Conventional least-squares method in X-ray crystal structure analysis was improved to take the orthonormal relation among wavefunctions into account. d-orbital wavefunctions in a low symmetry crystal field were obtained with this method. It is convenient to express an atomic orbital (AO) in terms of complete orthonormal basis set

\[ \Psi_{i}(k|q) = \sum_{m} C_{m}^{i}(k|q) \Phi_{m}(k|q), \]

where \( C_{m}^{i}(k|q) \) is a row matrix and \( \Phi_{m}(k|q) \) is a column matrix. \( C_{m}^{i}(q) \) allows AO to expand or contract in the crystal. Orthorormality of the AO's is expressed by

\[ C_{m}^{i}(k|q)^{T} C_{m}^{i}(k|q) = \delta_{m}, \]

where I is the unit matrix. By employing Lagrange's method of undetermined multiplier the present problem reduces to a minimization of

\[ S = V_{1} - V_{2}, \]

where

\[ V_{1} = \sum_{i} \sum_{k} \sum_{q} |\Psi_{i}(k|q)|^{2} R_{i}(k|q), \]

\[ V_{2} = \sum_{i} \sum_{k} \sum_{q} |\Psi_{i}(k|q)|^{2} \delta_{m}, \]

\[ \delta_{m} = \sum_{n} C_{n}^{m}(k|q)^{T} R_{n}(k|q). \]

\( V \) is a matrix of residuals of observed and calculated structure factors, i.e., \( |F_{o}| \times |F_{c}| \). Notation of \( F_{o} \) and \( X_{i} \) is the same as those given by Hamilton. Following usual procedure and using the orthonormality, the normal equation is obtained

\[ (1-R)(\delta_{m}) = \sum_{i} C_{m}^{i}(k|q)^{T} R_{i}(k|q), \]

where R is the matrix with elements expressed only by the coefficients in (11). Reorthogonalization after each cycle of refinement is carried out using Löwdin's method.

d-wavefunctions in a crystal field are usually expanded by the real basic functions \( \Phi_{m+1}(q) \) as

\[ \Psi_{i}(k|q) = \sum_{m} C_{m}^{i}(k|q) \Phi_{m+1}(k|q), \]

Scattering factors of metal atoms are thus given by

\[ C_{m}^{i}(k|q) = \sum_{m} C_{m}^{i}(k|q) \Phi_{m+1}(k|q), \]

where \( C_{m}^{i}(q) \) is the electron density on the i-th AO and \( \Phi_{m}(k|q) \) is the parametric to be determined.

The present method was applied to CuX on the center of symmetry in crystals of Cu(TII) (dicyclic cinnamate) (NO)\(_{2}\) (Space group: \( P2_{1}/c \)). Cu displays a square planar coordination geometry with Cu-N = 2.19 A. Cu-N = 2.034 (1) A and Zn-Cu-N = 85.98 (5)\(^{\circ}\). The deformation density shows four negative peaks around Cu\(^{2+}\) representing the hole d-orbitals.

After the refinement with the present method these peaks were deleted and a factor was reduced from 0.031 to 0.0296. Obtained wavefunctions are listed below.

The largest peaks along the direction perpendicular to the coordination plane were reduced to an insignificant level after successive analysis of \( \Psi_{i}(k|q) \) and anharmonic thermal vibration. Contour interval 0.05 e\(^{\text{A}}^{-2}\).

The present method enables us to analyze charge density on the basis of wavefunctions. It is also applicable to a molecular orbital model provided two-center scattering factors are calculated.

Table: d-orbital wave functions. \( \kappa \) values of \( \Psi_{i}(k|q) \) are greater than 1.0, those of the others less than 0.1.