06.2-13   X-RAY ANALYSIS OF WAVEFUNCTIONS BY THE
LEAST-SQUARES METHOD INCORPORATING ORTHONORMALITY.
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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
$$\Psi_i(\kappa_i q) = C_i'\Phi(\kappa_i q), \qquad (1)$$
where C_i' 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 $C_i'C_j = \delta_{ij}$.
By employing Lagrange's method of undetermined multiplier
the present problem reduces to a minimization of
$$S = V'M_f^{-1}V - \Sigma\Sigma\varepsilon_{ij}(C_i'\delta C_j + \delta C_i'C_j).$$
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 Hamilton[1]. Following
usual procedure and using the orthonormality, the normal
equation is obtained,
$$(I-R)(A'M_f^{-1}AX - A'M_f^{-1}F) = 0,$$
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
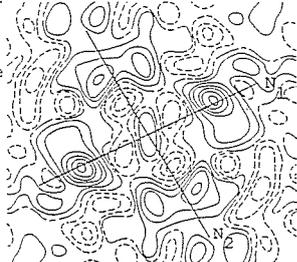$$\Psi_i(\kappa_i q) = \Sigma C_{im}\Phi_m(\kappa_i q).$$
Scattering factors of metal atoms are thus given by
$$f_M(\vec{S}) = f_{M,core}(\vec{S}) + \Sigma\Sigma\Sigma n_i C_{im}C_{im'}f_{mm'}(\vec{S}/\kappa_i),$$
where n_i ($0 \leq n_i \leq 2$) is the electron population on the i-th
AO and n_i, C_{im}, 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)$_2$(NO$_3$)$_2$
(Space group; P2$_1$/n, a=7.9040(7)Å, b=15.694(1)Å,
c=7.0886(7)Å, β=95.36(1)°). Cu^{2+} displays a square
planer coordination geometry with Cu-N$_1$=1.997(1)Å,
Cu-N$_2$=2.034(1)Å and $\angle$N$_1$-Cu-N$_2$=85.98(5)°. The deformation
density shows four negative
peaks around Cu^{2+} represent-
ing 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 wavefunc-
tions are listed below.
The large peaks along the
direction perpendicular to
the coordination plane were
reduced to an insignificant
level after successive   Deformation density on the
analysis of κ_i's and   coordination plane.
anharmonic thermal vibration. Contour interval 0.05eÅ^{-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
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Elastic electron scattering by gases involves
information on electron density distribution
in the molecules. The experimental scattering
intensities were compared with those calculat-
ed 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 molecu-
lar 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 wave-
functions and therefore the validity of the
electron density was tested.
The information on the electron densities of
these molecules will be discussed in   com-
parison with the results from the crystal
studies.

S.Shibata, F.Hirota, N.Kakuta and T.Muramatsu,
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