Theor Chem Acc (2002) 107:378–380
DOI 10.1007/s00214-002-0347-9

Theoretical
Chemistry Accounts

*Comment*

# Bader's interatomic surfaces are unique

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Received: 10 May 2001 / Accepted: 7 September 2001 /

**Abstract.** In this work we comment on the statement about the nonuniqueness of the solution of Bader's equation for defining atoms in molecules reported in the article of P. Cassam-Chenaï and D. Jayatilaka in *Theoretical Chemistry Accounts* (2001) 105: 213–218

**Key words:** Interatomic surface – Differential equation

## 1 Bader's interatomic surface as a solution of a partial differential equation

In the article "Some fundamental problems with zero flux partitioning of electron density", which appeared in *Theoretical Chemistry Accounts* (2001) 105: 213–218 [1], the authors point out the problem of the nonuniqueness of the solutions of Bader's equation

$$\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})=0;\quad \forall\,\mathbf{r}\in S(\mathbf{r}) \tag{1.1}$$

for defining topological atoms in molecules. In this section we comment on this point by performing a basic and simple mathematical analysis. Quoting the authors "... any surface that originates from a nucleus and follows the gradient of density satisfies Eq. (1.1) since the normal is orthogonal to $\nabla\rho(\mathbf{r})$ at every point. That is to say that Eq. (1.1) has an infinite number of solutions...". What the authors state is, rigorously speaking, true and, to our knowledge, it is also true that so far this problem has never been explicitly treated in a rigorous mathematical analysis; however, we can anticipate that this is not an argument which can be used to fully invalidate the application of the theory but can be certainly used to promote a further formal and mathematical development. The main reason why the validity of the theory, in the field of chemistry, is not touched by the previous statements is that among the "infinite number of solutions" the authors refer to, there exists only one solution which corresponds to a "proper chemical" topological interatomic surface, and this is the surface Bader explicitly refers to in all his work (see, for example, the most recent [2]). In the following part of this contribution, we show the formal uniqueness of this interatomic surface when the problem is mathematically defined in a proper way. However, we must underline that in the present formulation of Bader's theory and contrary to his opinion, the formal uniqueness of such a solution does not automatically emerge, but somehow is a consequence of what we require a posteriori from a chemical point of view rather than a natural consequence of the mathematical formulation of the theory itself; this point is a delicate one and we will try to make it clear. In our work [3, 4], we emphasized that Eq. (1.1) can also be interpreted in simple topological terms without any reference to the variational problem from which it is originated (and so to Bader's theory); the density $\rho(\mathbf{r})$ can be considered as a (regular) three-dimensional manifold, and the problem of finding interatomic surfaces is reduced to determining separatrix surfaces of a vector field $\nabla\rho(\mathbf{r})$. This procedure allows one to partition the electron density in real space in nonoverlapping regions, each of which is bounded by the local zero flux surface, and each of these disjoint regions contains a nucleus which can be considered as the "source" of the local atomic topology. This topological problem can be translated in mathematical terms via a partial differential equation which explicitly involves the zero flux surface, $S(\mathbf{r})$. To do so, first let us write the formal equation for the surface S, which takes the simple general form of $S(x,y,z)=0$, it follows that the components of the vector $\mathbf{n}(\mathbf{r})$ normal to the surface at every point take the following form:

$$n_x(\mathbf{r})=\frac{\partial S(\mathbf{r})}{\partial x};\quad n_y(\mathbf{r})=\frac{\partial S(\mathbf{r})}{\partial y};\quad n_z(\mathbf{r})=\frac{\partial S(\mathbf{r})}{\partial z}\quad . \tag{1.2}$$

Substituting Eq. (1.2) in Eq. (1.1) one obtains

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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

$$\frac{\partial\rho(\mathbf{r})}{\partial x}\frac{\partial S(\mathbf{r})}{\partial x}+\frac{\partial\rho(\mathbf{r})}{\partial y}\frac{\partial S(\mathbf{r})}{\partial y}+\frac{\partial\rho(\mathbf{r})}{\partial z}\frac{\partial S(\mathbf{r})}{\partial z}=0\ . \qquad (1.3)$$

The fundamental mathematical problem of the existence and uniqueness of a solution for such an equation is expressed by the theorem of Kovalevskaja for the existence and uniqueness of the solutions of partial differential equations (for more details about the whole procedure see Ref. [6]). What defines a differential equation and makes a particular solution unique, i.e. selects one solution within a class of solutions, is the initial or boundary condition. Such a condition consists of imposing a priori that the solution passes through a given curve. A partial differential equation can be solved only when an initial condition is explicitly assigned; this means that the existence and uniqueness of a particular explicit solution can be defined only when an initial condition is given. At this point if we analyze how the equation of the zero flux surface is formulated and presented in Bader's work (see Ref. [7] as the most representative reference) it is evident that is not linked to any explicit initial condition. In particular, one should not confuse the techniques used to define atoms in molecules based on Bader's theory [5, 8, 9, 10] and consisting in defining the atomic volume by following the gradient paths from a nucleus to their turning point, with the formal (and also numerical) solution of Eq. (1.3): in the current form, this equation is not uniquely defined since is not related to an explicit initial condition and as a consequence from a rigorous mathematical point of view it defines a class of solutions not a single and unique one. At this point the reason also becomes clear why we previously stated that, rigorously speaking, Cassam-Chenaï and Jayatilaka are right; an initial condition in a mathematical rigorous equation does not automatically emerge from the present formulation of Bader's theory as a consequence of the theory itself. We underline "present formulation" because, at least so far, this fact has never been pointed out in the literature in explicit terms. As a consequence the surface which properly defines atoms in molecules, and is the one Bader refers to, is only one of the possible solutions related to the choice of a particular initial condition. So how can we decide the way to choose an initial condition which leads to a proper chemical partitioning of the charge density?

As stated before, if one searches (given the proper curve as the initial condition) for the "separatrix surface" of the vector field $\nabla\rho(\mathbf{r})$, as is well known in topology, the results will be a unique surface which divides the electron density, $\rho(\mathbf{r})$, in disjoint regions, each of which contains a nucleus; this would be a chemically reasonable partitioning suitable for applications. On the other hand, if one chooses as the initial condition a curve which leads to the kind of solution Cassam-Chenaï and Jayatilaka refer to, then there would be several problems: one problem would be the partitioning of nuclear charge and how to assign it to a particular entity, but probably this is only a minor problem. A major problem would be the fact that one cannot even talk about atoms since there would be single entities which do not recover any of the properties of an atom (as Bader underlined very often in his work [2]). So from a chemical point of view the formal choice of an initial condition is not difficult: we search for the "separatrix surface" of $\nabla\rho(\mathbf{r})$ and we know that formally this is unique and is defined by the appropriate initial condition. In practical application we do not need to specifiy the initial condition; in fact the "techniques" of Refs. [5, 8, 9, 10] would be reasonable since in practical numerical terms the solution obtained by these techniques and a numerical solution of the partial differential equation with the appropriate initial condition produces the same chemical entities. In the light of what was stated previously we can conclude that the application of Bader's theory, having in mind the chemical idea of atoms and molecules, remain fully valid. This sort of chemical empirical argument is satisfying for practical applications, but still does not answer the major question. We are still left with a partial differential equation that in order to be uniquely and rigorously defined needs an explicit initial condition which must emerge from the mathematics of Bader's procedure in applying the Schwinger principle of stationary action. Although not in an explicit form, it seems that a boundary condition is automatically assigned by the variational problem. In Bader's procedure the necessary condition to obtain the zero flux equation is that an integral over a differentiable surface bounding a subvolume of the whole space (i.e. closed regular surface) must vanish; this is, as underlined before, a necessary condition to obtain what Bader refers to as a "proper quantum subsystem" [11] (quantum atom). A regular surface differentiable at every point and bounding a subvolume can certainly be obtained from solving the problem of finding the separatrix of $\nabla\rho(\mathbf{r})$ [given the condition of regularity of $\rho(\mathbf{r})$, which is usually fulfilled in quantum chemistry]; this is not true for solutions obtained from an initial condition of the kind suggested by Cassam-Chenaï and Jayatilaka. In this case one would find that the surface is not closed or is not differentiable everywhere or both. In fact, let us consider the nucleus to be a pointlike charge or a spherical extended region (as usually happens in applications and theoretical models). In these cases we have two possibilities:

1. The pointlike nucleus is part of the surface solution. In this case the partitioning of the whole atom will consist at least of two regions which overlap at the point where the nucleus is and create the problem of partitioning the nuclear charge. This is different from the case of the "separatrix surface" where the space is partitioned in disjoint regions and the electronic as well as the nuclear charge are uniquely assigned to one specific atomic entity.
2. The nucleus is a cusp or an extended spherical region, so a solution that originates from a nucleus and follows the gradient of density will lead to an open domain or to a surface which is not differentiable everywhere (this is evident in the case of a cusp); in fact the surface solution which contains the gradient paths in the neighborhood of the nuclear region is normal to the spherical surface of the nucleus. This means that in order to have a closed surface in the

neighborhood of the nuclear region one should join part of the surface of the nucleus to its normal surface which contains the gradient paths; this generates an irregular nondifferentiable topological region (a sort of step surface).

However, and to a first approximation this is the important point, what we can certainly have by accepting the "separatrix surface" as the solution of Eq. (1.3), is the consistency between the chemical idea of atoms and the mathematical variational procedure adopted by Bader. The kind of solution proposed by Cassam-Chenaï and Jayatilaka presents evident problems in practical applications as well as in mathematical terms; however, in this latter case a rigorous mathematical formulation should be carried out in order to make the theory of atoms in molecules formally complete. This task goes beyond this communication, and possibly will be presented elsewhere.

## 2 Conclusions

In the light of what was reported here, we can conclude that Cassam-Chenaï and Jayatilaka pointed out a delicate issue about the theory of atoms in molecules. The answer to their statement can be separated into two parts. On one hand, from a chemical point of view and for practical applications, we can be assured that the interatomic surface is unique since the partial differential equation related to this surface is uniquely defined by the initial condition, and as an initial condition we choose the one which leads to the "separatrix surface" of $\nabla\rho(\mathbf{r})$ which allows us to have "atomic entities" in multiatomic systems consistent with the chemical idea of atoms; however, at this level our choice is not governed by any rigorous mathematical principle connected to the mathematical formulation of the theory. On the other hand, a more profound problem arises and is connected with the formulation of the theory itself; does an initial condition for the partial differential equation emerge automatically from the mathematical procedure of Bader's theory, as should occur for a self-complete theory?

We conclude that this is possible, and again formally such a condition leads to the "separatrix surface" of $\nabla\rho(\mathbf{r})$. The final conclusion is that the separatrix surface" of $\nabla\rho(\mathbf{r})$ is consistent with the chemical idea of atoms and with Bader's theoretical framework; this surface is unique. As a final comment. we add that although the article of Cassam-Chenaï and Jayatilaka may be incorrect in some points, it shows the necessity of the further development of the theory of atoms in molecules, at least at a formal level.

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