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*Comment*

# Comments on "Some fundamental problem with zero flux partitioning of electron densities"

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**Abstract.** The article by P. Cassam-Chenaï and D. Jayatilaka (*Theor Chem Acc* (2001) 105: 213) is critically analyzed.

**Key words:** Atoms in molecules – Electron density – Zero flux surface

An article [1] has recently been published in *Theoretical Chemistry Accounts* which demonstrates the "fundamental problems" in the foundation of the atom-in-molecules (AIM) theory developed by Bader and coworker [2] (see also Refs. [3, 4]. According to the Bader definition, "an atom" (or equivalently, an atomic basin) in the given $N$-electron molecule in the quantum state $|\Psi\rangle$ is an open subsystem or domain, $\Omega$, of this molecule whose boundary, $\partial\Omega$, is determined by a so-called zero flux condition,

$$\nabla_{\mathbf{r}}\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0, \quad \mathbf{r} \in \partial\Omega \ . \tag{1}$$

In Eq. (1), $\rho(\mathbf{r})$ is the one-electron density associated with the $N$-electron wave function $\Psi$ (see Ref. [3] for the definition) and $\mathbf{n}(\mathbf{r})$ is the outward normal to $\partial\Omega$ at $\mathbf{r}$. Actually, Eq. (1) is the first-order differential equation which is well defined *iff* the correct boundary conditions are imposed [5]. Each domain, $\Omega$, determined by Eq. (1) usually includes a nuclear attractor; however, in general, some domain(s) may be located around nonnuclear positions. This takes place, for instance, for the ground-state molecule $Li_2$ and some other molecules and crystals [3, 6]; however, it does not mean at all that the Bader definition of "an atom in a molecule" is invalid. Rather, it is a physically sound approach although we have to admit that it is not in fact a "theory of everything" – it is one of many approaches to define atoms in multiatomic systems like, for instance, a recently launched one based on the Bohm potential [7]. Nevertheless, many chemists successfully operate with the AIM theory [8] owing to that the idea of the local zero flux surface in the gradient vector field of the electron density, $\rho(\mathbf{r})$, behind it is rather impressive and well grounded.

The present work aims to thoroughly analyze the "fundamental problems" posed in Ref. [1]. It is demonstrated that the objection arising in Sects. 2–5 of Ref. [1] are incorrect (notice that the "fundamental problem" treated in Sect. 1 has already been mentioned).

Let us start with Sect. 3 of Ref. [1], which introduces a family of one-electron trial wave functions

$$\Phi(\mathbf{r}; a) = \Psi(\mathbf{r}) + \varepsilon\chi(\mathbf{r}; a) \ , \tag{2}$$

where

$$\Psi(\mathbf{r}) = \frac{e^{-r}}{\sqrt{\pi}}, \chi(\mathbf{r}; a) = \frac{1}{2\sqrt{\pi a^3}}\left(1 - \frac{r}{a}\right)e^{-r/a} \ , \tag{3}$$

where $r$ is a length of $\mathbf{r}, \varepsilon$ is a constant, and $a$ is an arbitrary parameter. This family lies within a sphere of radius $\varepsilon/2$ (which is a stronger condition than that in Ref. [1]) centered at $\Psi(\mathbf{r})$.

Some algebra shows that the function $\chi(\mathbf{r}; a)$ defined in Eq. (3) as a function of $a$ has two extrema: the maximum $\chi_{\max}(a) = 1/(4\sqrt{\pi e a^3})$ at $r = a/2$ and the minimum $\chi_{\min}(a) = -1/(e^3\sqrt{\pi a^3})$ at $r = 3a$. They are distinct from each other *iff* $a \neq 0$. If $a = 0$ and $r \neq 0$, $\chi(\mathbf{r}; a)$ simply vanishes. On the other hand, it is undefined if $a = 0$ and $r = 0$. This implies that $a = 0$ is invalid in the analysis of the equation

$$e^{-3(a-1)}a^{3/2} = \varepsilon \tag{4}$$

derived in Ref. [1] under the condition that $\Phi(\mathbf{r}; a) = 0$ at $r = 3a$. Notice that its left-hand side reaches a maximum equal to

$$\varepsilon = (e/2)^{3/2} \simeq 1.3591409 \ . \tag{5}$$

The authors [1] then concluded that this "means that no matter how small $\varepsilon$ is chosen there are always at least two values of $a$ such that" $\Phi(3a\mathbf{r}/r; a) = 0$ "and so, where" $\nabla_{\mathbf{r}}\rho(3a\mathbf{r}/r; a)$ associated with $\Phi(\mathbf{r}; a)$ vanishes

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Comment to the article "Some fundamental problems with zero flux partitioning of electron densities" by P. Cassam-Chenaï and D. Jayatilaka, Theor Chem Acc (2001) 105: 213–218 over all direction in three dimensions. This statement is incorrect for two reasons. First, as already mentioned, the value $a = 0$ (and hence, $r = 0$) must be excluded from the variational calculus on a family (Eq. 2) of trial functions. Second, Eq. (5) demonstrates the $\varepsilon$ is fixed at about 1.3591409 and thus it cannot be chosen arbitrarily, particularly, small as claimed in Ref. [1]. Let us continue the arguments of Ref. [1]: "Therefore for either one of these values of $a$ there is, in addition to the surface at infinity, a surface of finite radius at $r = 3a$ satisfying Eq. (1) (inherited from the $2s$-like component of $\Phi$). This surface does not correspond to an attractor since it is a node of the density and it is not connected to the surface at infinity. Since a continuous mapping maps a connected set to a connected set, $\partial\Omega(\Psi)$ cannot be mapped continuously onto the two unconnected surfaces obtained for $\Phi$." The first sentence is correct, however, it is incorrect to require in the third sentence the existence of a continuous mapping between $\partial\Omega(\Phi)$ and $\partial\Omega(\Psi)$ where $\Psi$ and $\Phi$ are connected via Eq. (2) and where a continuous feature of $\varepsilon$ is lost because it is fixed by Eq. (5). Therefore, a variational limit $\varepsilon \to 0$ necessary to obtain the exact wave function of the ground-state hydrogen atom cannot be taken.

In Sect. 4 of Ref. [1], the authors considered the local zero flux condition. Precisely, on p.215, they wrote that within the AIM theory, "the local zero flux condition... was a stronger, sufficient but not necessary condition. However, ... it was argued ... that the zero flux condition was necessary. This is clearly false since the more general local condition for all $\Phi$

$$\nabla_{\mathbf{r}}\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = \nabla_{\mathbf{r}} \times \mathbf{A}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}), \quad \mathbf{r} \in \partial\Omega \tag{6}$$

where **A(r)** is an arbitrary vector field, is sufficient to obtain net zero flux for all $\Phi$." Equation (6) (or precisely, Eq. (9) in Ref. [1]) is incorrect for the following reason. As well known, any vector field, say **F(r)**, can be decomposed, according to the Helmholtz theorem [9], into two components

$$\mathbf{F} = \mathbf{F}^{||} + \mathbf{F}^{\perp} \ . \tag{7}$$

$\mathbf{F}^{||}$ is a component of $\mathbf{F}$ such that its curl, $\nabla_{\mathbf{r}} \times \mathbf{F}^{||}$, is identically zero. This is a longitudinal or irrotational component which can be represented as $\mathbf{F}^{||} = \nabla_{\mathbf{r}}P^{||}$, where $P^{||}$ is a scalar function. The other, transverse or rotational component, $\mathbf{F}^{\perp}$ has zero divergence, i.e., $\nabla_{\mathbf{r}} \cdot \mathbf{F}^{\perp} = 0$. Hence, $\mathbf{F}^{\perp} = \nabla_{\mathbf{r}} \times \mathbf{P}^{\perp}$. In Eq. (6), $\mathbf{F} = \nabla_{\mathbf{r}}\rho(\mathbf{r})$ and, therefore, its rotational component is zero, and that is why the initial assumption (Eq. 6) is incorrect. In the other words, the aforementioned proposal of Ref. [1] aimed to show that the statement of the AIM theory that Eq. (1) is the necessary condition "is clearly false" is simply invalid.

Let us now turn to the arguments presented in Sect. 5 of Ref. [1]. The authors' incorrectness stems from their misinterpretation of which density, the electron–nuclear density or the one-electron density, should be used in the AIM theory. Let us first suggest that the total electron–nuclear wave function in the form

$$\begin{aligned}\Psi_n(&\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{R}_1, \ldots \mathbf{R}_M) \\ &= \phi_{\mathrm{e}}(\mathbf{r}_1, \ldots, \mathbf{r}_N; \mathbf{R}_1, \ldots, \mathbf{R}_M)\chi_n(\mathbf{R}_1, \ldots, \mathbf{R}_M)\end{aligned} \tag{8}$$

is a rather good approximation to describe a given molecular system of $N$ electrons and $M$ nuclei. In Eq. (8), $\phi_{\mathrm{e}}(\mathbf{r}_1, \ldots, \mathbf{r}_N; \mathbf{R}_1, \ldots, \mathbf{R}_M)$ is the $N$-electron wave eigenfunction of the electronic sub-Hamiltonian $H(\mathbf{R}_1, \ldots, \mathbf{R}_M)$ (the colon in $\phi_{\mathrm{e}}$, Eq. 8, separates the electronic variables from the nuclear coordinates which are treated as parameters). Consider two total wave functions $\Psi_{\mathrm{n}_1}(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{R}_1, \ldots, \mathbf{R}_M)$ and $\Psi_{\mathrm{n}_2}(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{R}_1,\ldots,\mathbf{R}_M)$ having the form of Eq. (8). By assumption [1], these wave functions describe two distinct orthogonal vibrational states of a given molecular system corresponding to the same electronic state. By analogy with Ref. [1], we also suggest that $\chi_{\mathrm{n}_2}(\mathbf{R}_1,\ldots,\mathbf{R}_M)$ has a nodal nuclear configuration, say $\mathbf{R}_1^{\mathrm{o}},\ldots,\mathbf{R}_M^{\mathrm{o}}$, such that $\chi_{\mathrm{n}_2}(\mathbf{R}_1^{\mathrm{o}},\ldots,\mathbf{R}_M^{\mathrm{o}}) = 0$. This implies that the quantity

$$\rho_{\mathrm{n}_2}(\mathbf{r}, \mathbf{R}_1, \ldots, \mathbf{R}_M) = \rho_{\mathrm{e}}(\mathbf{r}; \mathbf{R}_1, \ldots, \mathbf{R}_M)|\chi_{\mathrm{n}_2}(\mathbf{R}_1, \ldots, \mathbf{R}_M)|^2 \tag{9}$$

defined by Eqs. (11), (12), and (13) or Ref. [1], where $\rho_{\mathrm{e}}(\mathbf{r}; \mathbf{R}_1, \ldots, \mathbf{R}_M)$ is the one-electron density associated with $\phi_{\mathrm{e}}(\mathbf{r}_1, \ldots, \mathbf{r}_N; \mathbf{R}_1, \ldots, \mathbf{R}_M)$, vanishes at $\mathbf{R}_1^{\mathrm{o}}, \ldots, \mathbf{R}_M^{\mathrm{o}}$. In contrast, except maybe in some pathological cases, $\rho_{\mathrm{e}}(\mathbf{r}; \mathbf{R}_1^{\mathrm{o}}, \ldots, \mathbf{R}_M^{\mathrm{o}})$ does not vanish everywhere in 3D space $\mathcal{R}^3$ because it corresponds to the square integrable eigenfunction $\phi_{\mathrm{e}}(\mathbf{r}_1, \ldots, \mathbf{r}_N; \mathbf{R}_1^{\mathrm{o}}, \ldots, \mathbf{R}_M^{\mathrm{o}})$ of the electronic sub-Hamiltonian $H_{\mathrm{e}}(\mathbf{R}_1^{\mathrm{o}}, \ldots, \mathbf{R}_M^{\mathrm{o}})$ depending parametrically on $\mathbf{R}_1^{\mathrm{o}}, \ldots, \mathbf{R}_M^{\mathrm{o}}$. This is precisely the one-electron density $\rho_{\mathrm{e}}(\mathbf{r}; \mathbf{R}_1^{\mathrm{o}}, \ldots, \mathbf{R}_M^{\mathrm{o}})$ to which the AIM theory should actually be applied. Therefore, the AIM theory cannot be applied to $\rho_{\mathrm{n}_2}(\mathbf{r}, \mathbf{R}_1, \ldots, \mathbf{R}_M)$ as treated in Ref. [1] because it is in fact the one-electron-nuclear density defined in $\mathcal{R}^{3(1+M)}$.

Concluding, it has been shown that the "fundamental problems" of the foundations of the AIM theory by Bader and coworker posed in Sects. 2–5 of Ref. [1] are incorrect. However, the article by Cassam-Chenaï and Jayatilaka [1] raised certain doubts in its foundations which will hopefully inspire further theoretical investigations in this area, directed particularly toward a well-grounded justification of nonnuclear attractors.

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## References

1. Cassam-Chenaï P, Jayatilaka D (2001) Theor Chem Acc 105: 213
2. Bader RFW (1990) Atoms in molecules, a quantum theory. Oxford University Press, Oxford
3. Kryachko ES, Ludeña E (1990) Energy density functional theory of many-electron systems. Kluwer, Dordrecht
4. Popelier PLA (2000) Atoms in molecules. An introduction. Pearson, Harlow
5. (a) Pontryagin LS (1974) Ordinary differential equations. Nauka, Moscow; (b) For application to AIM theory see, e.g., Popelier PLA (1996) Can J Chem 74: 829

6. (a) Cioslowski J (1990) J Phys Chem 94: 5496; (b) Sakata M, Sato M (1990) Acta Crystallogr Sect A 46: 263; (c) Edgecombe KE, Esquivel RO, Smith VH Jr, Müller-Plathe F (1992) J Chem Phys 97: 2593; (d) Jayatilaka D (1998) Phys Rev Lett 80: 798; (e) Pendás AM, Blanco MA, Costales A, Sánchez PM, Luaña V (1999) Phys Rev Lett 83: 1930
7. (a) Levit C, Sarfatti J (1997) Chem Phys Lett 281: 157; (b) Hamilton, IP (1998) Chem Phys Lett 297: 261; (c) Levit C, Sarfatti J (1998) Chem Phys Lett 297: 263
8. Bader RFW (2001) Theor Chem Acc 105: 276, and references therein
9. McQuistan RB (1965) Scalar and vector fields: a physical interpretation. Wiley, New York