

Pushing crystallography's frontiers through quantum mechanics

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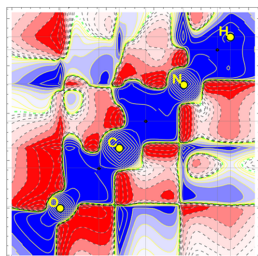
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1. Bridging the classical and quantum worlds in crystallography

Crystallography has long been a tool for understanding the structure of matter at the atomic level, rooted in classical physics concepts (*e.g.* diffraction and interference of waves by atomic planes of spheres) (Buerger, 1942; Rhodes, 2006; Sands, 1975; Stout & Jensen, 1989). Quantum mechanics does not typically play a direct role in data collection, data manipulation, and data processing. Perhaps the only indirect role of quantum mechanics at this stage is to compute the electron densities of spherical atoms in their ground state to generate the pseudoatomic density used to provide the first guess for the refinement cycles. This treatment yields good geometries and electron density maps. For more accurate work, especially for electron density analyzes such as those based on the Quantum Theory of Atoms in Molecules (QTAIM) (Bader, 1990), the refinement can be performed using a non-spherical (aspherical) multipolar representation of the atomic densities which yields accurate electron densities in bonding regions. A new frontier, initiated by Clinton and Massa more than five decades ago (Clinton *et al.*, 1973; Massa & Clinton, 1972) is now a booming emerging field termed Quantum Crystallography (QCr) (Genoni *et al.*, 2018; Gillet, 2023; Gillet & Macchi, 2021; Jayatilaka, 1998; Jayatilaka & Grimwood, 2001; Grimwood & Jayatilaka, 2001; Launay & Gillet, 2021; Macchi, 2022), a term coined in a landmark paper by Massa, Huang and Karle in 1995 (Massa *et al.*, 1995; Huang *et al.*, 1999; Huang *et al.*, 2010; Matta *et al.*, 2023), which seeks to extend the quantum mechanical description of matter into the realm of crystallographic techniques. The work of Yu and Gillet, published in this issue of *Acta Crystallographica Section B* (Yu & Gillet, 2025), represents a significant stride in this direction. This important contribution demonstrates how quantum-mechanical phase-space description of electron distributions, once considered a purely theoretical concept, can now be recovered from a combination of experimental scattering data.



2. Quantum crystallography: a paradigm shift

The fundamental challenge in quantum chemistry and condensed matter physics has been the accurate description of electron distributions accounting, for example, for static and dynamic correlation. The many-electron wavefunction, while

the most complete representation, is of such complexity that makes it infeasible for large systems. As an alternative, quantum crystallography, in Yu & Gillet (2025), focuses on reduced representations such as the one-electron reduced density matrix (1-RDM) and the Wigner function, both of which encode essential quantum information beyond the electron density while remaining experimentally accessible. Yu and Gillet's work highlights how a combination of high-resolution X-ray diffraction and Compton scattering measurements can provide a complete phase-space description of electrons in a crystal (Yu & Gillet, 2025). This marks a departure from conventional crystallography by switching from electron densities described in position space only to embrace a quantum mechanical view that incorporates dynamical information by describing the electron distribution in both position and momentum spaces.

3. The role of phase-space representations

A key innovation is the retrieval of the Wigner function — a quasi-probability distribution that offers a full phase-space description of electrons (Yu & Gillet, 2025). Unlike the classical probability distributions used in conventional crystallography, the Wigner function can exhibit *negative values*, a hallmark of non-classical behavior. This negativity is a direct consequence of quantum interference effects and serves as a fingerprint of the quantum nature of electronic states. Yu & Gillet (2025) demonstrate the experimental feasibility of reconstructing the Wigner function using data from both X-ray diffraction (elastic) and Compton (inelastic) scattering. While the first provides information about the electron density in position space, Compton scattering supplies complementary data on the electronic momentum distributions. By drawing on the complementary information of these two techniques, the authors propose a more complete picture of 'electronic structure' in crystals, bridging the gap between theoretical quantum mechanics and experimental crystallography.

To showcase the power of this approach, Yu & Gillet (2025) applied their methodology to a test-case molecular crystal, namely, urea ($(\text{NH}_2)_2\text{C}=\text{O}$). Using a combination of X-ray structure factors and directional Compton profiles, they successfully reconstructed the 1-RDM and its corresponding Wigner function. Their results not only corroborate quantum chemical predictions but also highlight subtle quantum effects that classical approaches would overlook. (See Fig. 2 of their paper reproduced with permission here as Fig. 1.)

One striking observation is the role of electronic delocalization, which is elegantly captured in the off-diagonal elements of the 1-RDM. These elements reveal long-range electronic correlations that govern bonding interactions. The corresponding Wigner function [in Fig. 3 of Yu & Gillet (2025)] indicates that electrons in the vicinity of OCN nuclei exhibit the highest momenta reflecting Heisenberg's indeterminacy, reinforcing the notion that electrons do not simply 'orbit' nuclei but exhibit intricate quantum behavior dictated by their quantum nature.

4. Closing comments

The work of Yu and Gillet has taken us a step closer to a quantum mechanical description of crystals. As experimental techniques continue to advance, particularly with the advent of ultra-high-resolution X-ray and electron diffraction methods, the potential for the general field of quantum crystallography will only grow. The study of these authors has far-reaching implications. It provides a combined *experimental-theoretical* approach to elucidate electron correlation offering additional insights into the nature of chemical bonding in crystals. Enabling an experimental access to phase-space quantum mechanical representation could aid, eventually, in designing novel materials with tailored electronic properties (functional materials) such as organic semiconductors.

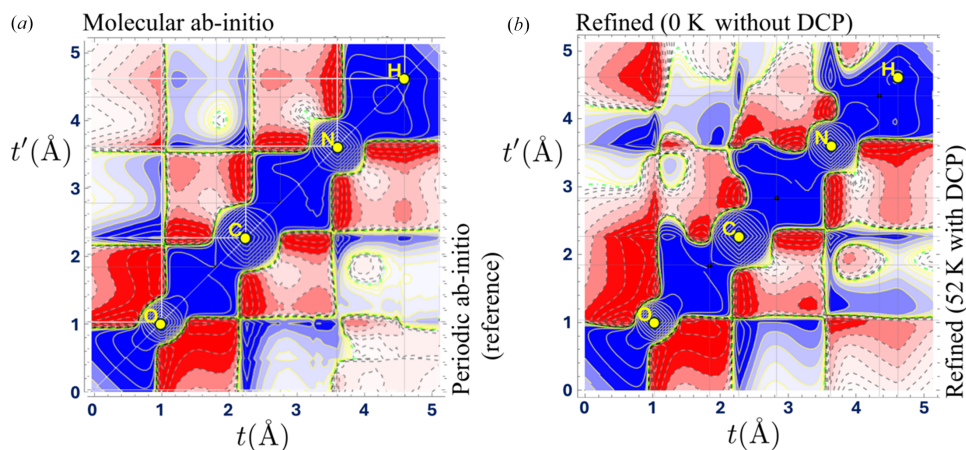


Figure 1
(a) Theoretical 1-RDM along the path $\text{O}=\text{C}-\text{N}-\text{H}$ within urea with the upper matrix representing the isolated molecule and the lower matrix showing periodic *ab initio* data. (b) The upper matrix depicts the 1-RDM refined using X-ray structure factors alone, determined at 0 K, whereas the lower matrix incorporates noisy directional Compton scattering data along with structure factors obtained at 52 K. Positive contours are solid in the blue regions while negative ones are dotted in red regions with step size = 0.01×2^n , $n = 0, 1, 2, \dots$

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