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Expanding the usage of the Source Function to experimental electron densities

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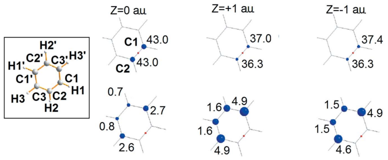

The concept of the Source Function (SF) for the reconstruction of the electron density first appeared in the seminal study published by Bader & Gatti (1998) where it was unambiguously shown how the density at any given point, $\rho(\mathbf{r})$, is the effect of the action of the cause, $\nabla^2\rho(\mathbf{r}')$, at all other points weighted by the influence function $(4\pi|\mathbf{r}-\mathbf{r}'|)^{-1}$

$$\rho(\mathbf{r}) = \int \frac{-\nabla^2\rho(\mathbf{r}')}{4\pi|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}r'.$$

Utilizing further the space-filling subdivision of charge into atomic basins using the zero-flux surfaces which lie at the root of Bader's Quantum Theory of Atoms in Molecules (Bader, 1990) allows one to write the density at any given point in space as a sum over atomic contributions $\mathrm{SF}(\mathbf{r};\Omega)$

$$\rho(\mathbf{r}) = \sum_{\Omega} \mathrm{SF}(\mathbf{r};\Omega).$$

One of the most important elements of the SF is the fact that it only depends on the value of the Laplacian of the density. This enables comparison of results from theoretical calculations with electron density studies based on high-resolution single-crystal X-ray diffraction.

Since its inception in 1998, several authors have contributed to illustrate the descriptive power of the SF. It has for instance been introduced into the study of hydrogen bonds (HBs), where in particular the contribution from the H atom was found to be a strong indicator of the nature of the given HB. As the HB changes character from normal and relatively weak HB to strong, single well, the SF contribution from the H atom to the H···O b.c.p. (bond criticial point) changes from negative to positive (Overgaard *et al.*, 2001; Gatti *et al.*, 2003). The strengths of the SF are also remarkably evident in the study of chemical bonding in the iron coordination compound with trimethylenemethane (TMM), where conventional topological analysis suggests a η^1-coordination mode for the TMM ligand while delocalization indices as well as the SF clearly portray a bonding scenario with significant contributions to bonding from the three methylene C atoms, thus a η^4 complex is a much better representation (Farrugia *et al.*, 2006). The SF provided a similar weighty argument in the rebuttal of hypervalency in the sulfate anion in K_2SO_4 (Schmøkel *et al.*, 2012).

In the featured paper by Gatti *et al.* (2016) it is indisputably illustrated, by resorting to clever choices of chemical systems, how the SF approach applied to experimental data is able to clearly reveal electron delocalization effects in aromatic systems. This was previously studied for theoretical densities (Monza *et al.*, 2011) and has now been expanded to experimental data. First, the authors establish reference electron delocalization properties of benzene (Fig. 1) and naphthalene as examples of non-perturbed aromatic systems, using the SF approach applied to the experimental electron densities of these two compounds. They then move on to study the effects on the delocalization of substituting some of the H atoms of these benchmark reference systems as it occurs in (±)-8′-benzhydrylideneamino-1,1′-binaphtyl-2-ol (BAB), which is a highly suitable molecular complex having two phenyl groups and two naphthalene-like moieties.

However, besides establishing the validity of the SF approach for experimental densities as will be described later, the authors devote the first half of the review to a detailed state-of-the-art of the SF method neatly summarizing the development of the method since its foundation, pointing out its strength in being able to provide a picture of

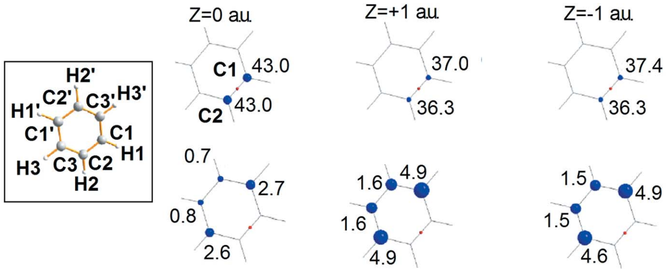

Figure 1
X-ray derived SF% patterns reflecting electron delocalization effects in benzene crystal. The top row shows SF% from bonded atoms at b.c.p. and above/below molecular plane. The second row shows the SF% from the other atoms in the same reference points (reproduced with permission from Gatti *et al.*, 2016).

bonding that correlates extremely well with that given by the delocalization index, δ, but without the need for the pair density or the first-order density matrix, which is only available through theoretical approaches (or the X-ray wavefunction refinement method by Jayatilaka & Grimwood, 2001). Importantly, it sets itself apart from the delocalization index, δ, which is 'symmetrically relating the action of two atoms or group of atoms Ω_1 and Ω_2', while the SF approach is asymmetric in nature and links a volume defined as one or more atoms to the density at a given point, typically at the defining b.c.p. between two bonded atoms.

Of particular significance in the introduction is the rebuttal of previously voiced criticism of the SF approach claiming that the SF approach will produce similar results if based on the physically meaningless promolecule density. This is done in the following way: For a series of three molecules with an increasing degree of electronic delocalization (cyclohexene; 1,3-cyclohexadiene; benzene) the IAM density has been calculated fixing the geometry at that of the higher level calculation, and it is found that the changes to the SF contributions from both bonded atoms, next-neighbors and other atoms, across the series of molecules show no resemblance to the trends observed for the SF based on the true density. By virtue of these results it is concluded that the SF approach will deliver pertinent information about the electronic delocalization when applied to a realistic approximation of the true density, and that it is able to distinguish electronic and structural effects.

The major impact of the work is found in its exposition of how well the SF is able to sense the tiny changes that follow upon substitution of H atoms on the naphthalene and phenyl rings. The substituted atoms are more electronegative than the H atoms previously residing there, and they have the effect of removing electron density from the ring-residing C atoms such that less ED is available for chemical bonding. The consequence is that the CC bonds become less covalent and thus slightly extended and the value of SF_{ba}% decreases. The ingenuity of the study is their choice of the molecule BAB which contains more or less substituted fragments of the reference molecules (naphthalene and benzene) and there is an amazing quantitative agreement between SF% numbers from the reference systems and those of the BAB crystal suggesting that the SF% parameters are transferable across systems.

With the present results, Gatti *et al.* enhance the position of the SF as a key property that holds absolutely vital information about chemical bonding in molecular systems. Its adaptation to experimental densities has been made available and it has been shown with exceptional accuracy that it is able to sense changes to the electronic environment in aromatic systems due to (distant) substitution effects.

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