Structure Determination from X-ray Powder Diffraction (XRD)

Determining a crystal structure from X-ray powder diffraction data typically involves **two main steps**:

1. **Indexing the diffraction peaks** to define the unit cell parameters.
2. **Determining atomic positions** within the unit cell.

Several methods have been developed over the years to accomplish these tasks efficiently. Below we present the most commonly used techniques and their principles.

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1. Methods for Structure Determination

1.1 Peak Indexing

- **Dichotomy Algorithm:**
  One of the earliest and most widely used approaches for indexing powder diffraction peaks. This method searches for Miller indices (h, k, l) that satisfy the interplanar spacing for observed peaks.
  Reference: DOI: 10.1107/S0021889804014876

1.2 Unit Cell Refinement

- **Pawley Method (1981):**
  After peak indexing, the Pawley method refines the unit cell parameters by minimizing the squared difference between calculated and observed peak positions. It does not require knowledge of atomic positions.
  Reference: DOI: 10.1107/S0021889881009618

1.3 Determining Atomic Positions

- **Le Bail Method:**
  This method fits the observed diffraction intensities using least-squares minimization to extract structure factors without prior atomic coordinates.
  Reference: DOI: 10.1016/0025-5408(88)90019-0
- **Charge Flipping Method:**
  Uses Fourier transforms of the observed intensities to generate possible electron density maps, which can then be used to determine atomic

positions.
Reference: DOI: 10.1107/S0108767303027569

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2. Software for Structure Solution

Several software packages implement these methods to facilitate crystal structure determination:

- **EXPO:**
  Widely used for ab-initio structure solution. Implements the SAE indexing algorithm and advanced methods such as **COVMAP** for structure refinement.
  References: DOI: 10.1107/S002188981201953X, DOI: 10.1002/crat.201500024
- **GSAS:**
  Developed in Python, GSAS supports Pawley refinement and the charge flipping method to solve crystal structures from powder data.
  Reference: DOI: 10.1107/S0021889813003531