

Using X-ray Constrained Extremely Localized Molecular Orbitals in the Theoretical Study of the Biscarbonyl[14]annulene Charge Density

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Nowadays, two of the main families of techniques to determine crystal electron distributions from high-resolution X-ray diffraction data are the multipole model methods [1, 2] and the wave function based approaches [3]. If on the one hand the former are linear scaling strategies and are characterized by an easy chemical interpretability of the obtained charge distributions, on the other hand the latter, although more computationally expensive, are intrinsically more quantum mechanically rigorous. In this context, to combine the typical ease of chemical interpretation of the multipole models with the quantum mechanical rigor of the wave function-based techniques, the X-ray constrained wave function approach proposed by Jayatilaka [3] has been recently extended in the framework of a quantum chemistry method for the determination of Extremely Localized Molecular Orbitals (ELMOs) [4]. This resulted in a novel strategy that enables to extract Molecular Orbitals strictly localized on small molecular fragments, (e.g. atoms, bonds or functional groups) directly from high-quality experimental X-ray diffraction data [5-7].

As example of the intrinsic chemical meaning associated with the X-ray constrained ELMOs (XC-ELMOs), we will present a recent study in which the new localized “experimental” Molecular Orbitals have been exploited to study the charge density of the syn-1,6;8,13 biscarbonyl[14]annulene (BCA). In particular, we will show that, using the XC-ELMOs and some new original methods based on them (e.g., the novel X-ray constrained ELMO Valence-Bond strategy), it is possible to clearly highlight how the BCA, which is a fairly aromatic molecule at ambient pressure, is able to progressively localize single and double bonds when pressure increases. This confirms some recent results obtained by Macchi and coworkers through unconstrained multipole model refinements of X-ray diffraction for the BCA crystal data collected at high pressures [8].

References:

1. R. F. Stewart, *Acta Cryst. A* **32**, 565 (1976).
2. N. K. Hansen, P. Coppens, *Acta Cryst. A* **34**, 909 (1978).
3. D. Jayatilaka, D. J. Grimwood, *Acta Cryst. A* **57**, 76 (2001).
4. H. Stoll, G. Wagenblast, H. Preuss, *Theoret. Chim. Acta* **57**, 169 (1980).
5. A. Genoni, *J. Phys. Chem. Lett.* **4**, 1093 (2013).
6. A. Genoni, *J. Chem. Theory Comput.* **9**, 3004 (2013).
7. L. H. R. Dos Santos, A. Genoni, P. Macchi, *Acta Cryst. A* **70**, 532 (2014).
8. P. Macchi, N. Casati, A. Kleppe, A. Jephcoat, *in preparation*.