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Reply to "Comment on the Comparative Use of the Electron Density and Its Laplacian"

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Abstract: In our reply to the preceding comment by Richard Bader we show that the statements of the author are not justified and that he contradicts his own previous work.

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Richard Bader starts the introductory section of his comment with the doctrinaire statement that scientists who "use some form of energy partitioning analysis (EPA) in studies of chemical bonding arrive at conclusions that are difficult to criticize because they lie beyond the boundaries of physics". We reject the declaration of Bader who apparently identifies his personal view of physical sciences with physics itself. We rather adhere to the view about chemical bonding which was expressed by Klaus Ruedenberg in his seminal paper entitled *The physical nature of the chemical bond*: "Many of these interpretations certainly are not "physical" in an operational sense, that is, they have no direct relationship to specific experimental observations. They are however "physical" in the sense that they try to provide a complete set of physical pictures which furnish a correct facsimile of the mathematical workings of the Schrödinger equation."[1] It is certainly legitimate to have a different view point, but we find it insulting to declare that chemists who are using EPA bonding models for explaining molecular structures and chemical bonding are operating outside of physics. The final statement of Bader has the same vilifying tone when he writes about using different bonding models: "Only the appeal to some teleological purpose lying beyond physics could lead to one description being favored over the other." This narrow view excludes nearly every chemist from the world of science except Richard Bader himself!

The concrete criticism raised in Baders comment against our paper[2] actually touches a very minor aspect of the work that is not relevant at all for the conclusions which are made. The author contradicts his own previous publications (see below) and he uses the method of selective citation of our text to find a criticizable point. He first cites our sentence: "The Laplacian distribution has been found to be a sensitive probe for the topology of the electron density distribution, $\rho(\mathbf{r})$." Bader then sets out to explain at great length that the Laplacian $\nabla^2\rho(\mathbf{r})$ and the electron density $\rho(\mathbf{r})$ have different topologies. He writes that we have a "misunderstanding regarding the different topologies of the two fields···". As a reply we give a *complete* citation from our work where we write: "We would like to point out that the Laplacian distribution does not show absolute charge concentrations. It indicates rather the differences in the charge concentration around the atoms with respect to monotonous decay. In a separated atom, the Laplacian distribution gives the shell structure of the electron density. For a bonded atom in a molecule, the Laplacian distribution gives the deformation of the spherical charge distribution which is caused by the interatomic interactions. The shape of the Laplacian distribution of a molecule shows the areas of charge concentration and charge depletion relative to the charge distribution of the free atom". It takes much fanciful misinterpretation to conclude from the above that we do not understand the different topologies of $\nabla^2\rho(\mathbf{r})$ and $\rho(\mathbf{r})$. A more precise statement would be that the Laplacian

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$\nabla^2\rho(\mathbf{r})$ indicates local maxima of $\rho(\mathbf{r})$ rather than charge concentrations, because it is the radial distribution function but not the charge concentration itself which has a shell structure. We repeat the citation given in Bader's comment which comes from the cited textbook of Morse and Feshbach: "If $\nabla^2\rho(\mathbf{r})$ is negative at some point there is a tendency for ρ to *concentrate* at that point."[3] There is no discrepancy between the latter assertion and our statement which was criticized by Bader!

The text which is cited by Bader in apparent support of his claim that we mistakenly equate charge depletion with lack of density accumulation actually comes from a footnote which more completely reads like this: "Also, as one referee pointed out, covalent interactions do not necessarily lead to an accumulation of the electronic charge in the bonding region. An example is the chemical bond in F_2. The Laplacian distribution of the electron density shows depletion of electronic charge in the bonding region of F_2. This was discussed by Cremer and Kraka who suggested that the energy density at the bond's critical point should be used as a sensitive probe for covalent bonding: D. Cremer, E. Kraka, *Angew. Chem.* **1984**, *96*, 612; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 62." (The page number in the latter should read 627). In the paper by Cremer and Kraka it was shown that the Laplacian at the bond critical point has a *positive* value, which indicates charge *depletion* rather than charge concentration. Richard Bader writes in his comment: "The F_2 molecule does in any event exhibit a negative value for $\nabla^2\rho_b$, of -0.04 au when calculated from a density obtained from a large basis set containing f functions." We want to confront the author with his own previous publishing which contradicts his statement! In his book *Atoms in Molecules*,[4] on page 429, Table A3, Bader gives a *positive* value for $\nabla^2\rho_b$, of 0.2287 au in F_2, which, according to the Table caption, comes from a calculation using Slater functions close to the Hartree-Fock limit. It was pointed out in the above cited paper by Cremer and Kraka that the existence of a bond critical point and a bond path does not rule out a positive value of $\nabla^2\rho_b$. This is because the Laplacian $\nabla^2\rho(\mathbf{r})$ is the sum of the principle curvatures in the three coordinates, one of them, belonging to the direction of the bond axis, being always positive while the other two in the orthogonal directions are always negative. It then depends on the absolute values of the three curvatures if the Laplacian is positive or negative.

We want to finally comment on the sentence "Arguing that the energy, rather than the density, is the driving force for bond formation is akin to arguing which came first—the chicken or the egg." The comparison is misleading. The crucial property of the charge is its energy which determines the course of chemical reactions and molecular structures. Hohenberg and Kohn have shown that, once we have a charge distribution, we may know its ground state energy provided that we know the correct functional. However, a given energy does not give us any information about the associated charge.

It is enlightening to consider the perceptions about chemical bonding offered by Bader in his recent work that are based on his understanding of physics. In a recent comment in this journal[5] which appeared as a rebuttal to a paper by Poater, Solà and Bickelhaupt[6] he wrote that "*The physics of bonding and the formation of a bond path between two hydrogen atoms in H_2 is indistinguishable from the bonding and the formation of a bond path between the ortho-H atoms in biphenyl*." (Italics by the author). A theory which does not distinguish between the interatomic interactions between a pair of atoms at equilibrium distance and in a transition state has severe limitations for the analysis of chemical problems. The problem also becomes obvious by the finding that similar bond paths and bond critical points are found for He_2 and H_2, which for a chemist have qualitatively different types of bonding. This clearly indicates that Bader's orthodox understanding of physics is unable to address fundamental questions of chemistry! Chemical research is based to a large degree on the ability to distinguish between different types of interatomic interactions. Chemistry has been called "the science of change, of transformations".[7] To this end, different bonding models for classifying molecular structures and chemical reactions have been developed that have been proven as very useful for explaining chemical phenomena. These bonding models are integral parts of chemical research. The AIM (Atoms In Molecule) model pioneered by Bader is one of them, complementary to, but not substituting, other approaches such as molecular orbital models. We do not share the reductionistic[8] view point of the author who does not recognize that the complexity of chemical phenomena requires specific models for different fields. *Chemical research begins where the physics of Richard Bader ends.*

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