The electron localization as the information gain of the conditional pair density

Luis Rincón, Andrés S. Urbina and F. Javier Torres

Universidad San Francisco de Quito (USFQ), Grupo de Química Teórica y Computacional (QCT-USFQ), Departamento de Química e Ingeniería Química, Colegio Politécnico de Ciencias e Ingeniería, Diego de Robles y Via Interoceanica, Quito 17-1200-841, Ecuador

The information gained by an electron located at r for "knowing" about the position of another electron with the same spin is calculated using the Kullback-Leibler divergence ($D_{KL}(r)$) between the same-spin conditional pair density and the marginal probability. $D_{KL}(r)$ is proposed as an electron localization measurement, based on the observation that regions of the space with high information gain can be associated with strong localized electrons.[1,2] Taking into consideration the scaling of D_{KL} with the number of s-spin electrons of the system,

$$D_{KL}(r) \leq \frac{1}{N^{\sigma}-1},$$

the quantity $\chi(r) = (N^{\sigma}-1) f_{cut} D_{KL}(r)$ is introduced as a general descriptor that allows the quantification of electron localization in the space. f_{cut} is defined such that it goes smoothly to zero for negligible densities. $\chi(r)$ is computed for a selection of atomic and molecular systems in order to test its capability to determine the region in space where electrons are localized. $\chi(r)$ is able to explain the electron localization of molecules on the basis of chemical grounds with a high degree of success and produce a clear differentiation of the localization of electrons that can be traced to the fluctuations in the average number of electrons in these regions.

1. A.S. Urbina, F.J. Torres, and L. Rincon, *J. Chem. Phys*. **144**, 244104 (2016).
2. L. Rincon, R. Almeida, P. L. Contreras, and F.J. Torres, *Chem. Phys. Lett*. **635**, 116 (2015).