

## Frequently asked questions on “Some fundamental problems with zero flux partitioning of electron densities”

P. Cassam-Chenaï

*Laboratoire d'étude théorique des milieux extrêmes, CNRS-OCA-UNSA, Physique-recherche,  
Faculté des Sciences, Parc Valrose, F-06108 Nice cedex 2, France  
E-mail: cassam@unice.fr*

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A number of fundamental problems with the topological analysis of molecular electron densities using the atoms in molecules (AIM) theory developed by Bader and coworkers have been highlighted recently. In the present article we provide complements and further details on this topics in the form of a frequently asked questions text.

**KEY WORDS:** atoms in molecules, zero flux surfaces, electron density partitioning, Schwinger variational principle

### Introduction

The theory of atoms in molecules put forward by Bader and coworkers claims that the boundaries of the “the atoms of Chemistry” are uniquely dictated by the Schwinger variational formulation of quantum theory. The observation by Dr. Jayatilaka that the local zero flux condition used to define these boundaries was sufficient but not necessary [1, section 4], and our own reflections on the molecular structure problem [2] and discovery that Bader and coworkers' application of Schwinger variational principle was mathematically incorrect [1, section 3], led the two of us to write the article entitled “Some fundamental problems with zero flux partitioning of electron densities” [1]. This latter work has attracted much interest and feedback from the quantum chemistry community. The first comments of Prof. Bader in July 1999 on our initial manuscript, those of the referees and the many questions raised at invited seminars and at the congresses where this work has been presented (6 or more including the 25th CHITEL in Napoli, September 1999, the 10th ICQC in Menton and its satellite in La-Colle-sur-Loup) helped us to make our arguments clearer. However, it appears from a number of comments we have received since the publication of our article, that there are still some misunderstandings. Moreover, a recent rebuttal by Prof. Bader [3] invokes a counter argument to remedy to the incorrect use of the Hilbert and Courant theorem we had noted in [1, section 3].

The purpose of the present document, which is presented in the form of a frequently asked questions document (FAQ) is to clarify some points made in [1] too succinctly and to demonstrate that the argument in [3] that “Schwinger’s principle requires the use of a special class of trial functions” is flawed.

**Question 1.** Figure 1 of [1] illustrates that one can construct an infinite number of local zero flux surfaces partitioning the electron density of a molecule. There are the surfaces which define atomic domains according to the AIM theory and extra ones which include a nucleus of the molecule. Can the problem of the extra surfaces be overcome by defining the AIM as attractor basins of the electron density in the frame of catastrophe theory [4]?

Yes, defining the AIM as attractor basins of the electron density rules out the extra surfaces that include an attractor such as a nucleus. In the conclusion of [1] it is only claimed that the difficulties due to excited vibrational states would subsist with such a definition. However, Bader considers the local zero flux surface as the fundamental concept to define AIM. He writes [3]: “Within this theory (the quantum theory of AIM [5]) an atom is defined as an open system, one that is bounded by a surface  $\partial\Omega$  (delimiting the domain  $\Omega$ ) of local zero flux in the gradient vector field of the electron density  $\rho(\mathbf{r})$ , as given in equation (1):

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0, \quad \forall \mathbf{r} \in \partial\Omega, \quad (1)$$

where  $\mathbf{n}(\mathbf{r})$  is the (outward) unit vector normal to the surface at  $\mathbf{r}$ .” This leads him to write erroneously [3]: “Topologically, a zero-flux surface always represents a partitioning between attractor domains” whereas it is the reverse that is true: “A partitioning surface between attractor domains is always a zero-flux surface.”

**Question 2.** In [1, section 1] the use of the cusp condition made by Bader in a footnote [6] for excluding nuclei from zero flux surfaces is criticised. In [3] Bader has expanded his idea in an entire section entitled “the cusp condition”. Is the objection of [1] answered by accepting that the AIM partitioning of space with zero flux surface be “contingent upon the use of the Coulombic Hamiltonian” (conclusion of [3])?

No, our objection still holds. Bader in [3] demonstrates that the cusps can be ignored by the chemist both experimentally (up to energies that would result in the formation of a plasma) and theoretically (they are homeomorphic to regular (3, -3) critical points), but at the same time he makes them play a critical role in the definition of an atom. We find that this is not consistent.

**Question 3.** Is it possible to consider the global attractors of the electron density (such as the “shell attractors” of excited electronic states mentioned in [1, section 2]) and their basins as “a separate entity with a definable set of contributing properties” [3]?

It is an interesting proposal to try to give a physical meaning to every attractor of the electron density. However as noted in [3] this violates Dalton’s dictum that an atom

be indivisible. Given this, can it still be argued that the atoms of the AIM theory are “the atoms of Chemistry”?

**Question 4.** Does the counterexample presented in [1, section 3] challenge Schwinger’s principle of stationary action [7]?

Absolutely not. Schwinger’s principle applied to the H atom example with the constraint that the wave function be square integrable, hence vanishing almost everywhere at infinity, gives (as expected) the Schrödinger equation. It is only claimed in [1] that the application of this principle to a system bounded with local zero flux surfaces as presented in the AIM theory is not correct because it relies on a theorem whose hypotheses are not met.

**Question 5.** If the answer to question 4 is negative, what is wrong with the claim that when applied to an isolated closed system such as the H atom example, the “generalised Schwinger’s principle” reduces to Schwinger’s original principle because the zero flux condition is fulfilled at infinity [8]?

Bader and co-workers’ application of Schwinger’s principle to an open system is based on the system being partitioned by zero flux surfaces as defined by equation (1). If it is a bona fide “generalisation” it has to work in the same way for the particular case of a closed system. That is, in both cases, one has to start from equation (1) and solve it to obtain the zero flux surfaces of the system. The fact that the zero flux condition is fulfilled at infinity is a necessary but not sufficient condition to recover the traditional derivation of Schrödinger equation from the “generalisation” of Schwinger’s principle. One has to show in addition that there is no other surface at finite distance in  $L^2$  satisfying equation (1) for the trial wave functions. Unfortunately, this is not the case.

**Question 6.** In the example of [1, section 3] is there any attempt to vary the “surface found at infinity” whose mathematical meaning is not clear?

No. The mathematically well-defined wave function is varied. In the AIM theory the boundaries of the subsystem depend upon the wave function through equation (1), so may vary accordingly. However, since all wave functions satisfy the zero flux condition at infinity, the “surface found at infinity” associated with the different wave functions were identified through the mappings  $g_\phi$  in [1]. Therefore, the “surface found at infinity” can be seen as “fixed” in our attempt to apply Hilbert and Courant’s theorem [9, p. 260]. However, we agree that one should avoid this language and that we should be blamed to have borrowed it from the AIM literature (see [5, p. 31] “the interatomic surfaces, along with *the surfaces found at infinity*, are the only closed surfaces of  $\mathbb{R}^3$  which satisfy the zero-flux condition of equation (1)”).

**Question 7.** Can the closed isolated system be considered as a limiting case of an open system for which the zero flux partitioning does not apply in the same way as in open systems?

Yes, one can. The problem is that the zero flux condition does not work any better with open systems. In a polyatomic molecule, the fact that in the vicinity of any square integrable function there are other square integrable functions with extra zero flux surfaces remains true and prevents the application of Hilbert and Courant theorem [9, p. 260].

**Question 8.** Bader in a recent reply [3] has a new argument that the variations of the wave function should avoid those functions with extra zero flux surfaces. Does this solve the problem?

Bader argues that the variation of the wave function  $\delta\Psi$  should be proportional to an Hermitian operator  $\widehat{G}$  applied to  $\Psi$ . The variation made in [1, section 3] can of course be cast into this form by setting:

$$\begin{cases} \widehat{G}^+\Psi = \Psi', \\ \widehat{G}^+\Phi = 0 \quad \text{if } \langle \Phi|\Psi \rangle = 0, \end{cases} \quad (2)$$

that is,  $\widehat{G}^+$ , is the operator which excites  $\Psi$  to  $\Psi'$  and is null on the orthocomplement of  $\Psi$  (in [1]  $\Psi$  was the hydrogen 1s function and  $\Psi'$  a scaled hydrogen 2s function),

$$\widehat{G}^- = (\widehat{G}^+)^{\dagger}, \quad (3)$$

and

$$\widehat{G} = \widehat{G}^+ + \widehat{G}^-, \quad (4)$$

that is,  $\widehat{G}$  is the sum of the operator,  $\widehat{G}^+$ , and its Hermitian conjugate,  $\widehat{G}^-$ . Bader adds that the operator  $\widehat{G}$  must be “physical” without defining what he exactly means. We guess, however, that our operator  $\widehat{G}$  is not “physical” because the resulting trial function does not belong to the special class of trial functions he considers. But then, how are we supposed to derive the Schrödinger equation from, say, [8, equation (6) or equation (47)] (see also the textbook [5]) or more simply from

$$\int (\widehat{H}\Psi - E\Psi) \delta\Psi^* = 0? \quad (5)$$

This step relies upon the application of the fundamental lemma of the calculus of variation [9, p. 185]. A more appropriate version of the lemma for the  $L^p$  spaces is employed in [10, p. 61]. With  $p = 2$  (the space of square integrable functions) it can be written as

$$\int uh = 0, \quad \forall u \in L^2 \quad \Rightarrow \quad h = 0. \quad (6)$$

According to Bader,  $u \equiv \delta\Psi^*$  is not free to vary in all  $L^2$  for it has to avoid all the functions with extra zero flux surfaces. Therefore this lemma cannot be invoked. How then can one conclude that  $h \equiv \widehat{H}\Psi - E\Psi = 0$  for  $\Psi \in L^2$ ? It is the derivation of the Schrödinger equation that is forfeited with Bader's argument.

Finally, we note that in Schwinger's article [7] there is no restriction on the variation of the field components  $\delta_0\phi^\alpha$  (equations (2.16) and (2.17)), therefore, one can legitimately obtain the equations of motion (equation (2.18)).

**Question 9.** When one follows the construction scheme of section 3, one usually finds functions which have more than one extra zero flux surface and can be high in energy. Is there a way to obtain more realistic functions?

In the construction of a trial function with at least one extra zero flux surface, we have looked for a function of the open sphere of radius  $\varepsilon$  centered on the ground state wave function that has a node. However, a zero flux surface also appears where the derivative of the trial function with respect to the radial distance vanishes (see [1, equation (6)]). Similarly, we have set the restriction  $r = 3a$  because we had more freedom than needed and this was simplifying the algebra. However, the wave function corresponding to a given  $a$  value may have other nodes at other radial distances. For these two reasons the function in our counter example may have more zero flux surfaces than that expected at  $r = 3a$  by construction. For instance, in [1, figure 2] we see that three zero flux surfaces would occur at finite distance. Having more than one non connected zero flux surfaces at finite distance does not affect the validity of our counter example. We were not solving variationally the Schrödinger equation (in which case a practical algorithm would probably not consider our trial function), we were dealing with the derivability of the Schrödinger equation itself from Bader's "generalisation" of Schwinger variational principle.

**Question 10.** Bader has emphasized in [3] that equation (1) is not a necessary but only a sufficient condition for the cancellation of the quantity

$$\delta I_\Psi = \delta \left\{ \int_{\Omega(\Psi)} \nabla^2 \rho_\Psi(\mathbf{r}) \, d\mathbf{r} \right\} \quad (7)$$

correcting the false statements noted in [1, section 4]. Does this address the criticism made in section 4?

No, our criticism has not been addressed, because Bader has not drawn from this statement the logical conclusion that the cancellation of the quantity  $\delta I_\Psi$  used to obtain his "operational statement of Schwinger's principle" [3, equation (8)] could only justify the net zero flux condition, equation (8) below, and not the local zero flux condition equation (1) which is a stronger, sufficient but not necessary condition.

**Question 11.** In [1, section 4] it is argued that the more general condition,

$$\nabla \rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}), \quad \forall \mathbf{r} \in \partial\Omega, \quad (8)$$

is sufficient to obtain equation (8) from equation (7) in [3]. However, does such an equation admit a solution for  $\mathbf{A}(\mathbf{r})$  nonconstant?

Let us exhibit a net zero flux surfaces that is not a local zero flux one. We set  $\mathbf{A}(\mathbf{r}) = (1/2)\mathbf{K} \times \mathbf{r}$ , with  $\mathbf{K}$  a constant vector. Then equation (8) becomes

$$\nabla \rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = \mathbf{K} \cdot \mathbf{n}(\mathbf{r}), \quad \forall \mathbf{r} \in \partial\Omega. \quad (9)$$

Using Cartesian coordinates and setting  $\mathbf{K} = (0, 0, -K)$  (without loss of generality) and  $\mathbf{r} = (x, y, S(x, y))$  (where  $S$  is the function to determine), we have more explicitly

$$\nabla \rho(x, y, S(x, y)) \cdot \left( \frac{\partial S(x, y)}{\partial x}, \frac{\partial S(x, y)}{\partial y}, -1 \right) = K, \quad (10)$$

$\forall \mathbf{r} \in \partial\Omega$ . We consider again the case of a hydrogen atom in its ground state so that

$$\nabla \rho(\mathbf{r}) = \frac{-2}{\pi} e^{-2r} \hat{\mathbf{r}}, \quad (11)$$

where  $\hat{\mathbf{r}}$  is the unit vector along  $\mathbf{r}$ . Because of the cylindrical symmetry of the problem, it is convenient to change to polar coordinates in the  $xy$ -plane by setting

$$x = t \cos \phi, \quad y = t \sin \phi. \quad (12)$$

Choosing  $K = 1/\pi$  (the normalisation factor of the density) equation (10) is then transformed into

$$t \frac{\partial S(t, \phi)}{\partial t} = S(t, \phi) - \frac{e^{2\sqrt{t^2 + S(t, \phi)^2}} \sqrt{t^2 + S(t, \phi)^2}}{2}. \quad (13)$$

We note that the derivative of  $S$  with respect to  $\phi$  does not appear in this expression as could be anticipated by symmetry. So, it reduces to a differential equation of the variable  $t$ , the dependency of  $S$  upon  $\phi$  can be suppressed and the partial derivative symbol replaced by a total derivative symbol. The condition at the limit  $t = 0$  is found by noticing that for symmetry reasons the normal must be aligned with  $\mathbf{K}$  for this value of  $t$  and so is the gradient of the density. Then equation (9) implies  $\nabla \rho(\mathbf{r}) = \mathbf{K}$  and we obtain  $S(0) = \log(2)/2$ . A numerical solution of equation (13) with this condition at the limit  $t = 0$  is depicted in figure 1.

**Question 12.** From section 5 on, why did you use the same symbol  $\mathbf{r}$  (respectively  $\mathbf{R}$ ) for the electronic (respectively nuclear) position vector and for the set of position vectors?

In fact, the position vectors,  $\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}, \mathbf{R}_1, \dots, \mathbf{R}_{N_n}$ , were meant to be in italic font and the sets of position vectors  $\mathbf{r} = (\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_{N_e})$  and  $\mathbf{R} = (\mathbf{R}_1, \dots, \mathbf{R}_{N_n})$  not in

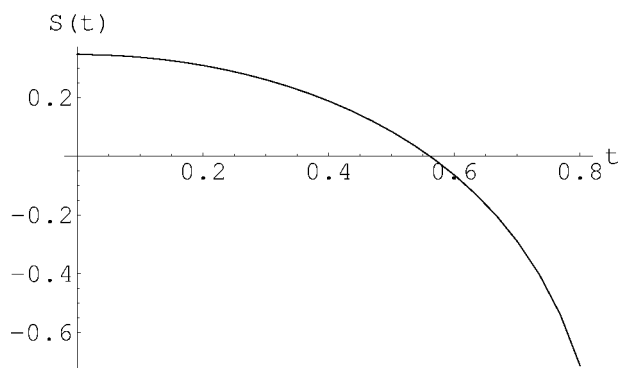


Figure 1. The curve  $S(t)$  solution of equation (13) with  $S(0) = \ln[2]/2$  and  $\phi$  arbitrary. The atomic surface  $S(t, \phi)$  is the surface of revolution of  $S(t)$  over the vertical axis. The hydrogen nucleus is at the origin.

italic fonts. This was OK in the proofs, but everything came out not in italic fonts in the published version.

**Question 13.** In [1, section 5], why is the adiabatic approximation used instead of the more usual Born–Oppenheimer (BO) approximation?

The “adiabatic” approximation we have referred to is the Born adiabatic approximation [11] for a given translation-free molecular Hamiltonian and with “electronic” wave functions,  $\{\Psi_e^k(\mathbf{r}, \mathbf{R})\}_k$ , that need not be exact solutions of the eigenvalue problem of the part of the Hamiltonian containing electronic operators. It differs from the related BO approximation by the fact that the integrals containing the gradient or the gradient square of the electronic wave function with respect to the nuclear displacements are not neglected. Since the cancellation of the latter integrals was not necessary for making our point, we placed ourselves in the general frame of the adiabatic approximation.

Similarly, the particular molecule-fixed coordinate system used to separate off the translation or the method employed to obtain the electronic wave functions were not specified as they were not of particular relevance to our point.

All that was needed at this stage of our demonstration was that the Born–Huang expansion of the wave function

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_k \Psi_e^k(\mathbf{r}, \mathbf{R}) \Psi_n^k(\mathbf{R}) \quad (14)$$

be reduced to a single term, (in equation (14)  $\{\Psi_e^k(\mathbf{r}, \mathbf{R})\}_k$  is an orthonormal basis set of “electronic” wave functions for every value of  $\mathbf{R}$ , and  $\{\Psi_n^k(\mathbf{R})\}_k$  is the set of the associated nuclear wave functions).

**Question 14.** Can the AIM approach be carried out at a node of the adiabatic nuclear function if an exact wave function expanded as in equation (14) is used?

Yes, of course. It seems extremely unlikely that all the terms in equation (14) could vanish for the same value of  $\mathbf{R}$ . This is why, in contrast with the adiabatic case, we did not claim that a “catastrophe” was occurring with such a wave function. We contended that an AIM analysis could be performed at a node of the dominant term (assuming that the adiabatic approximation is reasonable so that there exists such a term) but that it would not be chemically meaningful because it would only correspond to the structure of the tail of the wavefunction equation (14). We might be wrong on this point and the structure given by the application of Bader’s analysis could prove of some physical relevance. Unfortunately, as far as we are aware, this interesting problem has not yet been tackled.

**Question 15.** The adiabatic wave function is not dominant in the Born–Huang expansion near a node of its nuclear wave function. What do you mean by “dominant” in [1, section 5]?

Not only the adiabatic wave function is not dominant at a node of its nuclear wave function but it is zero and this is why we have argued that Bader’s analysis would not be meaningful at such a geometry. The word “dominant” must not be taken in a local sense which does not make sense in the context of our article. We meant “dominant” in the sense of the norm of the Hilbert space, that is, for all  $k$  different from  $j$

$$\sqrt{\langle \Psi_e^j \Psi_n^j | \Psi_e^j \Psi_n^j \rangle} > \sqrt{\langle \Psi_e^k \Psi_n^k | \Psi_e^k \Psi_n^k \rangle}, \quad (15)$$

where the Hermitian product  $\langle | \rangle$  corresponds to integration over both electronic and nuclear variables  $\int d\mathbf{R} d\mathbf{r}$ .

A nonadiabatic study on diatomics and a numerical example on  $H_2$  [12] has shown that the adiabatic wave function is dominant in this sense in the exact wave function.

**Question 16.** What is in Žislin’s article [1, reference [15]] which is in Russian?

It is a very important article which extends Hilbert and Courant nodal theorem [9, p. 451] to the case of the clamped nuclei Schrödinger equation and to the general translation-free molecular Schrödinger equation. Žislin also obtains as a corollary a general and rigorous proof that the ground state of this equation is nondegenerate. The article was quoted because the proof of the corollary makes use of the fact that two orthogonal eigenstates (which can be chosen real without loss of generality for the Hamiltonians of interest here) cannot have both a constant sign over their domain.

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