

06.2-13 X-RAY ANALYSIS OF WAVEFUNCTIONS BY THE LEAST-SQUARES METHOD INCORPORATING ORTHONORMALITY. By K. Tanaka and F. Marumo, Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta 4259, Midori, Yokohama 227, Japan.

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

$$\Psi_i(\kappa, q) = C_{ij}^{-1} \phi_j(\kappa, q), \quad (1)$$

where C_{ij} is a row matrix and ϕ is a column matrix. κ_i allows AO to expand or contract in the crystal. Orthonormality of the AO's is expressed by $C_i^{-1} C_i = \delta_{ij}$. By employing Lagrange's method of undetermined multiplier the present problem reduces to a minimization of

$$S = V^T M_F^{-1} V - \sum_i \lambda_i (C_i^{-1} \delta C_i + \delta C_i^{-1} C_i).$$

V is a matrix of residuals of observed and calculated structure factors, i.e. $V = F - AX$. Notation of F, A, X, M_F is the same as those given by Hamilton¹. Following usual procedure and using the orthonormality, the normal equation is obtained,

$$(I - R)(A^T M_F^{-1} AX - A^T M_F^{-1} F) = 0,$$

where I is the unit matrix and R is the matrix with elements expressed only by the coefficients in (1). 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 ϕ_m ($m=1$ to 5) as

$$\Psi_i(\kappa, q) = \sum_m C_{im} \phi_m(\kappa, q).$$

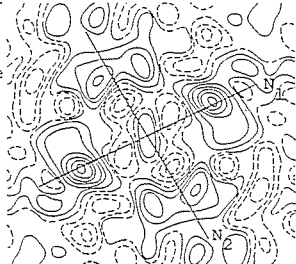
Scattering factors of metal atoms are thus given by

$$f_i(\vec{S}) = f_{i,core}(\vec{S}) + \sum_m C_{im} C_{im}^{-1} f_{mm}(\vec{S}/\kappa_i),$$

where n_i ($0 \leq n_i \leq 2$) is the electron population on the i-th AO and n_i , C_{im} , κ_i are parameters to be determined. The present method was applied to Cu^{2+} on the center of symmetry in crystals of $Cu(II)$ (diazacyclooctane)₂(NO₃)₂ (Space group; P2₁/n, a=7.9040(7)Å, b=15.694(1)Å, c=7.0886(7)Å, $\beta=95.36(1)^\circ$). Cu^{2+} displays a square planer coordination geometry with Cu-N₄=1.997(1)Å, Cu-N₁=2.034(1)Å and $\angle N_1-Cu-N_2=85.98(5)^\circ$. 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 R factor was reduced from 0.0311 to 0.0296. Obtained wavefunctions are listed below.

The large peaks along the direction perpendicular to the coordination plane were reduced to an insignificant level after successive analysis of κ_i 's and



Deformation density on the coordination plane.

anharmonic thermal vibration. Contour interval $0.05e^{-3}$. 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.

ϕ_i	n_i	$d_{x^2-y^2}$	d_{z^2}	d_{yz}	d_{zx}	d_{xy}
Ψ_1	1.38(6)	0.726(5)	0.25(2)	-0.00(2)	0.42(1)	-0.48(3)
Ψ_2	1.62(6)	-0.54(2)	0.106(9)	-0.188(6)	-0.07(2)	-0.81(2)
Ψ_3	2.0	0.31(2)	-0.302(6)	-0.813(1)	-0.39(2)	-0.02(2)
Ψ_4	2.0	-0.08(2)	-0.848(1)	0.046(7)	0.510(1)	-0.113(2)
Ψ_5	2.0	0.28(1)	-0.343(4)	0.550(2)	-0.637(1)	-0.306(1)

Table. d-orbital wave functions. κ values of Ψ_1, Ψ_2 are greater than 1.0, those of the others less than 0.1.

1. Hamilton, W. C. (1964). Statistics in Physical Science: Ronald Press.

06.2-14 MOLECULAR ELECTRON DENSITIES DISTRIBUTION FROM HIGH-ENERGY ELECTRON SCATTERING BY GASES. By S. Shibata, F. Hirota and K. Tachikawa, Department of Chemistry, Shizuoka University, Japan

Elastic electron scattering by gases involves information on electron density distribution in the molecules. The experimental scattering intensities were compared with those calculated in the Born approximation using electron densities from ab initio molecular orbitals. The elastic scattering cross sections for 30 keV electrons have been measured on the target gases of hydrocarbons such as methane, ethane, propane, cyclopropane, cyclobutane, cyclohexane, ethylene, acetylene and benzene in a small angle range up to $s = 12$ by means of the unit providing a retarding field energy filter and a scintillator and photo-counting system. The Hartree-Fock self-consistent field molecular orbitals were obtained using single-zeta, double-zeta, double-zeta plus polarization basis sets. The scattering intensities were very sensitive to the quality of the wavefunctions and therefore the validity of the electron density was tested. The information on the electron densities of these molecules will be discussed in comparison with the results from the crystal studies.

S. Shibata, F. Hirota, N. Kakuta and T. Muramatsu, Intern. J. Quant. Chem., XVIII, 281 (1980)