Insights into Atomic Bonding from Dynamical Multipole Refinement of Three-Dimensional Electron Diffraction Data

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Three-dimensional electron diffraction (3D ED) has emerged as a powerful tool for structural determination, particularly for nanocrystalline materials[1]. While recent advancements have improved the accuracy of structure refinements, the full potential of 3D ED for probing atomic interactions and charge transfer remains underutilized. Traditional refinement techniques rely on the Independent Atom Model (IAM), which assumes spherical atoms and neglects bonding effects—leading to chemically simplistic interpretations and potentially biased structural parameters[2].

In this study, we present an approach based on *dynamical multipole refinement*, which incorporates dynamical diffraction effects alongside an aspherical atomic model[3,4]. This method bridges the gap between experimental electron diffraction data and quantum crystallographic modeling, offering a more nuanced representation of electron density and bonding. We applied the technique across a diverse set of organic and inorganic crystals, encompassing variations in bonding character, symmetry, and atomic composition. The results demonstrate significant improvements in the accuracy of refined structural parameters—particularly for systems with light atoms—while providing chemically meaningful charge density information. These findings highlight the growing synergy between theoretical models and high-quality experimental data in advancing quantum crystallography through 3D ED.

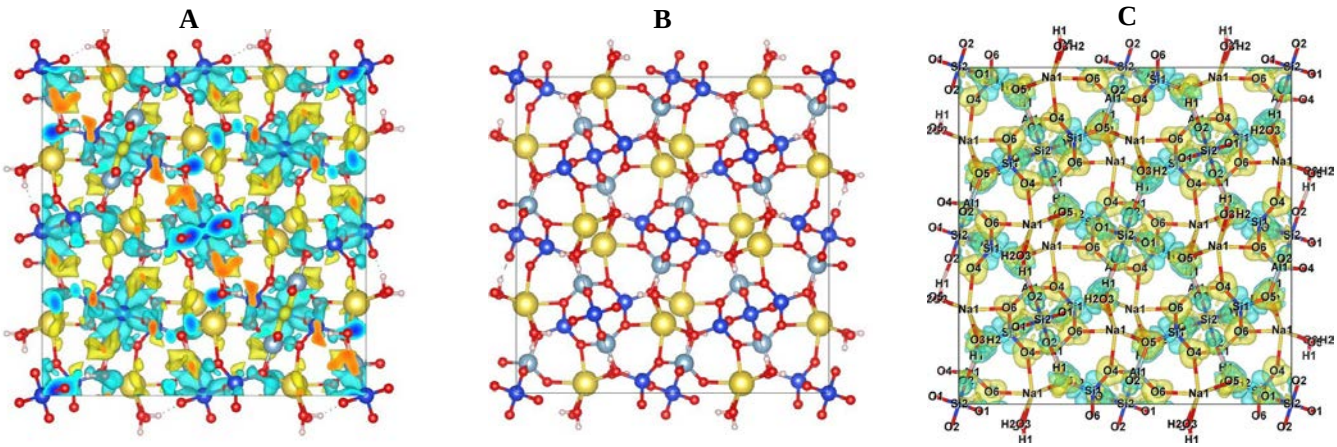

Figure 1. Evaluation of quality of refinements for natrolite ($Na_2Al_2Si_3O_{12}H_4$). The 3D difference fourier maps before (A) and after (B) charge density refinements plotted at the same isosurface value (0.18 e $Å^{-1}$). The static deformation map (C) of the molecule after the charge density refinement. Positive and negative isosurfaces are plotted in yellow and blue, respectively.

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