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Reply to comments

A complement to "Some fundamental problems with zero flux partitioning of electron densities"

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1 Introduction

Our work "Some fundamental problems with zero flux partitioning of electron densities" [1] has attracted many comments from the quantum chemistry community. Four of them are published in this issue. We address them in turn and take this opportunity to clarify some misunderstandings with the claims made in Ref. [1].

2 Mohallem's comment

Mohallem criticises Sect. 5 of Ref. [1], entitled "Vanishing of atomic domains at vibrational nodes", but appears to miss the point; he also quotes us erroneously.

Contrary to what the author says, we did not "suppose" a catastrophe. Instead we considered two cases:

1. The adiabatic case, where at a node of the nuclear function the total density is zero – hence a proven catastrophe.
2. The non-adiabatic case, where Bader's analysis can retrieve a structure – hence where no catastrophe is claimed. However, we argued that this structure is only due to the tail of the Born–Huang expansion, and hence would not be chemically meaningful.

Mohallem examined in detail the fact (understood as obvious in our original work) that, in the nonadiabatic case, the wave function does not usually vanish at a given value of $\mathbf{R}_0$ but did not address our criticism in case 2. We are not clear about what he means by the word "dominant" in his text. In our article we meant "dominant" in the sense of the norm in L^2 (the space of square integrable functions over both electronic and nuclear position variables minus the translation variables [2]) and in this sense (with the rotation variables also removed), the reference to Czub and Wolniewicz he quotes reports an exact wave function dominated by the adiabatic wave function. It is worth noting in this connection that we wrote that the Born–Huang expansion has "generally" a dominant term – not "always", as quoted by the author.

3 Kryachko's comment

This author has not understood the counterexample of Sect. 3, entitled "The Schwinger subsystem variation principle cannot be applied to zero flux surfaces". The author believes that ε is fixed at the value given in his Eq. (5), whereas it is fixed at an arbitrarily small value in the first step of the construction. More precisely, our construction proceeds as follows:

1. Choose $\varepsilon > 0$ to be arbitrarily small.
2. Solve Eq. (4) of Kryachko's comment for a and chose a solution a_0 (we showed in our article that there are always two solutions).
3. The function $\boldsymbol{\Psi}(\boldsymbol{r}; a_0)$ has a zero flux surface at $r = 3a_0$ and is on the closed sphere of radius $\frac{\varepsilon}{2}$ that is in the open sphere of radius ε as required.

As an example we considered the case $\varepsilon = 0.1$ and depicted the function $\boldsymbol{\Psi}(\boldsymbol{r}; a_0)$ obtained in Fig. 2 of our article. For those that are confused, we suggest trying another value of ε, say $\varepsilon = 0.001$, to see that the construction is correct.

Next, the author addresses Sect. 4, entitled "Non equivalence of net and local zero flux domains". He argues that his Eq. (6) is incorrect because the gradient of the density has no rotational part, a fact that is elementary. Note that since the zero flux condition, Eq. (1) of his comment, is a particular case of Eq. (6) with $\boldsymbol{A}(\boldsymbol{r})$ constant, this would mean that Bader's theory is also invalid, a consequence that we suppose the author did not intend. Apparently, the author has not realised that Eq. (6) does not stand for all $\boldsymbol{r}$ but is an equation to be solved for $\boldsymbol{r}$, yielding the set of solutions defining the

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Reply to the comments by J. R. Mohallem, E. S. Kryachko, L. Delle Site, and R. F. W. Bader, this issue surface $\partial\Omega$. In Ref. [2] we solved this equation in a concrete example.

Finally the author addresses Sect. 5 and says that we should have used the electronic density instead of the total density. Here it seems that the author stopped reading our article at the end of Sect. 5, or skipped the second sentence of Sect. 6. We precisely considered his solution to the problem raised in Sect. 5.

4 Delle Site's comment

Delle Site addresses the problem of the uniqueness of interatomic surfaces, but this is not the point we were really concerned with in our article, despite (perhaps) the misleading title of Sect. 1. The spurious surface problem illustrated in Fig. 1 of our article and that few people were aware of was indeed known to Bader and the latter made use of an argument based on the nuclear cusps to solve it. The aim of Sect. 1 as clearly stated in the last sentence was "not to invalidate the use of AIM as a practical tool but to emphasise that the spurious solutions cannot be excluded by using the cusp argument".

The problem of the extra zero flux surfaces that include an attractor can be easily dealt with by defining the atomic domains as attractor basins in the frame of catastrophe theory; or, as Delle Site suggests, by imposing on chemical grounds an appropriate boundary condition.

Delle Site asks further if such a boundary condition could emerge from purely theoretical arguments and replies positively because of the regularity of the surfaces required to apply Bader and coworkers' generalisation of Schwinger's principle. Suitable boundary conditions may indeed emerge from further theoretical considerations, but not from any theoretical considerations based on Bader and coworkers' application of the Schwinger principle, since we have shown that this principle has been applied incorrectly.

5 Bader's comment

Bader writes "An article (...) [3] written before the appearance of their article (but not before we sent it to him in July 1999), deals with many of the criticisms they put forth."

We disagree with this statement. We believe that his article only makes our criticisms appear sharper.

For example, in the section entitled "The cusp condition" he demonstrates at length that the cusps are unimportant to the chemist; at the same time, however, he makes them play a crucial part in the definition of the atoms in molecules (AIM). This contradiction was the problem of Sect. 1 in Ref. [1]. A second example concerns the global attractors of the electron density to which he also devoted a section in Ref. [3]. He states himself that the attractors we dealt with in Sect. 2 violate Dalton's dictum that an atom be indivisible. This seems in contradiction with his statement that the atoms of the AIM theory are "the atoms of chemistry" [4]. This was our point in Sect. 2. We have not been granted enough space here to go through all the old contradictions and new errors in Ref. [3] and refer the reader to Ref. [2] for a more complete discussion.

The author now contests the use of the hydrogen atom for our counterexample of Sect. 3; however, he claims that the AIM theory encompasses the closed isolated atom as a particular case [4] and he wrote in Ref. [5] "the partitioning obtained by excluding nuclei or attractors, in general, from a boundary surface is always unique, disjoint, and exhaustive and the surfaces of bound and free atoms are continuously transformable one into the other".

The author also says that our "variations of $\boldsymbol{\Psi}$ on the boundary of a closed system is both mathematically and physically incorrect". This is a puzzling statement. Our variation consists in adding a scaled 2*s*-like function with a small coefficient. All the functions considered are square integrable and vanish at infinity. No local variation on the boundary is attempted.

The references made to Schwinger and Schrödinger are irrelevant, as these authors were not dealing with systems defined by zero flux surfaces. This is why they could legitimately obtain the equation of motion.

When reading Bader's comment, it is important to keep in mind the difference between his ideas and those of Schwinger in regard to the generators of infinitesimal unitary transformation. Schwinger does not restrict the variations of the wave function to obtain the equation of motion, Eq. (18) of Ref. [6]. If, on the other hand, we follow Bader and restrict the variations to a special class of functions which exclude the square integrable functions with extra unconnected zero flux surfaces (despite the fact that the latter form a dense subset in L^2 as follows from the arguments developed in Ref. [1]!), then one cannot invoke the fundamental lemma of variation calculus to conclude that $\hat{H}\boldsymbol{\Psi} - E\boldsymbol{\Psi} = 0$ from $\int(\hat{H}\boldsymbol{\Psi} - E\boldsymbol{\Psi})\delta\boldsymbol{\Psi}^* = 0$. This is because this lemma relies on the variation $\delta\boldsymbol{\Psi}^*$ being arbitrary in the space of square integrable functions [7]. So, either no restrictions are made, but then the hypothesis of the Hilbert and Courant theorem is not met [8], or the variations are restricted, and the hypothesis of the lemma is not met. In both cases the Schrödinger equation cannot be obtained for a system defined by a zero flux surface.

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