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Revisiting the Foundations of Quantum Theory of Atoms in Molecules (QTAIM): The Variational Procedure and the Zero-Flux Conditions

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ABSTRACT: A rigorous mathematical procedure is proposed in order to employ the variational apparatus in "Quantum theory of atoms in molecules." This mathematical procedure is free from the previously reported mathematical obstacles. Although it is possible to apply the Schrödinger's variational procedure to derive the putative net zero-flux condition, no claim has been made to derive the equation of motion (Schrödinger equation) from subsystem variational procedure. In this regard, the problem of admissible and general neighborhoods and their relevance to the subsystem variational procedure has been discussed thoroughly in this article. In the end, a brief discussion has been offered to emphasize the difference between the net and local zero-flux conditions with particular emphasize on its logical consequences. © 2008 Wiley Periodicals, Inc. Int J Quantum Chem 108: 1477–1484, 2008

Key words: quantum theory of atoms in molecules (QTAIM); variational procedure; net zero-flux condition; local zero-flux condition; mathematical neighborhoods

1. Introduction

The quantum theory of atoms in molecules (hereafter abbreviated as QTAIM) has recently attracted a great deal of attention from both theoretical and computational aspects. Although foundations of this theory were formally completed in

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1981 [1, 2], and later comprehensively reviewed in 1990 [3]; the growing computational experiences in the previous decade have revealed interesting features of this theory, in the realm of molecular bonding, that were totally unprecedented in traditional approaches. This led to the emergence of struggles and controversies on the mathematical foundations [4–15], as well as the chemical interpretation of computational results [16–24]. This seems to have originated from the very nature of this theory (with respect to traditional standards of the chemical

community), which in turn has its roots in the fact that QTAIM is usually described in an axiomatic manner. On the other hand, this mathematical solidification is at variance with the fuzzy nature of chemical language and leaves less room for ad hoc interpretations [25, 26]. All these features bear certain methodological problems that need clarification possibly within the newly developed field of "philosophy of chemistry." However, in this article, we will try to concentrate exclusively on the mathematical foundations of this theory, and leave a thorough discussion on other aspects of QTAIM to another article.

2. The Nature of the Problem

The variational procedure within QTAIM is usually imagined as the very foundation of this theory [1–3]. Thus, any obstacle within this procedure may have fatal consequences on its applications. Indeed, some mathematical obstacles have been discussed in the case of the application of the variational procedure to deduce the zero-flux conditions [4, 15]. From our point of view, Bader's response to these criticisms [8, 27] cannot be regarded as mathematically adequate. In this article, we will introduce a detailed mathematical strategy to reorganize the subsystem variational procedure in order to circumvent the known obstacles. We hope that our procedure and the logic behind it will serve as a mathematically sound foundation for the application of the variational approach within context of QTAIM.

On the other hand, the difference between the *net* and *local* zero-flux conditions has also been emphasized [4, 15], and the authors have briefly stressed that the celebrated local zero-flux condition (the foundation of "topological" definition of atom [1, 3]) is a sufficient but not necessary condition for the very definition of "quantum atom." Therefore, this condition is not extractable from generalization of the quantum mechanics of proper open subsystems [1–3]. Accordingly, only net zero-flux condition may be regarded as a necessary condition. Although Bader discussed [8, 27] this problem in some detail, the difference between net and local zero-flux conditions may, indeed, bear interesting consequences that have not been considered yet (at least in formal publications). This issue will also be discussed in this account.

3. Subsystems Variations and Required Mathematical Toolbox

The details of mathematical procedure and entities employed in this section may be found in the relevant monographs [28, 29], thus they are not reiterated in the text.

3.1. CONTINUOUS DEFORMABILITY AND FUNCTION SPACE PARTITIONING

Let $C(R^3)$ be the space of all bounded continuous complex functions on R^3, and X be the subset of $C(R^3)$ contains on functions with specific boundary condition. Also, let $\hat{S}$ be a "rule" that relates a 2D manifold (we should call it a general surface that is embedded into R^3) to each function Ψ that is a member of X. We will denote this general surface related to Ψ by S_Ψ. In this stage, we do not assume anything regarding the very nature of the rule $\hat{S}$.

Definition 3.1.1. Let S and T be two general surfaces that are embedded into R^3. The surface S is continuously deformable into the surface T, if there is a family of functions $F_t: S \to R^3$, $t \in [0,1]$ that for each t, the function F_t is one-to-one continuously differentiable and $F_0(S) = S$ as well as $F_1(S) = T$. The family $\{F_t\}$ is called as continuous deformation between S and T.

Accordingly, the definition 3.1.1 allows us to define a relation on the space X via a specific rule $\hat{S}$. Let Ψ and Φ be two functions that are members of X, and $\hat{S}$ be a specific rule. One can define the relation $\overset{\hat{S}}{\leftrightarrow}$ on X as follows: "For two functions Ψ and Φ, we write $\Psi \overset{\hat{S}}{\leftrightarrow} \Phi$ if and only if the general surface S_Ψ is continuously deformable into the surface S_Φ."

Theorem 3.1.2. The relation $\overset{\hat{S}}{\leftrightarrow}$ is an equivalence relation on X.

We recall that a relation R on a set A is an equivalence relation if and only if:

I. R is reflexive: aRa for all $a \in A$.
II. R is symmetric: whenever aRb then bRa.
III. R is transitive: If aRb and bRc then aRc.

Proof of theorem 3.1.2:

I. The relation $\overset{\hat{S}}{\leftrightarrow}$ is reflexive.

Let Ψ be an arbitrary function in X and let $\{F_t\}$, $t \in [0,1]$ be a family of functions as is defined: $F_t =$

$id{:}S_\Psi \rightarrow R^3$ wherein id is the identity function. Therefore, for each t the function F_t is one-to-one continuously differentiable and $F_0(S_\Psi) = S_\Psi$ as well as $F_1(S_\Psi) = S_\Psi$. Thus, we have $\Psi \overset{\hat{s}}{\leftrightarrow} \Psi$.

II.   The relation $\overset{\hat{s}}{\leftrightarrow}$ is symmetric.

Let Ψ and Φ be two functions in X and $\Psi \overset{\hat{s}}{\leftrightarrow} \Phi$. Consequently, there is a continuous deformation $\{F_t\}$ between S_Ψ and S_Φ, such that $F_0(S_\Psi) = S_\Psi$ and $F_1(S_\Psi) = S_\Phi$. We set $G_t = F_{(1-t)} \circ F_1^{-1}$ and claim that $\{G_t\}$ is a continuous deformation between S_Φ and S_Ψ. Indeed, for each t the function G_t is one-to-one continuously differentiable and $G_0(S_\Phi) = F_1 \circ F_1^{-1}(S_\Phi) = S_\Phi$ as well as $G_1(S_\Phi) = F_0 \circ F_1^{-1}(S_\Phi) = F_0(S_\Psi) = S_\Psi$. Therefore, we have $\Phi \overset{\hat{s}}{\leftrightarrow} \Psi$.

III.   The relation $\overset{\hat{s}}{\leftrightarrow}$ is transitive.

Let Ψ, Φ, and Θ be three functions in X such that $\Psi \overset{\hat{s}}{\leftrightarrow} \Phi$ and $\Phi \overset{\hat{s}}{\leftrightarrow} \Theta$. Therefore, there are two continuous deformations $\{F_t\}$ and $\{G_t\}$ between S_Ψ and S_ϕ as well as between S_Φ and S_Θ, such that $F_0(S_\Psi) = S_\Psi$, $F_1(S_\Psi) = S_\Phi$, $G_0(S_\Phi) = S_\Phi$, and $G_1(S_\Phi) = S_\Theta$. We set $H_t = \begin{cases} F_{(2t)} & \text{if } 0 \leq t \leq 1/2 \\ G_{(2t-1)} \circ F_1 & \text{if } 1/2 \leq t \leq 1 \end{cases}$. It is easy to check that $H_t{:}S_\Psi \rightarrow R^3$ is one-to-one continuously differentiable for each t. Furthermore, we have $H_0(S_\Psi) = F_0(S_\Psi) = S_\Psi$ and $H_1(S_\Psi) = G_1 \circ F_1(S_\Psi) = G_1(S_\Phi) = S_\Theta$. Consequently, the family $\{H_t\}$ is a continuous deformation between S_Ψ and S_Θ. Thus, we have $\Psi \overset{\hat{s}}{\leftrightarrow} \Theta$.

Accordingly, a specific rule $\hat{S}$ leads to a specific equivalence relation $\overset{\hat{s}}{\leftrightarrow}$ on X. So, for a function Ψ in X, the subset of X containing all elements of X that are equivalent to Ψ under the relation $\overset{\hat{s}}{\leftrightarrow}$ is called an equivalence class of Ψ and is denoted as $[\Psi]_{\hat{s}}$. This equivalence class is mathematically expressed as follows:

$$[\Psi]_{\hat{s}} = \{\Phi \in C(R^3) \therefore \Phi \overset{\hat{s}}{\leftrightarrow} \Psi\}. \quad (1)$$

The equivalence classes of relation $\overset{\hat{s}}{\leftrightarrow}$ form a partition (a disjoint collection of nonempty subsets whose union is the X) of X.

3.2. ADMISSIBLE NEIGHBORHOODS

Suppose that $\hat{B}$ is a rule that relates a general surface B_Ψ to the eigenfunction Ψ that is a member of X with following properties:

1. The general surface B_Ψ is defined as:

$$B_\Psi = \{(x, y, z) \in R^3 \therefore F(x, y, z) = 0\}. \quad (2)$$

2. The function F that is defined in relation (2) is a "proper solution" [7, 30] of the following PDE:

$$\partial_x \rho_\Psi \partial_x F + \partial_y \rho_\Psi \partial_y F + \partial_z \rho_\Psi \partial_z F = 0. \quad (3)$$

We point out that the phrase "proper solution" in statement (2) implies that the surface B_Ψ, be defined via relation (2), is the union of closed surfaces so that each of which is referred to as what Bader termed a "*topological atom*" [3, 31]. Thus, one should call the rule $\hat{B}$ as *Bader's Rule*. In other words, for Bader's rule the set $R^3 - B_\Psi$ is the union of nonoverlapping connected regions, in a way that, each of them is bounded by a local zero-flux surface.

Suppose that $\|.\|$ is the norm induced by the scalar product. The space X together with $\|.\|$ is the normed space denoted by $(X, \|.\|)$. The normed space $(X, \|.\|)$ is a metric space (X, d) that the induced metric is defined as $d(\Psi, \Phi) = \|\Psi - \Phi\|$. Now, based on this mathematical background, we are ready to define an admissible neighborhood for a function Ψ in the function space X.

Definition 3.2.1. Let $\hat{B}$ be Bader's rule. The admissible neighborhood with the center Ψ and the radius ε is defined as follows:

$$N_a(\Psi, \varepsilon) = \{\Phi \in X \therefore d(\Psi, \Phi)$$
$$< \varepsilon \text{ and } \Phi \in [\Psi]_{\hat{B}}\}. \quad (4)$$

We point out that the neighborhood of a given statefunction Ψ in Bader's monograph [3] (as well as others [4, 15]) is a general neighborhood namely

$$N(\Psi, \varepsilon) = \{\Phi \in X \therefore d(\Psi, \Phi) < \varepsilon\}. \quad (5)$$

Replacing the admissible neighborhood (expression (4)) instead of the general one leads to a change in the topology of the function space X. The importance of this topological change will be highlighted in the forthcoming subsection.

To summarize what has been mentioned so far, one may state that based on the definition of equiv-

alence relation on a function space and with the help of equivalence classes, a new type of neighborhoods, namely, admissible neighborhoods was constructed. Indeed, the topology of function space will be changed with this new structure. As will be demonstrated, this modification is done in a manner that avoids the problematic trial functions that cause obstacles in standard variational procedure of QTAIM (this seems to be a precise mathematical version of the concept of "well-behaved neighborhoods" that was emphasized by Bader in a less-formal context [27]).

3.3. PROPER STEPS IN THE SUBSYSTEM VARIATIONAL PROCEDURE

The variational method of Hilbert and Courant [32] has a pivotal role in the variation of the subsystem energy functional within QTAIM [3]. On the other hand, there appears to be some ambiguity about the application of Hilbert and Courant's variational theorem within QTAIM. In this section, we will dig more into the nature of the variational problem and its mathematical content based on the background that was provided in previous subsections.

The problem of variation of energy functional of subsystem that was discussed extensively elsewhere [3], may be divided into two main steps:

1. Variation of the energy functional (see the relation 5.74 in [3]) based on the Hilbert and Courant generalization of the variational method to the case of variable domains (see page 262 of [32]).

In this general variational form (5.74 in [3]), the first integral on the right hand side may be separated, by integration by part (see 5.77 in [3]):

$$\delta_\Psi \left\{ \int_\Omega d\tau_1 \int d\tau' F(\Psi, \nabla\Psi) \right\} = \int_\Omega d\tau_1 \int d\tau' [F]_\Psi \delta\Psi$$

$$+ \oint_{\partial\Omega} dS \int d\tau' \frac{\hbar^2}{2m} (\nabla\Psi^* \cdot n)\delta\Psi$$

$$+ \oint_{\partial\Omega} dS \int d\tau' F(\Psi, \nabla\Psi)\delta_\Psi S \quad (6)$$

wherein,

$$F(\Psi, \nabla\Psi) = \frac{\hbar^2}{2m} \sum_i \nabla_i\Psi^* \cdot \nabla_i\Psi + (V - E)\Psi^*\Psi \quad (7)$$

and $[F]_\Psi = \partial F/\partial\Psi - \nabla \partial F/\partial\nabla\Psi$ is Euler functional derivative as well as $d\tau' = \prod_{i=2}^N d\tau_i$.

2. Extracting the Euler theorem to discriminate physical state of system and also extracting (or imposing) the desired boundary conditions based on the physical problem under consideration.

It is important to note that calculus behind Eq. (6) is merely a mathematical procedure that is always true if:

I. The functional density F is twice continuously differentiable with respect to the both of its variables Ψ and $\nabla\Psi$.

II. The variation of any local reign, Ω is continuously deformable.

The condition (I) is always satisfied for the functional density F (as the basic functional employed in [3]). On the other hand, the condition (II) may be satisfied if we employ an infinitesimal variation $\delta\Psi$ in the variational point Ψ such that $\Psi + \delta\Psi \in [\Psi]_{\hat{B}}$ ($\hat{B}$ is Bader's rule that was defined in section 3.2). It is important to recognize that such selection of infinitesimal variations $\delta\Psi$ imposes no mathematical restriction to the validity domain of Eq. (6), and one may perform the whole mathematical calculations for every $\delta\Psi$ such that $\Psi + \delta\Psi \in [\Psi]_{\hat{B}}$. However, the derivation of Euler–Lagrange equation lies on a different mathematical ground. Mathematically, if the Eq. (8):

$$\int_\Omega d\tau \int d\tau' [F]_\Psi \delta\Psi = 0 \quad (8)$$

holds for every $\delta\Psi$ that is twice continuously differentiable, then the celebrated Euler equation, namely, $[F]_\Psi = 0$ is obtained. However, in the standard formulation of QTAIM it is not necessary (nor claimed to be possible) to derive the corresponding Euler equation (time-independent Schrödinger equation) from the subsystem variational procedure. The derivation of Euler equation must be done when the variational expression is written for the whole system:

$$\delta_\Psi \left\{ \int d\tau F(\Psi, \nabla\Psi) \right\} = \int d\tau [F]_\Psi \delta\Psi$$

$$+ \oint dS \frac{\hbar^2}{2m} \nabla\Psi^* \cdot n\delta\Psi = 0. \quad (9)$$

Given the celebrated natural boundary condition, namely, $\nabla\Psi \cdot n = 0$, $\nabla\Psi^* \cdot n = 0$ when $r \to \infty$, one can rewrite relation (9) as follows:

$$\int d\tau [F]_\Psi \delta\Psi = 0. \qquad (10)$$

Indeed, this is what has been done in [3], prior to the introduction of the variational principle of subsystems (see 5.59 in [3]). It is important to note that in Eqs. (9) (or equivalently the relation 5.59 in [3]) and (10), there is no constraint on $\delta\Psi$ except the boundary condition of whole system. Thus, the equation $[F]_\Psi = 0$ may be derived unequivocally. On the other hand, in relation (8), the trial function $\Psi + \delta\Psi$ must be a member of the set of admissible neighborhoods. This means that the equation $[F]_\Psi = 0$ is not derived from relation (8), but it is rather a constraint imposed thereon. In other words, the relation $[F]_\Psi = 0$ is a known fact that is derived for the whole system and not a result that comes from the subsystem variational procedure. Accordingly, one may summarize these facts as below:

A. For the whole system:
{Optimization of total system's energy functional} $\to$ Equality (9)
{Equality (9) + natural BC for total system} $\to$ Equality (10)
{Equality (10) + applying the Euler lemma} $\to$ $[F]_\psi = 0$

B. For the subsystem:
{Variation (not optimization) of the subsystem energy functional} $\to$ Expression (6)
{Expression (6) + the fact that total system is in the stationary state} $\to$ Omit the first term in the right hand side of Expression (6).

Accordingly, the previous discussion highlights the obstacles that are associated with the subsystem variational procedure and based on these problems, in our opinion, what follows is a logical extraction of the main expressions of QTAIM.

In the first step, the functional $\Gamma(\Psi)$ must be optimized.

$$\Gamma(\Psi) = \int d\tau F(\Psi, \nabla\Psi), \qquad (11)$$

where, F is defined in expression (7). We represent the total variation of the functional $\Gamma(\Psi)$ as follows:

$$\delta\Gamma = \delta_\Psi \Gamma + \delta_{\Psi^*}\Gamma. \qquad (12)$$

The expression (12) is nothing other than expression (9) plus its complex conjugate. In this step, no constraints need to be imposed on the trial functions $\Psi + \delta\Psi$. Accounting the natural boundary conditions for every point on a hypothetical boundary at infinity, as well as assuming that expression (12) holds for any arbitrary functions $\delta\Psi$, one arrives to the Euler equations (time-independent Schrödinger equation):

$$\begin{cases} (H - E)\Psi = 0 \\ (H - E)\Psi^* = 0 \end{cases}. \qquad (13)$$

Consequently, the variational procedure unambiguously discriminates the physical state of the whole system.

In the second step, and before introducing the variational procedure for subsystems, we need to define $\hat{S}$-atoms. If Ψ is a variational state of Eq. (11) and $\hat{S}$ is a rule (that was defined in subsection 3.1) then every connected component (a set that cannot be represented as the disjoint union of two or more nonempty open subsets) of $R^3 - S_\Psi$ is called as $\hat{S}$-atom. Since we are interested in atoms defined within context of orthodox QTAIM, we consider $\hat{S}$-atoms to be those constructed based on Bader's rule. According to the definition of Bader's rule, the set of $R^3 - B_\Psi$ is the "union of the nonoverlapping connected regions, each of which is bounded by a local zero-flux surface. In other words, each $\hat{B}$-atom is a topological atom. This definition of atom will be adopted for the subsystem variational procedure in the next step.

In the third step, Ψ is considered as a stationary point of the functional (11) and also $A(\Psi)$ an $\hat{S}$-atom (of course, in this stage, we do not need to assume anything about the nature of the rule $\hat{S}$). We define the functional $\bar{\Gamma}(\Psi)$ as follows:

$$\bar{\Gamma}(\Psi) = \int_{A(\Psi)} d\tau_1 \int d\tau' F(\Psi, \nabla\Psi), \qquad (14)$$

where, F is defined in expression (7). For every $\Phi \in [\Psi]_{\hat{S}}$, $A(\Phi)$ will be adopted for a connected component region analogous to $A(\Psi)$ in $R^3 - S_\Psi$. In other words, the subspace $A(\Phi)$ acts as variation of subspace $A(\Psi)$. Based on the previous discussion, such variations are allowed without obstacles. Consequently, assuming that $\Phi - \Psi = \delta\Psi$, one may

apply the standard variational procedure to the expression (14) as follows:

$$\delta\bar{\Gamma} = \bar{\Gamma}(\Phi) - \bar{\Gamma}(\Psi) = \int_{A(\phi)} d\tau_1 \int d\tau' F$$

$$- \int_{A(\Psi)} d\tau_1 \int d\tau' F = \int_{A(\Psi)} d\tau_1 \int d\tau' \{H\Psi^* - E\Psi^*\}\delta\Psi$$

$$+ \oint_{\partial A(\Psi)} dS\left\{\frac{1}{2}(\Psi^* H\Psi + (H\Psi)^*\Psi) - E\Psi^*\Psi\right\}\delta_\Psi S$$

$$+ \oint_{\partial A(\Psi)} dS\frac{\hbar^2}{2m}\nabla\Psi^* \cdot n\delta\Psi + \frac{\hbar^2}{4mN}\oint_{\partial A(\Psi)}^2 \rho_\Psi \delta_\Psi S$$

$$+ (complex\ conjugate), \quad (15)$$

where $\delta_\Psi S$ describes the variation of $\hat{S}$-atom's boundary in the 3D space. The variation of $\bar{\Gamma}$ is constructed from four terms, each of which contains information about the whole system and also the corresponding subsystems. Since the statefunction Ψ shows the state of the whole system, according to the first step, it satisfies Eq. (13). Therefore, the first two terms on the right hand side of expression (15) will be vanished. By some mathematical manipulations, one arrives at the following expression:

$$\delta\bar{\Gamma}(\Psi) = \frac{\hbar^2}{4m}\int_{\partial A(\Psi)} dS\delta_\Psi J \cdot n$$

$$- \frac{\hbar^2}{4mN}\delta_\Psi\left\{\int_{A(\Psi)} d\tau\nabla^2\rho\Psi\right\} + (complex\ conjugate)$$

$$= T_1 + T_2 + (complex\ conjugate). \quad (16)$$

Before further progress, it is worthwhile discussing the nature of the variational procedure and also the precise meaning of the terms in expression (16).

In contrast with the total system, no assumption will be made that expression (16) must be totally optimized. In other words, we are faced with a total system that has an intrinsic tendency to optimize expression (11), but not the corresponding expression (14) in a subset of the 3D space $\Omega \in R^3$. In this regard, one may easily find other well-known examples of such dual tendencies. For instance, as in isolated systems in classical thermodynamic, the natural trends of physico-chemical processes are toward optimization of the total entropy of the system (one of myriad versions of the second law of thermodynamics), but this optimization does not hold for any arbitrary open subsystem. So, one may question: "What really matters with expression (16)?" Or more precisely: "What kind of information may be gained from expression (16)?" Indeed, if we assume a general variational expression for $\bar{\Gamma}(\Psi)$ like $\delta\bar{\Gamma}(\Psi) = \Sigma_i T_i$, then every term in this expression contains some information. Since no real optimization is invoked in this procedure, there is no "general physical principle" (like least action principle) to guide us as to how to extract useful information from this expression. Accordingly, even if we impose the constraint that one or some of these terms be zero, this must be viewed as a mathematical procedure to extract some information regarding the very nature of desired subsystems. In this direction, assuming that the $\hat{S}$ rule and corresponding $\hat{S}$-atoms are those satisfying the local zero-flux condition (Bader's rule that was defined in subsection 3.2), the second term on the right hand side of the expression (16) T_2 is vanished. Accordingly, one arrives at expression (17):

$$\delta\bar{\Gamma}(\Psi) = \frac{\hbar^2}{4m}\int_{\partial A(\Psi)} dS\delta_\Psi J \cdot n$$

$$+ (complex\ conjugate). \quad (17)$$

Expression (17) is the final result of the variational procedure pursued in this subsection. It is important to realize that this expression is the "identity" of $\hat{S}$-atom or in Bader's own words: "the proper open quantum subsystem" [3].

4. The Difference Between the Net and Local Zero-Flux Conditions

The delicate differences existing between the local and net zero-flux conditions have also been considered by different authors [4, 15, 27]. The formalism developed in previous section also clearly highlights this issue. Although the variational procedure employed in QTAIM only demands the net zero-flux condition namely $\int_A d\tau\nabla^2\rho = 0$, the topological definition of atom, that is based on ideas that were first introduced by Collard and Hall [33] and further developed by Bader et al. [1, 3], is based on the local zero-flux condition namely $\nabla\rho \cdot n = 0$,

$r \in \partial A$. The expression (18) offers correspondence based on the Gauss's theorem.

$$\oint_{\partial A} dS \nabla \rho \cdot n = \int_{A} d\tau \nabla^2 \rho = 0. \qquad (18)$$

A delicate point to consider is that although the local zero-flux condition is sufficient for satisfaction of the net zero-flux condition, the reverse is not true. One may look at local zero-flux condition as a special solution of the "integral equation" (18). In a recent article [27], Bader clearly stressed that it is possible to impose the local zero-flux condition as a sufficient condition to vanish the term T_2 in the subsystem variational procedure and then to demonstrate that a topological atom is also a "quantum atom." From this point of view, it is safe to claim that every topological atom contains not only topological and geometrical characteristics, but also the whole set of physical properties (generalized observables) attributed to a quantum atom.

Accordingly, one may ask the interesting question whether it is possible to imagine quantum atoms that are not equivalent to the topological atoms or in other words, if the integral Eq. (18) contains other solutions instead of the local zero-flux condition. Although it seems that Bader denies such possibility [34], yet to the best of our knowledge, there is no published positive (and general) mathematical proof regarding this assumption. If we accept the priority of the definition of quantum atoms in regard to topological atoms within QTAIM, then, this logical gap seems to be an obstacle. However, neglecting an initial "abstract" attempt [15], it is interesting that no one has yet explicitly described even an example of a 3D partitioning scheme that satisfies the net zero-flux condition that is different from the 3D partitioning, based on the local zero-flux condition. In this accord, the possibility of simultaneous double or even multiple partitioning of a single molecule to the corresponding quantum atoms based on both putative local and some unknown rule could not be ruled out (in such a hypothetical case, in one partitioning scheme, quantum atoms would be equivalent to the topological atoms, while this will not be the case in other partitioning schemes). Taking such a background into account, it is possible to propose a set of general conditions for the hypothetical well-behaved quantum atoms (hypothetical basins that satisfy the net zero-flux condition) that are not equivalent with the topological atoms. Since the importance and practical utility of the orthodox QTAIM is the resemblance of general topological as well as geometrical properties of 3D atoms that are defined by this theory, with those that are usually prescribed based on experimental facts and chemical intuition, one may also constrain the well-defined quantum atoms by the following general topological and geometrical criteria. Accordingly, one may emphasize on these minimum (and of course more or less arbitrary) criteria as:

A. Every partition (or basin) of the 3D space must contain one single nucleus or a single non-nuclear attractor of charge density.

B. Every nucleus must be contained in a 3D basin.

C. The atoms must be path connected.

D. The partitioning must be "physically" exhaustive. In other words, summing up the physical properties of all quantum atoms, one must arrive to the corresponding expectation values associated with the whole molecule.

Of course, one may complement this list by further restricting the criteria. This list may also be a starting point for individuals interested in offering a positive mathematical proof of Bader's assumption, namely, the general equivalence of quantum and topological atoms.

Moreover, it is worthwhile to stress that the lack of a formal proof of uniqueness of the quantum atom affects the logical structure of QTAIM, particularly if one is interested in an axiomatic construction of this theory. Consequently, if the local zero-flux condition is not the necessary condition for the presence of quantum atoms, then one cannot claim that atoms within the context of QTAIM are directly extractable from the basic principles of quantum mechanics (although they are certainly compatible with principles of formal quantum mechanics). In other words, we need to add some "external guiding principle" to the formal quantum mechanics in order to extract the desired quantum atoms that are equivalent to the topological atoms. Indeed, this problem will be more serious when one deals with finite nuclear models, since one may even divide the usual topological atom based on the local or net zero-flux conditions to tighter basins [4] (this point will be discussed thoroughly in a subsequent article). It seems to the authors that there is an urgent need for a rigorous mathematical procedure that completely addresses this problem.

5. Conclusion

In this article, we introduced a mathematical procedure devised to tackle obstacles relevant to variational procedure. This procedure demonstrates that, careful classification of neighborhoods and a correct ordering of variational stages, makes it indeed possible to circumvent the usual mathematical problems and employ the Schrödinger's variational procedure within the context of QTAIM (although, strictly speaking, one may formulate QTAIM even without invoking variational procedure [35]). On the other hand, the discussion on the differences between the net and local zero-flux conditions clearly reveals that there is yet no straightforward relationship between the topological and quantum atoms. After all, more remains to be done for a better understanding of the formal mathematical structure of QTAIM and its potential applications in novel domains.

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