda)$ is the representative of the regional kinetic energies. Relation (5) is similar to relation (5.53) in [1]; that is expressed for 3D regions bounded by a local zero-flux surface. Moreover, the generalized regional virial theorem [1] is also valid for the QDB, Λ:

$$-2T_\alpha(\Lambda) = \int_\Lambda d\tau\{-r \cdot \nabla \cdot \vec{\sigma}\} + \int_{\partial\Lambda} dAr \cdot \vec{\sigma} \cdot n = V_b(\Lambda)$$

$$+ V_s(\Lambda) = V(\Lambda) \quad (A6)$$

Or equivalently:

$$E(\Lambda) = 1/2 \, V(\Lambda) = -T_\alpha(\Lambda) \quad (A7)$$

In these relations, $V_b(\Lambda)$, $V_s(\Lambda)$, $V(\Lambda)$, are the basin, surface, and total virial of Ehrenfest forces acting on the region Λ, respectively. Also, the quantities σ and $E(\Lambda)$ are stress tensor density and total energy of the region Λ, respectively [1] (note that expression (7) for $\Lambda \equiv R^3$ is the usual virial theorem for a quantum system). It is important to realize that this regional virial theorem could not be written for an arbitrary 3D region Σ because the relation (7) converts into following form:

$$-2T_\alpha(\Sigma) = V(\Sigma) - \frac{\alpha''(0)}{m}\int_\Sigma \nabla^2\rho(r)d\Sigma \quad (A8)$$

Consequently, although QDBs are not TAs they share all properties of well-defined quantum subsystems (or in Bader's own words [1]: "proper open quantum subsystems") and the generalized local virial theorem may be applied to these regions as well. Hence, TAs are a special subclass of 3D regions and the regional theorems (like generalized local virial theorem) may be applied to them.

It is straightforward to extend our argument to other more complex atoms or even molecules. Because the Laplacian of the electronic charge density of more complex atoms contains separate positive and negative regions [1, 22, 23], thus, it is possible to combine them in a manner that certain 3D regions fulfill the net zero-flux condition. This approach is similar to what has been described for the hydrogen atom and the only difference is the explicit mathematical expression of the Laplacian of charge density in more complex atoms. The appropriate radial variables for integration in general may be derived from the roots of the equation $\nabla^2\rho(r) = 0$. In molecules, the inner structure of the Laplacian of charge density (inner electronic shells) is similar to the free atoms but in the internuclear regions (outer or valence electronic shells), because of polarization of the constituent atoms, QDBs (in contrast to spherically symmetric atoms) would not have the symmetric angular structure and so these variables could not be chosen arbitrarily. Nevertheless, the presence of negative and positive regions of the Laplacian of charge density guarantees that there are always certain regions satisfying the net but not local zero-flux conditions.

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