
Revisiting the Foundations of the Quantum Theory of Atoms in Molecules: The Subsystem Variational Procedure and the Finite Nuclear Models

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ABSTRACT: The role of finite nuclear models (FNMs) is scrutinized within the context of the quantum theory of atoms in molecules (QTAIMs). It is demonstrated that the newly proposed analytic-algebraic definition of the topological atoms is consistently extendable to the cases where a FNM is employed to construct the molecular hamiltonian. The whole variational procedure is reconsidered, and the insensitivity of final results relative to the employed FNMs is explicitly demonstrated. The analysis once again clearly demonstrates that the analytic-algebraic condition is an independent axiom that must be added to the subsystem variational procedure to construct the QTAIMs. © 2009 Wiley Periodicals, Inc. *Int J Quantum Chem* 110: 1188–1196, 2010

Key words: quantum theory of atoms in molecules; zero-flux conditions; topological atom; subsystem variational procedure; finite nuclear model; analytic-algebraic condition

1. Introduction

Recently, in two separate articles [1, 2], we have considered some of the fundamental traits of the quantum theory of atoms in molecules (QTAIMs) [3]. In these contributions, the varia-

tional procedure that is devised within the QTAIM as well as the very definition of the topological atom were scrutinized. It was demonstrated that a careful examination of the relevant mathematical neighborhoods and also the precise ordering of the variational steps could devise a consistent subsystem variational procedure. On the other hand, it was also illustrated that this variational procedure is not sensitive enough to discriminate topological atoms from a large set of other acceptable 3D regions. These excessive 3D regions were collectively called: quantum divided basins (QDBs). The re-

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gional virial theorem holds for these 3D regions. It means that the whole set of regional properties that are definable for topological atoms could also be defined and calculated for the QDBs. In one sense, taking purely mathematical standards into account, within the general framework of the quantum theory of proper open subsystems (QTPOS) the QDBs are indistinguishable from the topological atoms. To make a distinction, we proposed a novel and succinct definition of the topological atoms namely, the analytic-algebraic condition. This condition is not extractable from the subsystem variational procedure or the general condition for uniqueness of the regional kinetic energy. It must be assumed as an axiom or as an ad hoc assumption. If we add this condition to the subsystem variational procedure, then the QTAIM emerges automatically. In this contribution, we want to go further and consider the effect of generalized kinetic and potential energy functionals on this condition. This problem is also tied with the role of finite nuclear models (FNMs) within the framework of the QTAIM. Before considering technical details, some words on our strategy in dealing with the foundations of the QTAIM are worth mentioning in some detail. This will highlight our general philosophy and the goal of our research program.

2. The QTAIM and its Relevance to the Quantum Mechanics

Theoretical chemistry is full of ad hoc assumptions. They are not extractable from first principles. Quantum chemistry is not an exception as well. In the micro-world, it is possible to compute the mean value of physical observables and the probabilities of quantum transitions by employing quantum mechanics. These are the physical information. However, this is not usually the end of a quantum chemical calculation. Chemists need more. They want to extract *chemical* information. Contrary to the physical information that is defined uniquely within the formal framework of quantum mechanics, chemical information is not part of the formal structure of quantum mechanics. Usually, we cannot attribute proper hermitian operators to them [4–10]. Strictly speaking, they are not quantum observables. Accordingly, there are no universal recipes to extract them from the formal structure of quantum mechanics. Inevitably, one must take chemical intuition into account; something vague but respectable in the chemical community. This is

the source of ad hoc assumptions and the appearance of nonobservables in quantum chemistry [8, 9]. They could not be solely justified within the formal framework of quantum mechanics. This fact has been the rule of game since the advent of quantum chemistry. The well-known tales of the invention of hybridization, resonance, etc. are the first attempts in this direction [11–13]. Although quantum chemistry and its methods were (and are) under constant development in the last 80 years, the rule of the game is yet similar for most quantum chemists [8, 9]. Eventually, for a theoretical chemist, quantum mechanics serves to chemistry. In fact, quantum chemistry is a bridge between these two autonomous disciplines [13].

One of these ad hoc assumptions is the very concept of an atom in a molecule (AIM); something that is usually assumed to be part of the chemical rather than physical information [14]. Hence, it is justified based on the chemical intuition. Chemist's molecule is composed of atoms in 3D space rather than a complex function in an abstract mathematical space [15–17]. This chemical concept is usually assumed implicitly or explicitly in most (if not all) usual computational procedures that extract chemical information from molecular state functions. This includes the Mulliken population analysis [18–21], various atomic charges [22, 23], and the natural bond orbital method (NBO) [24]. One may always add to this list.

Although the explicit formulation of this concept goes back to the early 50s [25], today AIM is usually synonym to the approach that was formulated by Bader [3], the QTAIM. This approach now enjoys a widespread recognition and several computational studies are published employing this approach as part of their analysis to extract chemical information from molecular state functions; the properties of atoms in molecules and their mutual interactions [26]. On the other hand, contrary to growing applications, the QTAIM was (and is) a matter of debate in the last years as well (see the references cited in [1, 2]). It is usual to challenge the theoretical methodologies that aim to extract chemical information from quantum mechanics, but the debates around the QTAIM and its applications are unusually intense and heated. In our opinion, the origin of this problem seems to be the very claim that the QTAIM is directly extractable from the principles of quantum mechanics, and it is the *natural* extension of the formal quantum mechanics to the open quantum subsystems [3, 7, 27]. This is a unique claim since it challenges the usual view that the ad hoc assump-

tions are an inevitable part of every theoretical framework that aims to extract chemical information from quantum mechanics. If true, this claim poses the QTAIM a special position in quantum chemistry: the only AIM approach that is completely rooted in quantum mechanics with no appeal to the chemical intuition.

The initial motivation of our research program was (and is) to verify this claim in detail [1, 2, 8, 9]. Our fundamental question is: "Is the QTAIM directly extractable from quantum mechanics without any appeal to ad hoc assumptions?" To verify this fundamental question, one must consider the mathematical structure of the QTAIM and its relationship with quantum mechanics. Thus, in our research program it is not important how much the QTAIM and its entities are natural (in accord) or unnatural (against) relative to the usual chemical intuition.

Although part of our answer to this fundamental question may be found in our previous articles [1, 2], in this contribution we want to go further and consider the QTAIM in cases where the interaction of ingredients of system are not completely columbic: the slightly noncolumbic systems. The importance of this problem will be discussed in the following section.

3. The Nature of Problem and a Brief Review of Previous Studies

The role of FNMs within the context of the QTAIM was discussed previously [28–31]. The main question was (and is): "What will happen to the orthodox QTAIM if one replaces the point charge nuclear model with a finite nuclear model?" In all previous contributions, the main concern was the local zero-flux equation ($\vec{\nabla}\rho(r) \cdot \vec{n}(r) = 0$). Thus, the authors were considering the consistent solution of this differential equation assuming a FNM instead of the usual point charge model of nucleus. Although there are desperate views on details, it seems that there is a general (or almost general) consensus on two important issues:

- 1 Mathematically, the usual zero-flux surfaces or the so-called inter-atomic surfaces are only a subset of the zero-flux surfaces that satisfy the local zero-flux equation. The others include an infinite number of surfaces that cross the finite nucleus.
- 2 Chemical intuition and computational obser-

vations could be employed to justify the orthodox partitioning of 3D space into topological atoms, but this intuition is not directly extractable from the subsystem variational procedure. It must be somehow added to its mathematical fabric.

Consequently, auxiliary conditions are usually invoked to discard these extra but undesired surfaces [28]. The analytic-algebraic condition is a rigorous version of these attempts to discard what is not compatible with the usual chemical intuition [2]. However, the problem of extra surfaces is not the only consequence of incorporating the FNMs into the orthodox QTAIM. This point that is in the central focus of this contribution needs some clarification.

The local zero-flux equation is a part of an intricate mathematical network that includes the subsystem variational procedure for the open quantum subsystems, generalization of the usual quantum theorems to 3D subspaces (QTPOS), the topological analysis of charge densities, catastrophe theory, etc [3]. This network is collectively called the QTAIM. Various assumptions were made in the construction of this intricate network. If one replaces an assumption with a new one, the consequences must be traced in every part of this network. In the orthodox QTAIM [3], the whole variational procedure is based on an energy functional that explicitly employs the usual form of molecular hamiltonian within the clamped nuclear approximation. The potential energy functional has a coulomb form in this hamiltonian. This is also true for the QTPOS. The regional virial theorem is also derived for a coulombic system. On the other hand, any FNM is a deviation from completely coulombic interactions. Indeed, the electron-nuclear potential energy term must be modified [32]. This means that the whole network must be reconsidered. In this contribution we aim to explore this problem in detail.

Accordingly, we concentrate on the slight deviations from the coulombic potentials. This is justified since our primary interest is the role of FNMs. Hence, we assume that the regional properties are insensitive to this slight modification of the coulomb potential. Consequently, the variational procedure and the analytic-algebraic condition are in central focus. The strong deviations from the usual coulomb potentials that are routinely considered in many exactly solvable models will be considered in a separate contribution.

4. The QTAIM and the Slightly Noncoulombic Systems

The family of FNMs is the set of the modified nucleus-electron potentials that are designated to take the finite extension of nuclear matter into account [32]. Although their role is crucial in the relativistic quantum chemistry [33], they are usually (but not always) neglected in the nonrelativistic quantum chemical calculations (the point charge nuclear model is suitable for most applications in chemistry). In this study, we are interested in the general traits of these interactions and our arguments are not tied with a special model of nuclear matter's distribution. Thus, in the first step, the concept of a proper Hamiltonian family is introduced. Based on this concept, a general family of Hamiltonians is used to construct a generalized energy functional. This functional, the representative of the whole FNMs, is employed in the variational procedure.

4.1. THE PROPER HAMILTONIAN FAMILY

Although it is usually possible to construct a proper hamiltonian for the problem at hand (hereafter denoted as H_∞), mathematically, one may always find or construct a new hamiltonian that can reproduce the relevant properties (within experimental errors) with a precision comparable to H_∞ . The details are as follows:

Let σ be the experimental received precision and Σ_σ be the set $\{\chi\} = \{\chi_1, \chi_2, \dots, \chi_k\}$ such that:

$$|\langle \hat{H}_{\{\chi\}} \rangle - \langle \hat{H}_\infty \rangle| < \sigma \quad (1)$$

where $\langle \dots \rangle$ denotes the expectation value of energy and $\{\chi\} = \{\chi_1, \chi_2, \dots, \chi_k\}$ is the set of indices specifying the mathematically constructed hamiltonians. In this way, one may introduce a family of proper hamiltonians of H_∞ as follows:

$$N(H_\infty, \sigma) = \{H_{\{\chi\}} : \{\chi\} \in \Sigma_\sigma\} \quad (2)$$

Since the inequality (1) states that the expectation values of hamiltonians, $\langle \hat{H}_{\{\chi\}} \rangle$ and $\langle \hat{H}_\infty \rangle$, are physically indistinguishable, $N(H_\infty, \sigma)$ in (2) could be regarded as a neighborhood with the center H_∞ and radius σ such that all of its members are physically equivalent. In other words, for a specific Hamiltonian H' and the experimental received precision σ

each Hamiltonian H'' that is a member of $N(H', \sigma)$ is physically (but not necessarily mathematically) indistinguishable from H' .

Accordingly, assuming H_∞ to be the usual coulomb hamiltonian which employs the point charge nuclear model (PNM), one may suppose that $H_{\{\chi\}}$ is a member of $N(H_\infty, \sigma)$; it is a certain type of FNMs. It is always possible to define the parameters of a certain FNM (that control the size or the internal structure of the nucleus) unambiguously and consequently guarantee the proper asymptotic behavior; that is the reconstruction of the PNM in the limit of zero radius of nucleus [34–37]. Therefore, employing different physical models for the charge distribution of nucleus, one may always construct an infinite number of such $(H_{\{\chi\}})$ hamiltonians all with the same physical content.

4.2. THE GENERALIZED ENERGY FUNCTIONAL

The orthodox energy functional that was employed for the subsystem variational procedure is constructed by employing the usual kinetic energy expression $(\hbar^2/2m)\nabla\psi \cdot \nabla\psi^*$ and assuming the coulomb interactions between electrons and nuclei [1, 3]. In this study, we are interested in the whole set of FNMs. So, no special analytical form is assumed for the potential energy operator. We only assume that they are real functions of the electronic and nuclear coordinates. Since these systems are only slightly noncoulombic systems, the general traits of the corresponding potential energy operators are virtually indistinguishable from the coulomb interactions beyond nuclear domain. The noncoulombic part of the potential energy, within and near the nuclear region, acts as a perturbation to the original coulomb problem. On the other hand, instead of the usual kinetic energy expression, Cohen's general family of the local kinetic energies is employed in the construction of the generalized energy functional [38, 39]. The details are as follows:

Consider a wide class of energy functionals including Lagrange's multiplier E :

$$\begin{aligned} \Gamma_\nu^\alpha &= \int dq H_{\{\alpha, \nu\}} - E \int dq \Psi^* \Psi \\ &= \int dq \{T_\alpha + \Psi^*(\hat{V}_\nu - E)\Psi\} \end{aligned} \quad (3)$$

where \hat{V}_v is the representative of the potential energy operators of the FNMs and T_α is the class of Cohen's local kinetic energies with the following analytical form:

$$T_\alpha(q) = (2\pi)^{-6} \int \exp(-i\tau \cdot p + i\theta \cdot (u - q)) \alpha(\theta, \tau) p^2 / 2m \times \Psi^*(u - \hbar/2) \Psi(u + \hbar/2) d\theta d\tau du dp \quad (4)$$

The function α in this expression satisfies the condition [38, 39]:

$$\alpha(0, \tau) = \alpha(\theta, 0) = 1 \quad (5)$$

Note that for every α and β with the property (5) one obtains [38]:

$$|\langle T_\alpha \rangle - \langle T_\beta \rangle| = 0 \quad (6)$$

Thus, relation (1) is valid for $\{\chi\} = \{\alpha, \nu\}$ if and only if:

$$|\langle V_\nu \rangle - \langle V_\infty \rangle| < \sigma \quad (7)$$

More precisely, one should assert the following proposition:

Proposition 4.2.1. $H_{\{\alpha, \nu\}} \in N(H_\infty, \sigma)$ if and only if α and ν satisfy (5) and (7). This proposition guarantees that the proposed variational procedure (that is discussed in the following subsections) and all the results that are gained from this procedure are physically reliable as well.

In a special case where the function α has the property $\alpha(\theta, \tau) = \alpha(\theta \cdot \tau)$, T_α reduces to:

$$\tilde{T}_\alpha(q) = \{1/2 + 2\alpha''(0)/\hbar^2\}G(q) + \{1/2 - 2\alpha''(0)/\hbar^2\}K(q) + \alpha'(0)\nabla \cdot J(q) \quad (8)$$

where

$$G(q) = (\hbar^2/2m)\nabla\Psi^*\nabla\Psi \quad (9)$$

$$K(q) = -(\hbar^2/2m)\text{Re}\{\Psi^*\nabla^2\Psi\} \quad (10)$$

and $J(q) = (i\hbar/2m)\{\Psi^*(\nabla - \nabla)\Psi\}$ is the current density [3].

For a molecular system in a stationary state we then arrive at the following energy functional:

$$\Gamma_\nu^\alpha(\Psi) = \int dq F(q, \Psi, \nabla\Psi, \nabla^2\Psi; \alpha; \nu) \quad (11)$$

where the functional density F is given by:

$$F = F_{\{\alpha, \nu\}} = \{1/2 + 2\alpha''(0)/\hbar^2\}G(q) + \{1/2 - 2\alpha''(0)/\hbar^2\}K(q) + \Psi^*(\hat{V}_\nu - E)\Psi \quad (12)$$

This is the energy functional that is employed in the following subsections.

4.3. THE VARIATIONAL PROCEDURE FOR $H_{\{\alpha, \nu\}} \in N(H_\infty, \sigma)$

The variational procedure could be performed employing both the single and many particle energy functionals [3]. In this study, for the sake of simplicity, we restrict ourselves to the single particle energy functional. The extension of the whole procedure into the many particle functional is trivial (details may be found elsewhere [1, 3]). In the first step, the variational procedure is done for the whole system. This is the original variational problem of Schrödinger [40]. In the second step, by employing the results of the original variational problem, the subsystem variational procedure is done. The details are as follows:

In the case of single particle energy functional, variation with respect to variable Ψ leads to:

$$\begin{aligned} \delta_\Psi \Gamma_\nu^\alpha(\Psi) = & \int dq [F_{\{\alpha, \nu\}}]_\Psi \delta\Psi \\ & + (\hbar^2/2m) \oint ds (\nabla\Psi^* \cdot n) \delta\Psi + (\alpha''(0)/2m \\ & - \hbar^2/8m) \int dq \nabla^2(\Psi^* \delta\Psi) \end{aligned} \quad (13)$$

Applying either of the standard boundary conditions for the wave function [1, 3], the last two terms on the right-hand side of (13) vanish. Thus one obtains:

$$\delta_\Psi \Gamma_\nu^\alpha(\Psi) = \int dq [F_{\{\alpha, \nu\}}]_\Psi \delta\Psi = 0 \quad (14)$$

Taking the Euler-Lagrange lemma into account [41] leads to the Schrödinger equation (Euler-Lagrange equation):

$$\delta F_{\{\alpha, \nu\}} \big|_{\Psi} = 0 \quad (15)$$

where the Euler functional derivative is given by:

$$[F_{\{\alpha, \nu\}}]_{\Psi} = [\partial / \partial \Psi - \nabla \cdot (\partial / \partial \nabla \Psi) + \nabla^2 (\partial / \partial \nabla^2 \Psi)] F_{\{\alpha, \nu\}} \quad (16)$$

At this stage, based on what mentioned above, one can rearrange this procedure for subsystems. To do so, we appeal to the Hilbert and Courant generalization of the variational method to the case of variable domains [41]. According to this theorem, one obtains:

$$\begin{aligned} \delta_{\Psi} \int_{\Omega} dq F \\ = \text{Variation of } F \text{ while the surface is constant} \\ + \text{Variation of the surface while } F \text{ is constant} \end{aligned} \quad (17)$$

The variation of F while the surface is constant contains three terms, similar to (13). The only difference lies on the integration domain; the integral is taken over subsystem, Ω . Taking the relation $G = K - L$ into account the parametric functional density $F_{\{\alpha, \nu\}}$ may be re-expressed as follows:

$$F_{\{\alpha, \nu\}} = F_{\{\lambda, \nu\}} + \left(\frac{1}{2} - \frac{2\alpha''(0)}{\hbar^2} \right) L \quad (18)$$

where ([38, 39]):

$$\lambda(\theta \cdot \tau) = \exp\left(\frac{\hbar^2}{8}(\theta \cdot \tau)^2\right) \quad (19)$$

and

$$L = -(\hbar^2/4m)\nabla^2(\Psi^*\Psi) \quad (20)$$

In other words:

$$F_{\{\alpha, \nu\}} = G + \Psi^*(V_{\nu} - E)\Psi + \left(\frac{1}{2} - \frac{2\alpha''(0)}{\hbar^2} \right) L \quad (21)$$

Accordingly, the subsystem variation is expressed as follows:

$$\begin{aligned} \delta_{\Psi} \int_{\Omega} dq F_{\{\alpha, \nu\}} = \int_{\Omega} dq [F_{\{\lambda, \nu\}}]_{\Psi} \delta \Psi \\ + (\hbar^2/2m) \oint_{\partial \Omega} ds (\nabla \Psi^* \cdot n) \delta \Psi + \delta_{\Psi} \{ (1/2 \\ - 2\alpha''(0)/\hbar^2) \int_{\Omega} dq L(q) \} - \oint_{\partial \Omega} ds L(q) \delta_{\Psi}(\partial \Omega) \end{aligned} \quad (22)$$

If the Schrödinger equation (Euler-Lagrange equation):

$$[F_{\{\lambda, \nu\}}]_{\Psi} = [\partial / \partial \Psi - \nabla \cdot (\partial / \partial \nabla \Psi)] F_{\{\lambda, \nu\}} = 0 \quad (23)$$

is assumed to apply for the total system then (22) reduces to:

$$\begin{aligned} \delta_{\Psi} \int_{\Omega} dq F_{\{\alpha, \nu\}} = (\hbar^2/2m) \oint_{\partial \Omega} ds (\nabla \Psi^* \cdot n) \delta \Psi \\ + \delta_{\Psi} \{ (1/2 - 2\alpha''(0)/\hbar^2) \int_{\Omega} dq L(q) \} \\ - \oint_{\partial \Omega} ds L(q) \delta_{\Psi}(\partial \Omega) \end{aligned} \quad (24)$$

This expression is the generalized form of the relation (5.85) in [3]. To proceed further, we consider the following relation between the quantity $L(q)$, the Laplacian of the charge density, and the current density $J(q)$:

$$L(q) = \nabla \cdot \{ (\hbar/2i) J(q) - (\hbar^2/2m) \Psi \nabla \Psi^* \} \quad (25)$$

variation with respect to Ψ yields:

$$\delta_{\Psi} L(q) = \nabla \cdot \{ (\hbar/2i) \delta_{\Psi} J(q) - (\hbar^2/2m) (\delta \Psi) \nabla \Psi^* \} \quad (26)$$

The application of Hilbert and Courant's variational method for the regional integration of L yields:

$$-\int_{\partial\Omega} ds L(q) \delta_{\Psi}(\partial\Omega) = \int_{\Omega} dq \delta_{\Psi} L(q) - \delta_{\Psi} \int_{\Omega} dq L(q) \quad (27)$$

Then, incorporating (26) and (27) into (24) gives:

$$\delta_{\Psi} \int_{\Omega} dq F_{\{\alpha, \nu\}} = (\hbar/2i) \oint \partial\Omega ds \delta_{\Psi} J \cdot n - \delta_{\Psi} \{ (1/2 + 2\alpha''(0)/\hbar^2) \int_{\Omega} dq L(q) \} \quad (28)$$

As was mentioned earlier, this relation is valid for every parameter $\{\chi\} = \{\alpha, \nu\}$ that was expressed in the proposition 4.2.1. Particularly, this equality stands for the slightly noncoulombic systems.

To proceed further, we must eliminate the second term on the right hand side of (28). Neglecting the special case ($\alpha''(0) = -\hbar^2/4$), this means that we must seek for 3D regions Ω satisfying:

$$\delta_{\Psi} \left\{ \int_{\Omega} dq L(q) \right\} = 0 \quad (29)$$

The net zero-flux condition:

$$L(\Omega) = \int_{\Omega} dq L(q) = 0 \quad (30)$$

as well as the local zero-flux condition:

$$\vec{\nabla} \rho(r) \cdot \vec{n}(r) = 0 \quad (31)$$

that fit into this requirement, give rise to extra solutions apart from the usual topological atoms (see [2] for explicit examples). To get rid of this issue we assume that the 3D space is partitioned by means of the following condition [2]:

$$\begin{cases} \nabla \xi \cdot \nabla \rho_{\psi} = 0 \\ \chi[\xi] - |\Delta_{\rho}| = 0 \end{cases} \quad (32)$$

Where $\xi: R^3 \rightarrow R$ is a function that defines the inter-atomic surface S :

$$S = S_{\xi} = \{r \in R^3 : \xi(r) = 0\} \quad (33)$$

also χ and $|\Delta_{\rho}|$ are the characteristic function and the number of the (3, - 3) critical points, respectively (see [2] for details). In fact the second equation of (32) is a mathematical condition that selects the appropriate function ξ among the solutions of the partial differential equation [31]:

$$\partial_x \rho \partial_x \xi + \partial_y \rho \partial_y \xi + \partial_z \rho \partial_z \xi = 0 \quad (34)$$

For a fragment Ω that is derived from (32), namely the usual topological atoms, the last term on the right-hand side of (28) drops and the relation reduces to:

$$\delta_{\Psi} \int_{\Omega} dq F_{\{\alpha, \nu\}} = (\hbar/2i) \int_{\partial\Omega} ds \delta_{\Psi} J \cdot n \quad (35)$$

And thanks to the symmetry properties of the functional density ${}^*F_{\{\alpha, \nu\}}$, i.e. $F_{\{\alpha, \nu\}}^* = F_{\{\alpha, \nu\}}$ and $(\delta_{\Psi} F_{\{\alpha, \nu\}})^* = \delta_{\Psi} \cdot F_{\{\alpha, \nu\}}$, one obtains:

$$\delta \int_{\Omega} dq F_{\{\alpha, \nu\}} = (\hbar/2i) \int_{\partial\Omega} ds \delta_{\Psi} J \cdot n + c \cdot c \quad (36)$$

This is the standard outcome of the variational procedure that was obtained by taking PNM into account [1, 3]. Its persistence for a whole set of FNMs indicates that the variational procedure is not sensitive to the details of the energy functional. Thus, it is equally valid for the proper Hamiltonian family.

5. Conclusions, Prospects, and the Summary of Results

In the preceding section, it was demonstrated that the analytic-algebraic definition of topological atoms is consistently extendable into an infinite series of FNMs. This finding clearly demonstrates that this new condition is robust against minor deviations of the molecular Hamiltonian and corresponding energy functional from the usual coulombic interactions. On the other hand, because of this robustness, it seems that there is no need to invoke the cusp condition [42–44] to exclude the zero-flux surfaces that cross the finite nuclei. It is always

possible to consider another member of this proper set namely another hamiltonian that does not satisfy the cusp condition; a FNM.

The FNMs may also affect the orthodox topological analysis of the electronic charge densities. This includes both the classical treatments [3, 45] as well as our recent elaborations [46]. Accordingly, it is probable that beyond simple FNMs [32] one encounters a nontrivial topology of the electronic charge density distribution within the nuclear region. The complex layered structures of heavy nuclei (as a realistic model of charge density distribution within heavy nuclei [48]) may trigger very small ripples in the electronic charge density and this could facilitate the presence of more than a single local maximum (or a (3, -3) critical point [3]) in the electronic charge density within the nuclear region. Although in first glance this situation does seem to be probable, such possibilities demand a more thorough study of FNMs and their effect on the electronic charge density near and in the region of nucleus. After all, the analytic-algebraic condition may be easily extended even to such cases.

Taking above conclusions and the other results from our previous studies [1, 2] one may compress the outcomes. The very concept of topological atom is *uniquely* extractable only if both the subsystem variational procedure and the analytic-algebraic condition are employed simultaneously. At present state, the employment of analytic-algebraic condition, namely the topological atoms, within the QTAIM is based on chemical observations [47, 49]. So, this selection is *not* justified or tied with the employment of point charge model of nucleus. Somehow, this condition acts as an *auxiliary condition* that discriminates the true object from a vast set of other mathematical artifacts namely the QDBs. This is also comparable with the general attitude in the standard quantum mechanics since apart from Schrödinger's equation, we need to employ proper auxiliary conditions to derive the true observable quantum states [50]. The external conditions (that are usually introduced as independent axioms) like Born's probabilistic interpretation of state functions and the resulting boundary condition as well as the Pauli exclusion principle and the resulting symmetry properties of many particle state functions all complement Schrödinger's equation to reach the proper physical states. This seems to be the rule of game also within the context of the QTAIM.

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