MS19-2-1 X-ray constrained wavefunction approach: further developments and future outlooks
#MS19-2-1

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Abstract
The X-ray constrained wavefunction (XCW) technique [1-4] is a modern quantum crystallographic method that aims at extracting plausible electronic wavefunctions from X-ray diffraction data. This is done by minimizing the energy of the system under exam and simultaneously maximizing the statistical agreement between calculated and experimental structure factor amplitudes.
In this presentation, two unsolved problems of the XCW technique will be addressed: i) the possibility of introducing a weight for each considered reflection; ii) the need of determining a clear halting point during the XCW calculations (also known as the long-standing problem of determining the value of the parameter).
Pertaining to the former problem, we have recently proposed [5] a weighting scheme based on the results of a previous investigation on the capability of extracting electron correlation effects through X-ray constrained wavefunctions [6]. In that study we observed that the high-angle data largely predominate and are already very well described at unconstrained level (i.e., when =0), with the consequence that the significant electron correlation effects contained in the low- and medium-angle reflections cannot be fully captured by the XCW method. Based on these observations, we introduced a weighting scheme to up-weight the low- and medium-angle data and to down-weight the high-angle ones. The results obtained by means of this strategy will be shown and discussed, both in the case in which we exploited theoretically generated data and in the one in which we used experimental reflections.
Concerning the second point, we will present how the X-ray constrained wavefunction method can be revisited if the stationary condition of the Jayatilaka functional with respect to the auxiliary variable is introduced [7]. In fact, following a reasoning analogous to the one used in constrained Density Functional Theory [8, 9], regains its original meaning of Lagrange multiplier and it is possible to prove that the correct value of is always a maximum stationary point of the functional to optimize. Based on this finding, we will propose a reformulation of the XCW method that will be intrinsically more physically meaningful since it will enable to straightforwardly evaluate the highest level of confidence with which the experimental X-ray diffraction data can be reproduced. Finally, the new variant of the XCW technique will allow to better distinguish between “X-ray constrained” and “X-ray restrained” wavefunctions.

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