Beyond $\nabla^2\rho_b$: Chemical Bond Analysis using the Local Form of the Source Function

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The sign of the Laplacian of the density at the bond critical point, $\nabla^2\rho_b$, has been largely used for discriminating the closed-shell-like ($\nabla^2\rho_b>0$) from the shared-shell-like ($\nabla^2\rho_b<0$) interactions. This dichotomous bond classification has the merit of being simple, but it has also proved to be often inadequate. This is the case of bonding between heavy atoms missing the outermost regions of charge depletion and concentration in their atomic Laplacian distributions and/or the case of interactions having very low $|\nabla^2\rho_b|$, a fact which makes the sign of $\nabla^2\rho_b$ quite indeterminate and the use of $\nabla^2\rho_b$, as the only classification index, deceiving. Other quantities, based on the first and/or the second order density matrices, have in these cases been proposed as more suitable indices. However, both matrices are generally not directly amenable to experimental determination.

Recently, it has been shown [1-3] how the sign of $\nabla^2\rho$ at $\mathbf{r}'$ determines whether this point acts as a *source* or as a *sink* for ρ at any other point $\mathbf{r}$ in a system, with the effectiveness as a source or as a sink being related to $|\nabla^2\rho|$ and to the inverse of the distance between the two points, $\rho(\mathbf{r}) = \int -(1/4\pi)\nabla^2\rho(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^{-1}\cdot d\mathbf{r}' = \int LS(\mathbf{r}, \mathbf{r}')\cdot d\mathbf{r}'$.

The profile of the *local source function* LS $(\mathbf{r}, \mathbf{r}_{bcp})$ along the bond path is here used to unravel the different mechanisms by which covalent bonding between light or heavy atoms realizes in crystals.

[1] Bader R.F.W., Gatti C., *Chem. Phys. Lett*., 1998, **287**, 233. [2] Gatti C., Cargnoni F., Bertini L., *J. Comput. Chem*., 2003, **24**, 422. [3] Gatti C., Bertini L., *Acta Cryst.*, 2004, A**60**, 438.

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