Novel quantum crystallography methods for modeling of pressure-and temperature effects in minerals with cation disorder

Przemyslaw Dera
Hawaii Institute of Geophysics and Planetology,
University of Hawaii at Manoa

Conventional crystallographic investigations primarily focus on determining the geometric arrangement of atoms within the crystal lattice. This involves ascertaining unit cell parameters, space group symmetry, and the precise positions of atoms within the crystal. It serves as a foundational technique for understanding the three-dimensional arrangement of mineral components, providing information about bond lengths, bond angles, and overall crystal symmetry. This approach is invaluable for identifying the mineral's crystal system and lattice parameters. Conventional crystallographic technique uses an approximation assuming spherical distribution of electron density around atoms (IAM, or independent atom model), which restricts the resulting information to the spatial arrangement of atoms without delving into the finer details of electron charge distribution. In contrast, charge density studies using X-ray and neutron diffraction data account for aspherical features of the electron distributions and seek to unravel the fine details of electron charge, including bonding electrons, lone electron pairs, etc. This level of detail is crucial for understanding chemical bonding, interatomic interactions, and subtle electronic effects that influence mineral properties.

Traditionally, mineralogical charge density investigations have centered exclusively around the analysis of end-member compositions, wherein minerals are considered to have an ideal crystalline structure with fixed chemical composition, devoid of cationic disorder. Experimental charge density analysis has also been applied to investigate high pressure phenomena in only a handful of cases. However, geological reality often presents us with minerals exhibiting complex solid solution substitutional disorders and nonlinear mixing effects and in geophysical and geodynamic modeling there is a strong need to address these solid solution effects on the electronic and thermodynamic level.

Advances in experimental techniques, computational methodologies, such as Hirshfeld Atom Refinement (HAR), and enhanced access to high-quality diffraction data have created opportunities to explore the intricate world of non-spherical electron density in earth forming minerals not only at ambient, but also at extreme conditions. This presentation will review the current state of the art in Quantum Crystallography, present some examples of studies utilizing the HAR approach to minerals with cation disorder and hydrogen atoms at ambient conditions as well as at high pressure and temperature, and will discuss future outlook and possible applications.