A Quantum Crystallography journey to Phase-Space

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It is often considered that the birth of quantum chemistry coincides with that of the Schrödinger equation in 1925-1926[1]. This possibility of predicting the wavefunction paved the way to calculating the quantum expectation value of a range of measurable properties in atoms, molecules, and crystals. Nevertheless, it quickly became apparent that an N electron wavefunction often contained more information than necessary and yet was insufficient.

No more than two years after Schrödinger's discovery, von Neuman [2] and Landau [3] were already exploring an alternative approach to quantum physics using an object which could account for a statistical mixture of quantum states. They proposed consideration of the density matrix. Progressively, it appeared that the complexity of the wavefunctions and the associated density matrix could be reduced, which would still allow for the full quantum description needed to predict the properties of the system. The reduced density matrix (RDM) can be seen as an intermediate between the electron density and the set of N-electron wavefunctions. Almost simultaneously, other scientists were concerned about abandoning the phase space, which had been the natural ground of classical statistical physics. Eugene Wigner [4] was one of those physicists, and in 1932, he introduced a phase-space approach to quantum physics using what is now called the Wigner quasi-probability distribution. These alternative descriptions to Schrödinger's theory have long been shown to bear the same physical content and provide identical predictions. However, depending on the purpose, one can only acknowledge that one approach is sometimes more suitable.

While the computation of electron wavefunctions has become increasingly accurate, the experimental side of the exploration has also met with tremendous success. Indeed, Quantum Crystallography is a rapidly developing field of research where electron behaviour is observed in its finest details by using the strong complementarity of computational chemistry methods and experimental techniques developed mainly by the crystallography community.

Because of its obvious connection to X-ray diffraction (XRD), electron density is still at the focal point of Quantum Crystallography. In this respect, other techniques, such as polarized neutron diffraction or electron convergent beam diffraction, have often been considered as a happy supplement to refine our knowledge of XRD-based electron density [5]. From another perspective, Jayatilaka

[6] put forward a powerful extension of electron distribution refinement by judiciously combining ab initio computation and XRD fitting. It was an important milestone as it provided the community with a tool for extracting a pure-state wavefunction from X-ray diffraction data.

However, the ideas promoted by von Neumann, Landau and Wigner have persisted. Clinton, Massa and coworkers [7] have developed a strategy to extract a density matrix from a set of X-ray structure factors. Adopting a radically different philosophy, pioneering works conducted by Schmider, W. Weyrich and coworkers demonstrated that the rich information content carried by density matrices and Wigner functions was within reach if one also dared to explore the momentum part of the phase space. From the experimental perspective, this implies considering measurements obtained from different techniques. It necessitates gathering data from coherent-elastic and incoherent-inelastic scattering of X-ray photons and combining them through a common model.

This talk will retrace electrons' conquest of phase space, showing how experiments can mutually benefit from their complementarity and what it takes to reach an experimental description of electrons beyond the position representation.

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