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Extracting Extremely Localized Molecular Orbitals from X-ray Diffraction Data

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The accurate determination of electron densities in crystals from high-resolution X-ray diffraction data has become more and more important over the years. The existing techniques to accomplish this task can be subdivided into two great families: the multipole models and the wave function-based strategies. The former, which are the most widely used, are essentially linear scaling and allow an easy chemical interpretation of the obtained molecular charge densities, but they are also characterized by some drawbacks, such as the possible presence of unphysical negative regions in the resulting electron distributions. On the contrary, the latter always provide quantum mechanically rigorous electron densities, but they are more computationally expensive and, above all, the ease of chemical interpretation is almost completely lost. In this context, in order to combine the easy chemical interpretability of the multipole models with the quantum mechanical rigor of the wave-function based methods, we have recently extended the X-ray constrained wave function approach proposed by Jayatilaka in the framework of a quantum chemistry technique for the a priori determination of Extremely Localized Molecular Orbitals (ELMOs), namely we have developed a new strategy that allows to extract from X-ray diffraction data a single Slater determinant built up wit Molecular Orbitals strictly localized on small molecular fragments (e.g., atoms, bonds or functional groups). Preliminary tests have shown that the determination of X-ray constrained ELMOs is really straightforward. Furthermore, given the reliable transferability of the obtained Molecular Orbitals, we are constructing new ELMOs databases that can be used as alternative to the existing pseudo-atoms libraries for refining crystallographic structures and electron distributions of large systems. A detailed comparison between the new technique and the multipole models is also currently under investigation.

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