The Topology of Electron-Electron Interactions within the Chemical Bond

A. J. Proud, B. J. H. Sheppard, D. Mackenzie, D. Hennessey, Z. Zielinski and J. K. Pearson*

Department of Chemistry, University of Prince Edward Island, Canada

*Author for correspondence e-mail: jpearson@upei.ca

Since the days of G.N. Lewis [1] chemists have been enamored with the concept of a localized electron pair to represent the now intuitive features of electronic structure such as the so-called lone pair and even the chemical bond itself. Despite its simplicity the Lewis model yields an impressive wealth of predictive ability in terms of molecular structure [2] and chemical properties and is ubiquitous in the literature. To study electronic structure in terms of such pairs of electrons seems natural, however it is complicated by the dimensionality of the pair density and the generally delocalized canonical molecular orbitals. In this talk, I will describe our work to circumvent these challenges by using condensed pair densities of localized molecular orbitals (LMOs). These include the intracular (relative separation) and extracular (center of mass) densities for electron pairs within LMOs that describe the chemical bond and lone pairs in both position and momentum space. I will show that these may be interpreted as the distribution of electrons within a chemical bond and illustrate several applications. We have been interested in the prediction of electronic pair distributions for reasons including the analysis of electronic structure [3,4,5,6], the interpretation of correlation effects [5-7] and the calculation of the correlation energy [8].

References

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