Visualization and characterization of intermolecular interaction based on the electron difference density

Kota Daigoku

College of Liberal Arts and Sciences, Kitasato University

Noncovalent interactions (NCI) play an important role in chemistry and biochemistry. Since these are usually weak and obscure compared with covalent bonding, some extra efforts are needed to characterize and visualize it. Johnson et al. developed a noncovalent interaction index[1] based on the electron density and its derivatives(reduced density gradient in density functional theory), which is an effective tool for biological system. We investigated the intermolecular NCI by a simple and straightforward method based on the so-called difference density for molecular complexes

$$\Delta\rho(\boldsymbol{r}) = \rho_{complex-AB}(\boldsymbol{r}) - \left[\rho_{molecule-A}(\boldsymbol{r}) + \rho_{molecule-B}(\boldsymbol{r})\right]$$

where ρ is not only electron density, but also its laplacian and electrostatic potential(ESP). These difference quantities represent the NCI-induced change of electronic structure straightforwardly. We calculated these quantities for a few kinds of molecular complexes bound by van der Waals interactions such as the Hydrogen bonding and dispersion interactions. The difference densities of the electron and the laplacian represent the NCI-induced electron transfer, concentration or depletion visually although they look somewhat complicated. These pictures are also emphasized in the motion of intermolecular vibration (Some of animated illustrations are found in Ref. 2). On the other hand, the difference ESPs, which indicate a change of local polarity, make the existence of the NCI clear and distinct. These three difference quantities amplify the buried character of the NCI, and provide direct information for understanding it.

(This work was supported by JSPS KAKENHI Grand Number 23730842.)

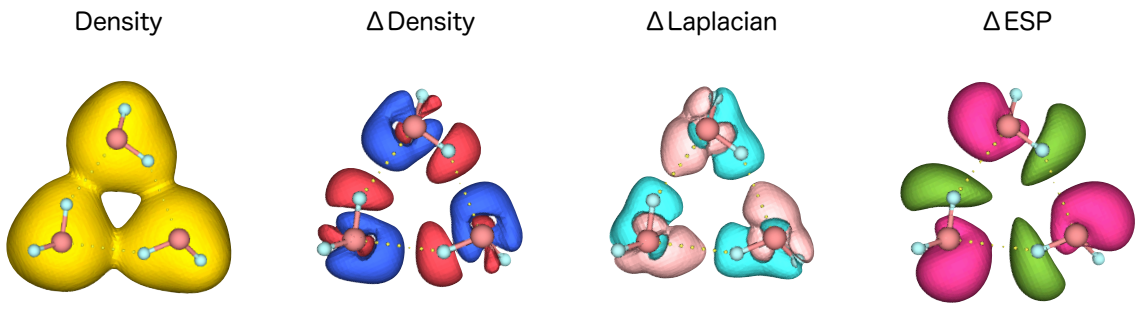

Figure 1. Molecular difference quantities of water trimer at the HF/aug-cc-pVTZ levels.

[1] Johnson, E. R., Keinan, S., Mori-Sanchez, P., Contreras-Garcia, J., Cohe, A. J., Yang, W. *J. Am. Chem. Soc.*, 132:6498-6506, 2010.

[2] Daigoku, K. *Clip Art of Quantum Chemistry*, http://www.kitasato-u.ac.jp/ippan/kagaku/daigoku/clipartQC.html.