X-ray constrained wave function: new developments and insights

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Nowadays the electron density can be considered as a crucial physical quantity whose prominent role relies both on the Hohenberg & Kohn theorem and on the observation that the knowledge of the charge distribution and of its properties is extremely important for a complete understanding and rationalization of chemical bonding. Therefore, the determination of crystal electron distributions from high-resolution X-ray diffraction data has become a mature field of science and, in order to accomplish this task, different strategies have been devised over the years.

In this context, the multipole models methods [1, 2] are certainly the most widely used techniques. They are characterized by a small computational cost and, above all, by an easy chemical interpretability of the resulting charge densities. Nevertheless, besides the multipole models, a primary role is also played by the wave function- (or density matrix-) based strategies [3, 4], among which the X-ray constrained wave function (XC-WF) approach proposed by Jayatilaka [4] is probably the most promising one.

Although more computationally expensive, the Jayatilaka's method has the non-negligible advantage of extracting wave functions associated with X-ray diffraction data. Therefore, unlike the multipole models, it enables to provide both more quantum mechanically rigorous electron distributions and properties not directly related to the collected structure factors used to determine the wave function itself.

In our lab, the XC-WF approach has been the object of our recent studies. In particular, the technique has been extended into the framework of the Extremely Localized Molecular Orbitals (ELMOs) [5], which allowed to combine the quantum mechanical rigor of the wave-function based strategies with the chemical interpretability of the multipole models [6-8]. Furthermore, a XC-ELMO Valence Bond method has been recently devised and afterwards applied to study the charge density of the biscarbonyl[14]annulene (BCA) at different pressures [9]. Finally, we are currently investigating some open problems associated with the Jayatilaka's strategy, such as the termination of the fitting procedure and the capability of the X-ray constrained wave functions of capturing at least part of the electron correlation effects. A brief overview and discussion of our recent developments and insights of the X-ray constrained wave function strategy will be presented.

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