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Comment on the Comparative Use of the Electron Density and Its Laplacian

Richard F. W. Bader*[a]

Abstract: This correspondence, in response to a paper published in this Journal, comments on the use of the Laplacian of the electron density, stressing that its topology and the physics it determines are distinct from those of the density itself, and their descriptors are not interchangeable.

Keywords: Atoms in Molecules theory · bond theory · chemical bonding · density functional calculations · energy-partitioning analysis

Introduction: Those who use some form of energy partitioning analysis (EPA) in studies of chemical bonding[1–4] arrive at conclusions that are difficult to criticize because they lie beyond the boundaries of physics.[5,6] However, the proponents of EPA occasionally make statements that clearly violate particular theorems or make use of physical properties of a system that lie within the realm of physics and in such cases they are beholden to abide by the strictures imposed by physics. A recent paper by Kovács, Esterhuysen, and Frenking illustrates the wrong physics that results with the impingement of an EPA analysis into the real world of physics.[7]

Differing topologies of the density and its Laplacian: The criticism of the paper by Kovács, Esterhuysen, and Frenking centers around their use of the Laplacian of the electron density, the function $\nabla^2\rho(\mathbf{r})$. The study of this function was initiated and its properties introduced into mainstream chemistry, by the research group at McMaster University[8–11] endowing the present author with some authority in its application and interpretation.[12] We begin with their statement: "The Laplacian distribution has been found to be a sensitive probe for the topology of the electron density distributions, $\rho(\mathbf{r})$." with a reference to "*Atoms in Molecules: A Quantum Theory*"[12] Now of course, $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ exhibit totally different topologies, as different as is the physical information they impart. The topology of $\rho(\mathbf{r})$ provides the basis for the definition of molecular structure, and does so because of its relatively simple topology, that of exhibiting maxima at the positions of nuclei.[13] This dominant topological property of $\rho(\mathbf{r})$ is a consequence of the dominance of the nuclear-electron force, one that leads directly to the definition of an atom in a molecule.

The more complex topology of $\nabla^2\rho(\mathbf{r})$ on the other hand, affords a theoretical model of the spatial localization of electrons, exhibiting alternating shells of charge concentration and charge depletion in accordance with the orbital model of shell structure,[9] together with multiple valence maxima in the function $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$. The maxima in $L(\mathbf{r})$ are found to coincide with the number and relative positions of the localised electron pair domains that have been invoked in models of the Lewis electron pair.[11,14] The topology exhibited by the Laplacian of the electron density has been shown to be a consequence of the electron pairing determined by the conditional pair density in six-dimensional space, its topology exhibiting a homeomorphism with the Laplacian of the conditional pair density, one that approaches an isomorphic mapping of one field onto the other when the reference pair is maximally localized.[15] The local concentrations of the Laplacian of the conditional pair density indicate the positions where the remaining electron pairs will most likely be found relative to a reference pair and correspondingly, the VSCCs displayed in $L(\mathbf{r})$ signify the presence of *regions of partial pair condensation, that is, of regions with greater than average probabilities of occupation by a single pair of electrons.*[5]

Differentiating between charge accumulation and charge concentration: Their misunderstanding regarding the differing topologies of the two fields, leads to a further error in their incorrectly relating particular topological features of

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[a] Prof. R. F. W. Bader
Department of Chemistry, McMaster University
1280 Main St W. Hamilton ON, L8S 4M1 (Canada)
Fax: (+1) 905-522-2509
E-mail: bader@mcmaster.ca

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the two fields. One may refer to a recent article stating: "One distinguishes between charge *concentrations* (CCs) and charge *depletions* (CDs) determined by the topology of L(**r**), and charge *accumulations* and charge *reductions* determined by the differing topology of $\rho(\mathbf{r})$."[5] Two separate sets of descriptors are purposely used to differentiate the ability of one function, determined by the second derivative of $\rho(\mathbf{r})$, to locate regions of CC and CD in an absolute sense, from the ability of the other to determine regions where the electron density attains maximum, minimum or saddle-like characteristics. The phrase "concentrate" comes directly from Morse and Feshbach in their demonstration, using the fundamental definition of a derivative of a scalar function such as ρ, that "If $\nabla^2\rho$ is negative at some point there is a tendency for ρ to *concentrate* at that point."[16] (Their italics).

The term "accumulation" may also be used to describe the change in the distribution of the density between different states or nuclear configurations of a molecule, such as the "accumulation of density in the internuclear region or regions" as required for the formation of a bound state of a molecule. Thus the Laplacian is determined by the operation $\nabla^2\rho$ while the topology of ρ may be used to determine density differences, the operation $\Delta\rho(\mathbf{r})=\rho(\mathbf{r})-\rho(\mathbf{r}')$.

This brings us to the statements by Kovács, Esterhuysen, and Frenking to the effect that "…covalent interactions do not necessarily lead to an accumulation of the electronic charge in the bonding region.",[7] a statement that violates the virial theorem[17,18] and the Feynman[19] and Ehrenfest[20] force theorems. This statement is followed by: "An example is provided by the chemical bond in F_2. The Laplacian distribution of the electron density shows a depletion of electronic charge in the bonding region of F_2." Thus Kovács, Esterhuysen, and Frenking mistakenly equate a *charge depletion* in $\nabla^2\rho(\mathbf{r})$ with a lack of an *accumulation* of density, two entirely unrelated physical properties of the density. As already discussed, whether or not electron density is *accumulated* is a property determined by the topology of the density, not by its Laplacian. Electron density is accumulated in the bonding region of F_2 as demonstrated by the formation of a bond path linking the nuclei, with a ρ_b value of 0.367 au, a value that is decreased to 0.268 au with electron correlation, identical to the value found for the correlated density in H_2.[21]

A bond path meets all of the physical requirements set by the Ehrenfest, Feynman, and virial theorems that the atoms be bonded to one another; the two atoms experience an attractive Ehrenfest force drawing their atomic basins together: no Feynman force, neither attractive nor repulsive, acts on the nuclei because of the balancing of the repulsive and attractive forces by the *accumulation* of electron density in the binding region: this same accumulation leads to a lowering of the electron-nuclear potential energy whose magnitude exceeds the increases in the electron and nuclear repulsion energies and the increase in the kinetic energy, as demanded by the virial theorem. *Thus a bond path is indicative of the accumulation of density between the nuclei that is necessary for the presence of attractive Ehrenfest forces, for a balancing of the Feynman forces on the nuclei and for the decrease in energy.* Its presence is both necessary and sufficient for two atoms to be bonded to one another.[22] A bond path is mirrored by a "virial path", a line along which the potential energy density is maximally stabilizing and the formation of the line of maximum density is associated with a local lowering in the energy.[23]

Kovács, Esterhuysen, and Frenking make reference to a calculation by a 1989 paper by Schwarz et al,[24] to the effect that a density difference map between the molecular density and that of the overlapped free atoms for F_2 exhibits an accumulation of electronic charge in the bonding region when referenced to the 'properly arranged fluorine atoms'. (Use of spherical atom densities in the construction of the $\Delta\rho$ map for F_2 leads to a depletion of density in the central bonded region.) The correct phrase is when "referenced to fluorine atoms in their proper *valence states*", something that has been known since 1967 when an extensive series of papers appeared providing the first definitive study of the rearrangement of atomic densities on bond formation,[25–29] studies that made use of the near Hartree–Fock densities obtained by the Mulliken–Roothaan group at the University of Chicago from large STO basis sets with optimized exponents for both the free atoms and the molecule.[30–32]

A disadvantage of density difference maps is that their form depends upon the choice of atomic references states, as noted for F_2. A consistent physical choice can however, be made in diatomic molecules, by appeal to physics. This is accomplished by the use of the valence state of the atom determined by perturbation theory in the limit of a vanishing axial electric field where the quantum number λ begins being a good quantum number, breaking the m_l degeneracy into σ, π…. sets.[25,26] The resulting $\Delta\rho$ maps yield a single pattern for the redistribution of density for atoms past He: a quadrupolar polarization with a density accumulation along the axis in both the bonded and nonbonded regions of the atom, and its removal from perpendicular torus-like region encircling the axis at the position of the nucleus. This pattern of charge reorganization is the universal response of an atom to an axial electric field, be it an applied static field or a dynamic one arising from nuclear displacements, vibrational or bond formation.[33] As an example, one notes that the density of a F atom 13 au from an approaching Li atom exhibits a quadrupolar polarization along the axis of approach consistent with the valence state configuration $2p\sigma^1 2p\pi^4$,[34] the same configuration that yields a build-up of density in the binding region of the bond density map for F_2.[26] This is the valence state that is defined by the energy of interaction of arising from the approach of the atoms and the consistent use of physics avoids all contradictions in the response of the density to a particular perturbation.

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.[35] A value of ρ_b lying within the "shared" range of interactions[12] coupled with a value of $\nabla^2\rho_b$ in the neighborhood of zero, indicates a bonding type wherein density is both accumulated and concentrated along the bond path, as evidenced by the large magnitude of the negative perpendicular curvatures, but one in which the final distribution is dominated by the stress parallel to the bond path, as measured by the positive curvature. This stress is a consequence of the exceptional degree of localization of the pair density within the fluorine atomic basins, the per cent localization equalling 94.4% in F_2 compared to 84.2% in N_2 in CI calculations.[21] Attention was drawn to the exceptional localization of electrons within the basin of a F atom and the resulting weakness of the bonding in F_2 in the original paper that related the localization of electrons to the corresponding localization of the Fermi density.[36] Correspondingly, the exchange of electrons between the atomic basins is greater in N_2 than in F_2, 2.2 pairs being exchanged in the former compared to 1.0 in the latter, as determined by the correlated exchange indices.[21] The "α,β spin-exchange resonance" deemed necessary for "covalent bonding" in VB theory is proportional to the exchange indices, the exchange energy being determined by a weighting of the exchange density by $1/r_{12}$, and the interbasin exchange energy is significantly reduced in F_2 compared to N_2.

Independence of ρ and $\nabla^2\rho$ from reference states: Contrary to what is stated by Kovács, Esterhuysen, and Frenking,[7] the topology of $\nabla^2\rho(\mathbf{r})$ does provide absolute measures of charge concentration and depletion, a consequence of the integral of $\nabla^2\rho(\mathbf{r})$ vanishing over the entire space of a molecule, ensuring an equality in the overall formation of regions of charge concentration and charge depletion within a molecule and within the basin of every atom in the molecule, a consequence of the zero-flux boundary condition.[12] Thus the concentrations are most definitely not, as KEF state, measured "with respect to monotonous decay" or "relative to the charge distribution of the free atoms."[7] Of primary importance, is the number, relative size and orientation of the CCs in the VSCC of an atom that form the bridge with the Lewis electron pair model[37,38] and the VSEPR model of geometry,.[39] While it is the outer shell of charge concentration of the free atom that is distorted in the formation of a molecule, *the topology of the VSCC is independent of any reference to the free state of the atom.* Also important, is the extent to which the CCs, determined by the (3,−3) and (3,−1) critical points (cps) in L($\mathbf{r}$) exceed the values of the CDs determined by the (3,+1) and (3,+3) cps in the VSCC. Such comparisons are provided by the listing of the VSCC cps of L($\mathbf{r}$) for a large number of A_nH_m and A_nB_m molecules[40] and more recently for the Cr, Fe and Ni atoms in their carbonyl complexes.[5] The absolute topology of $\nabla^2\rho(\mathbf{r})$ also determines the relative weighting of the kinetic and potential energy densities, G(r) and v(r) respectively, at each point in space, because of its appearance in the local statement of the virial theorem,[12]

$$(\hbar^2/4m)\nabla^2\rho(\mathbf{r}) = 2\mathrm{G}(\mathbf{r}) + v(\mathbf{r})$$

One is free of course, to determine changes in any property between any pair of quantum states, between the separated atom states and the molecular state for example, but the physical information provided by the topologies of ρ(r) and $\nabla^2\rho(\mathbf{r})$ and the physical information they provide are independent of the choice or use of a reference state. Thus the use of ρ(r) and $\nabla^2\rho(\mathbf{r})$ in a discussion of bonding differs from the use of EPA whose implementation requires the definition of a number of reference states that are non-physical, as well as arbitrary.

Concluding remarks: Kovács, Esterhuysen, and Frenking state that "energy is a more direct criterion for chemical bonding than charge distribution.", also stating ".that the accumulation of electronic charge in the bonding region is a result of chemical interactions but not the driving force.",[7] statements that reflect Frenking's criticism of the use of the electron density in the interpretation of chemical bonding.[41] 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 two statements that "accumulation of density in the bonding region lowers the potential energy and decreases the total energy"—or that "density is accumulated in the bonding region because it lowers the potential energy and decreases the total energy", are equivalent physical descriptions of chemical bonding. Only the appeal to some teleological purpose lying beyond physics could lead to one description being favoured over the other.

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