

QUANTIFYING DEGREES OF LOCAL AROMATICITY THROUGH MULTICENTER INDICES

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Although aromaticity is a notoriously undefined concept, it remains a vital idea in much of chemistry. As the concept is not defined, one cannot know what quantities play a determining role in any discussion on whether a molecule is aromatic or not. Nevertheless, there seems to have grown some degree of consensus that a molecule is considered aromatic if it has a delocalized electronic system, it shows bond length equalization, exhibits a diamagnetic ring current when exposed to an external magnetic field, shows a remarkable extra energetic stabilization and has specific chemical reactivity characteristics.

In this presentation, multicenter indices are introduced and some critical tests are performed to investigate the merits of such an index. Their application towards the quantitative study of local aromaticity is studied and the results carefully checked against conclusions from other indices. It will be shown how the lack of definition of aromaticity has even worse consequences in local aromaticity. Careful statistical analysis of correlations between different indices is performed, showing that for polyaromatic hydrocarbons several indices that are commonly considered orthogonal or divergent in fact correlate relatively well and can thus not be considered separate entities in the so-called multidimensional character of (local) aromaticity.

It is then shown how, despite the lack of a proper definition, a relative degree of aromatic character for benzenoid rings can be derived from a quantum similarity approach in which each benzenoid ring is compared to benzene as a truly *defined* aromatic standard. The remarkable agreement between such similarity measures and multicenter indices is shown for a set of polyaromatic hydrocarbons.