O - 33 Full electron population analysis through the integration of the source function descriptor

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The electron density evaluated at any point **r** in a system, $\rho(\mathbf{r})$, can be seen as due to the contributions from a local source, LS(**r**,**r'**), operating at any other point **r'**.[1] When the local sources are integrated over Quantum Theory of Atom In Molecules (QTAIM) atomic basins Ω, $\rho(\mathbf{r})$ can be decomposed and reconstructed as a sum of basin contributions, each one named *Source Function* (SF) from the atom Ω to the point **r**, S(**r**,Ω). Through this topological descriptor, one is able to reveal how and to which extent atoms or group of atoms contribute to determine the electron density in any reference point within a *cause-effect* relationship.[2] When the SF contributions are integrated over a basin Ω', a "full population matrix" M is retrieved, where the matrix element M(Ω',Ω) represents the contribution of the Ω basin to the population of Ω'. At variance with other population analyses, such as Mulliken population[4], Natural Bond Orbital analysis[5] and that based on the Hirshfeld partitioning[6], this method has some advantages: i) it is only based on the electron density and its laplacian; ii) it can be obtained from both experiments and theoretical calculations; iii) the atoms are quantum mechanical objects; iv) the matrix is generally not symmetric, M(Ω',Ω)≠M(Ω,Ω'). However, the application of this method has been undermined by severe drawbacks such as large computational costs, numerical integration errors and the impossibility to assign all the electrons.[7]

Methodological improvements on this analysis are here reported. The SF contributions are integrated over a variable resolution grid box, where the resolution is dynamically calculated according to the theoretical $\rho(\mathbf{r})$. High resolutions are used where the $\rho(\mathbf{r})$ rapidly changes, while low resolutions are adopted for smooth regions. This strategy allows to reduce the number of integration points, saving computational time without losing any important density feature. Each point is uniquely associated to a basin according to $\nabla\rho(\mathbf{r})$ field. To reduce the effect of numerical errors, a double cutoff (k and k') is used. The SF contributions are evaluated only on those points where $\rho(\mathbf{r})\geq k$. The density thus reconstructed is corrected and integrated only if ERR%≤k', where ERR% is the percentage error calculated with respect to the true value of the density in the point **r**. The two cutoffs are chosen so that only a small amount of electrons is lost (usually lower than 1%). Numerical population matrices and comparisons with other population analyses are also discussed.

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