Integrating the Laplacian of electron density in fuzzy overlap space as a measure of covalent bond order

Tian Lu and Feiwu Chen

Department of Chemistry and Chemical Engineering, School of Chemical and Biological Engineering, University of Science and Technology Beijing, Beijing, P. R. China

E-mail: Sobereva@sina.com

Bond order is an important concept for understanding the nature of chemical bond. In this work, we propose a novel definition of covalent bond order based on the Laplacian of electron density $\nabla^2\rho$ in fuzzy overlap space, called Laplacian bond order (LBO).[1] The LBO between atom A and B can be simply written as

$$\mathrm{LBO}_{A,B} = -10 \times \int_{\nabla^2\rho<0} w_A(\mathbf{r}) w_B(\mathbf{r}) \nabla^2\rho(\mathbf{r})\,\mathrm{d}\mathbf{r}$$

Where w is a smoothly varying weighting function and represents fuzzy atomic space, hence $w_A w_B$ corresponds to fuzzy overlap space between A and B. Note that the integration is only restricted to negative part of $\nabla^2\rho$. The physical basis of LBO is that the larger magnitude the integral of negative $\nabla^2\rho$ in the fuzzy overlap space, the more intensive the electron density is concentrated in the bonding region, and therefore, the stronger the covalent bonding.

The reasonableness and usefulness of LBO were demonstrated by applying it to a wide variety of molecules and by comparing it with many existing bond order definitions.[1] It is shown that LBO has a direct correlation with the bond polarity, the bond dissociation energy and the bond vibrational frequency. The computational cost of LBO is low, also LBO is insensitive to the computational level used to generate electron density. In addition, since LBO is inherently independent of wavefunction, one can in principle obtain LBO by making use of accurate electron densities derived from X-ray diffraction data.

LBO has been implemented in our wavefunction analysis program Multiwfn,[2] which can be freely downloaded.

[1] Lu, T., Chen, F. *J. Phys. Chem. A*, 2013. DOI: 10.1021/jp4010345
[2] Lu, T., Chen, F. *J. Comput. Chem., 33: 580-592*, 2012.