

because the author forgot to mention whether or not the symmetry centre is at the origin of the unit cell.

We thank Professor Theo Hahn (Aachen, Federal Republic of Germany) for useful comments, Professor H. Wondratschek (Karlsruhe, Federal Republic of Germany) for pointing out ambiguities in two space groups which we overlooked and Dr M. Penzo for the calculation of the interatomic distances in the examples and a comparison of the two editions of *International Tables*. This study was supported by the Swiss National Science Foundation under contract 2.857-0.88.

Acta Cryst. (1988). **A44**, 1002-1008

X-ray Analysis of Wavefunctions by the Least-Squares Method Incorporating Orthonormality. I. General Formalism

BY KIYOAKI TANAKA

Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 227, Japan

(Received 9 December 1987; accepted 17 May 1988)

Abstract

The least-squares method incorporating the orthonormal relation between wavefunctions is formulated. The method fulfils the idempotency condition and allows the representation of wavefunctions to be obtained from charge-density distributions measured by the X-ray diffraction method. The present method can be applied to both the atomic-orbital (AO) and the molecular-orbital (MO) models. The scattering-factor formalisms are also described for both models. One of the most important applications of the present method to the AO models is the determination of the d wavefunctions in a general crystal field. The restrictions among the coefficients of d wavefunctions in the 32 point-group-symmetry fields are derived. The effect of expansion and contraction of electron clouds in crystal fields is highly important, since it allows the possibility of determining all the unknown d wavefunctions. Even the wavefunctions of atoms with spherical electron configuration like Zn^{2+} and high-spin Mn^{2+} ions can be determined when this effect is significant. From the scattering factors of two-center terms, the temperature factors for these terms are derived.

Introduction

Charge-density distribution has been extensively studied with diffraction methods in the last two decades. Charge densities obtained in various molecular, ionic and metallic crystals revealed

References

- BEZNOŠIKOVA, A. V., CHEBOTAREV, N. T., LUK'YANOV, A. S., CHERNYI, A. V. & SMIRNOVA, E. A. (1975). *Sov. At. Energy*, **37**, 842-846.
- EISENMANN, B., JAKOWSKI, M. & SCHÄFER, H. (1982). *Rev. Chim. Miner.* **19**, 263-273.
- International Tables for Crystallography* (1983). Vol. A, edited by TH. HAHN. Dordrecht: Reidel. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- International Tables for X-ray Crystallography* (1952). Vol. I, edited by N. F. M. HENRY & K. LONSDALE. Birmingham: Kynoch Press.
- PACCARD, D., LEROY, J. & MOREAU, J. M. (1979). *Acta Cryst.* **B35**, 1315-1319.

features of bondings. Quantitative analysis of the measured charge-density distributions was carried out with electron-population analysis (Stewart, 1969; Coppens, Willoughby & Csonka, 1971) and with the method of multipole refinement (Kurki-Suonio, 1968; Hirshfeld, 1971; Stewart, 1972; Hansen & Coppens, 1978). Multipole refinements showed remarkable success in representing charge-density distribution in crystals by analytical functions, and various electrical physical quantities such as electric moments were calculated from them. However, these methods failed to give more fundamental quantities such as first-order density matrices and the representation of wavefunctions. This is because of the lack of conditions imposed by the antisymmetric property of wavefunctions.

Assume that M electrons occupy M molecular spin orbitals (MO's) ψ_i and that each MO is represented in terms of a linear combination of N basic functions, $\varphi_n(\mathbf{r})$, which are normalized and orthogonalized, as follows,

$$\psi_i(\mathbf{r}) = \mathbf{c}'_i \boldsymbol{\varphi}(\mathbf{r}), \quad (i = 1, 2, \dots, M) \quad (1)$$

or

$$\boldsymbol{\Psi}(\mathbf{r}) = C \boldsymbol{\varphi}(\mathbf{r}),$$

where $C = \{c_{in}\}$ consists of M orthonormal rows \mathbf{c}'_i . $\boldsymbol{\Psi} = \{\psi_i\}$ and $\boldsymbol{\varphi} = \{\varphi_n\}$ are $M \times 1$ and $N \times 1$ matrices, respectively. A prime means a row vector or a transposed matrix in the following discussion. M is the number of MO's to be determined and is not more

than N . $\varphi_n(\mathbf{r})$ is an atomic orbital or a linear combination of atomic orbitals. In the Hartree-Fock scheme the necessary and sufficient condition for reducing the total wavefunction to a single Slater determinant is expressed by the two equations (Löwdin, 1955):

$$P^2 = P, \quad (2)$$

$$\text{tr}(P) = M, \quad (3)$$

where tr means the diagonal sum and P is a first-order density matrix defined as

$$P = C^\dagger C. \quad (4)$$

The $N \times N$ matrix P is a Hermitian matrix and from (2) P is an idempotent matrix. McWeeny (1960) gave the iterative equation

$$P_{k+1} = 3P_k^2 - 2P_k^3 = P_k \quad (5)$$

for the purpose of calculating an idempotent matrix from a nearly idempotent one. Clinton, Galli & Massa (1969) proposed iterative equations by imposing the physically important constraints of (5) in addition to that in (3). The X-ray structure-factor constraint was introduced by Clinton, Frishberg, Massa & Oldfield (1973) to obtain a first-order density matrix from the experimental charge density. Tsirel'son, Mestechkin & Ozerov (1977) introduced the idempotency property (2) in the minimization of the functional

$$Q = (1/V_c) \sum |F_{\text{obs}}(\mathbf{S}) - F_{\text{calc}}(\mathbf{S})|^2, \quad (6)$$

where F_{obs} and F_{calc} are observed and calculated structure factors and V_c is the volume of the unit cell. \mathbf{S} is the scattering vector defined as $|\mathbf{S}| = (\sin \theta)/\lambda$.

If the system is described on the basis of wavefunctions instead of density matrices, the orthonormal condition between the wavefunctions, which is equivalent to the condition (2) (McWeeny, 1960), should be considered. The conventional least-squares method does not incorporate the condition (2) as pointed out by Frishberg & Massa (1982). The present method introduces the constraint of orthonormality into the conventional least-squares method. By adding the constraint (3), which can be easily done even in the conventional least-squares program, the least-squares method of the present study ensures the Hartree-Fock representability. Therefore the present method leads to the direct determination of the representation of wavefunctions by the X-ray diffraction method. It is to be noted, however, that the assumption of the strict validity of the Hartree-Fock approximation or a single-Slater-determinant assumption is a serious limitation for many transition-metal complexes and the extension of the present method to one which incorporates the method of configuration interaction will be necessary.

The charge-density distributions of transition metals in the O_h crystal fields were analyzed using the well defined orthonormal wavefunctions by the

crystal field theory (Kijima, Tanaka & Marumo, 1982, 1983; Miyata, Tanaka & Marumo, 1983). The shift of one electron from the $d\gamma$ orbital to the $d\epsilon$ orbital, that is, the transition from the high-spin state to the low-spin state in KCoF_3 crystals, for example, causes so enormous a change in the deformation density maps that the Co^{2+} ion was shown definitely to be in the high-spin state. The charge-density distribution in Jahn-Teller-distorted KCuF_3 crystals was measured and the 3D wavefunction of Cu^{2+} ions was determined, keeping the orthonormal relation between the E_g orbitals (Tanaka, Konishi & Marumo, 1979). The wavefunction of the ds hybridized orbital of the Cu^+ ion in CuAlO_2 crystals was also determined in the same way (Ishiguro, Ishizawa, Mizutani, Kato, Tanaka & Marumo, 1983). The method proposed in the present study was applied to the wavefunction analysis of the Cu^{2+} ion in $[\text{Cu}(\text{diazacyclooctane})_2](\text{NO}_3)_2$. The 3D wavefunction in a crystal field C_1 was obtained by optimizing the charge-density distribution. This will be published in a subsequent paper (Tanaka & Marumo, 1988).

Formalism of the least-squares method incorporating orthonormality

A conventional least-squares method in X-ray crystallography was improved to obtain the representation of wavefunctions by taking the orthonormal relation between wavefunctions into account. The orthonormal condition is expressed by

$$\sum_m \sum_n c_{im}^* c_{jn} \int \varphi_m^* \varphi_n \mathbf{dr} = \delta_{ij}, \quad (7)$$

where $\int \varphi_m^* \varphi_n \mathbf{dr} \equiv s_{mn}$ is an overlap integral of φ_m and φ_n . δ_{ij} equals 1 if $i = j$ and 0 otherwise. Equation (7) is expressed by matrices C, S, I as

$$CSC^\dagger = I \quad (8)$$

where $S = \{s_{mn}\}$ is an $N \times N$ matrix. Idempotency condition (2) still holds in this case (see Appendix).

In the subsequent discussion, real wavefunctions ψ_i and φ_m are assumed and c_{im} are taken as real. The present formulation can easily be extended to that for complex values. By employing Lagrange's unknown multiplier method, the value Q to be minimized in the least-squares method reduces to

$$Q = \mathbf{v}' M_f^{-1} \mathbf{v} - \sum_{i=j}^M \sum_{i=j}^M \lambda_{ij} \left(\sum_m \sum_n c_{im} c_{jn} s_{mn} - \delta_{ij} \right), \quad (9)$$

where

$$\mathbf{v} = \mathbf{f} - \mathbf{A}\mathbf{x}, \quad (10a)$$

$$\mathbf{f} = \{F_{\text{obs}}^i - F_{\text{calc}}^i\}, \quad (10b)$$

$$\mathbf{A} = \{a_{ij}\} = \{\partial F_{\text{calc}}^i / \partial x_j\}, \quad (10c)$$

$$\mathbf{x} = \{x_j - x_j^0\} = \{\Delta x_j\}, \quad (10d)$$

and M_f is a variance-covariance matrix. A is a design matrix. F_{obs}^i and F_{calc}^i are observed and calculated structure factors, respectively. \mathbf{x} is a $P \times 1$ matrix of the shifts of P unknown parameters to be determined in the least-squares method. All the notations are the same as those given by Hamilton (1964) except those of vectors, which are written in bold lower-case letters. The second term is linearized by expanding c_{im} by the small shift Δc_{im} ,

$$c_{im} = c_{im}^0 + \Delta c_{im}. \quad (11)$$

Putting this into (9) and ignoring the terms higher than second order, we have

$$Q = \mathbf{v}' M_f^{-1} \mathbf{v} - \sum_{i \leq j}^M \sum_{m}^M \lambda_{ij} \sum_{n}^N \sum_{n}^N (\Delta c_{im} c_{jn}^0 + c_{im}^0 \Delta c_{jn}) s_{imn}. \quad (12)$$

By differentiating with respect to Δx_j and putting $\lambda'_{ij} = \lambda'_{ji} = (1 + \delta_{ij}) \lambda_{ij} / 2$, we obtain

$$\begin{aligned} \delta Q &= 2\delta \mathbf{x}' (A' M_f^{-1} A \mathbf{x} - A' M_f^{-1} \mathbf{f}) \\ &\quad - 2 \sum_i^M \sum_j^M \lambda'_{ij} \sum_m^N \sum_n^N \delta(\Delta c_{im}) c_{jn}^0 s_{imn} \\ &= 0. \end{aligned} \quad (13)$$

The first term is obtained following the usual procedure. In the following discussion we put

$$\mathbf{b} = A' M_f^{-1} A \mathbf{x} - A' M_f^{-1} \mathbf{f}. \quad (14)$$

For simplicity, MN small shifts Δc_{im} are placed at the bottom of \mathbf{x} , and the superscript of c_{im}^0 and the prime of λ'_{ij} are omitted in the following discussion. The second term in (13) is further rewritten since $s_{mn} = s_{nm}$,

$$\begin{aligned} &\sum_i^M \sum_j^M \lambda_{ij} \sum_m^N \sum_n^N \delta(\Delta c_{im}) c_{jn} s_{imn} \\ &= \sum_i^M \sum_m^N \delta(\Delta c_{im}) (\Lambda CS)_{im} \\ &= [\delta(\Delta c_1)', \delta(\Delta c_2)', \dots, \delta(\Delta c_M)'] \mathbf{m} \\ &= \delta \mathbf{x}' \mathbf{n}, \end{aligned} \quad (15)$$

where $A = \{\lambda_{ij}\}$ is an $M \times M$ matrix and \mathbf{m}' is a $1 \times MN$ matrix with the form

$$\mathbf{m}' = (\mathbf{n}'_1, \mathbf{n}'_2, \dots, \mathbf{n}'_M). \quad (16)$$

Each \mathbf{n}'_i is a $1 \times N$ matrix defined as

$$\begin{aligned} \mathbf{n}'_i &= [(\Lambda CS)_{i1}, (\Lambda CS)_{i2}, \dots, (\Lambda CS)_{iN}] \\ &= \lambda'_i CS. \end{aligned} \quad (17)$$

\mathbf{n}' is an augmented $1 \times P$ matrix made by adding $P - MN$ zero elements to the top of \mathbf{m}' ,

$$\mathbf{n}' = (\mathbf{o}'_{P-MN}, \mathbf{n}'_1, \mathbf{n}'_2, \dots, \mathbf{n}'_M), \quad (18)$$

where \mathbf{o}'_i is a $1 \times I$ zero matrix. From (13) and (15),

the next equation,

$$\mathbf{b} = \mathbf{n}, \quad (19)$$

is obtained.

In order to calculate λ_i , we define an operator \mathbf{v}'_{ij} , a $1 \times P$ matrix, as follows.

$$\mathbf{v}'_{ij} = (\mathbf{o}'_{P-MN+(i-1)N}, \mathbf{c}'_j, \mathbf{o}'_{MN-iN}). \quad (20)$$

\mathbf{v}'_{ij} operates only on \mathbf{n}_i if (19) is multiplied by it on the left as

$$\mathbf{v}'_{ij} \mathbf{b} = \mathbf{c}'_j \mathbf{n}_i = \mathbf{c}'_j SC' \lambda_i. \quad (21)$$

Then the operator N'_i , the $P \times M$ matrix, is further defined as

$$N'_i = (\mathbf{v}_{i1}, \mathbf{v}_{i2}, \dots, \mathbf{v}_{iM}). \quad (22)$$

Equation (19) is multiplied on the left by N_i and λ_i is obtained by using (17) and the orthonormal condition (8),

$$N_i \mathbf{b} = CSC' \lambda_i = \lambda_i. \quad (23)$$

To satisfy the condition $\lambda_{ij} = \lambda_{ji}$, we further put

$$\lambda_i = \frac{1}{2} M_i \mathbf{b}, \quad (24)$$

where M'_i is a $P \times M$ matrix defined as

$$M'_i = (\mathbf{v}_{i1} + \mathbf{v}_{1i}, \mathbf{v}_{i2} + \mathbf{v}_{2i}, \dots, \mathbf{v}_{iM} + \mathbf{v}_{Mi}). \quad (25)$$

Putting λ_i into (17), we get

$$\mathbf{n}_i = R_i \mathbf{b}, \quad (26)$$

where R_i is an $N \times P$ matrix and has the form

$$R_i = \frac{1}{2} SC' M_i. \quad (27)$$

From (19) and (26), the next equation is obtained:

$$\mathbf{b} = R \mathbf{b}, \quad (28)$$

where R' is a $P \times P$ matrix with elements

$$R' = (O_{P,P-MN}, R'_1, R'_2, \dots, R'_M), \quad (29)$$

where $O_{P,P-MN}$ is a $P \times (P - MN)$ zero matrix. The explicit form of the normal equation is obtained from (14) and (28) as

$$(I - R)(A' M_f^{-1} A \mathbf{x} - A' M_f^{-1} \mathbf{f}) = 0. \quad (30)$$

This is different from the normal equation of the least-squares method having no condition of orthonormality in the existence of R . Matrix $I - R$ acts as an ill-condition modifier of the matrix $A' M_f^{-1} A$, the inverse matrix of which cannot be calculated because of severe parameter interaction.

Error in \mathbf{x} is formulated in the following way. From (30), \mathbf{x} is evaluated as

$$\begin{aligned} \bar{\mathbf{x}} &= \{(I - R) A' M_f^{-1} A\}^{-1} (I - R) A' M_f^{-1} \mathbf{f} \\ &= C^{-1} D A' M_f^{-1} \mathbf{f} \end{aligned} \quad (31)$$

where

$$C = (I - R) A' M_f^{-1} A = D A' M_f^{-1} A, \quad (32a)$$

$$D = I - R. \quad (32b)$$

Then the variance-covariance matrix of \mathbf{x} is given by

$$\begin{aligned} M_x &= \varepsilon\{(\bar{\mathbf{x}} - \mathbf{x})(\bar{\mathbf{x}} - \mathbf{x})'\} \\ &= \varepsilon\{C^{-1}DA'M_f^{-1}(\mathbf{f} - \mathbf{f}^0)(\mathbf{f} - \mathbf{f}^0)'(C^{-1}DA'M_f^{-1})'\} \\ &= C^{-1}DA'M_f^{-1}\varepsilon\{(\mathbf{f} - \mathbf{f}^0)(\mathbf{f} - \mathbf{f}^0)'\}M_f^{-1}AD'C'^{-1}, \end{aligned} \quad (33)$$

where $\varepsilon\{A\}$ means an expected value of A . By definition

$$\varepsilon\{(\mathbf{f} - \mathbf{f}^0)(\mathbf{f} - \mathbf{f}^0)'\} = M_f. \quad (34)$$

Then M_x is finally obtained as

$$\begin{aligned} M_x &= C^{-1}DA'M_f^{-1}AD'C'^{-1} \\ &= D'C'^{-1}. \end{aligned} \quad (35)$$

Evaluation of the scattering expressions

1. The d wavefunctions in a general crystal field and their scattering factors

If overlap density is ignored, d wavefunctions in a crystal field are generally expressed in terms of five basis functions. In this case, the parameter κ which represents the expansion ($\kappa < 1$) and contraction ($\kappa > 1$) of electron clouds in crystals is introduced. By replacing MO in (1) with AO ψ_i , (1) is rewritten as

$$\psi_i(\kappa_i\mathbf{r}) = \sum_{m=1}^5 c_{im}\varphi_m(\kappa_i\mathbf{r}). \quad (36)$$

The values of κ_i of symmetrically equivalent AO's or degenerate AO's should be the same. The parameter κ was first introduced by Coppens, Guru Row, Leung, Stevens, Becker & Yang (1979). In the present study κ is assigned for each AO. The least-squares method described in the previous section needs a minor modification accompanying the introduction of κ . Since the normalization constant $\kappa^{3/2}$ is necessary for each $\varphi(\kappa\mathbf{r})$ and since the overlap density is ignored, the orthonormal condition (8) is modified to

$$(\kappa_i\kappa_j)^{3/2} \sum_m c_{im}c_{jm} = \delta_{ij}. \quad (37)$$

Therefore by rewriting $\kappa^{3/2}c_{im}$ as c_{im} and taking S as I , we can apply the procedure in the previous section to the d -wavefunction analysis.

d wavefunctions in higher point-group symmetries have no off-diagonal components of c_{im} and it is not necessary to determine the coefficients c_{im} . However, for the other symmetry fields, mixing of basic orbitals is permitted and the analysis of d wavefunctions or determination of the coefficients c_{im} becomes necessary. The relationship among coefficients c_{im} in crystal fields of various symmetries is listed in Table 1. Real wavefunctions of d_{yz} , d_{zx} , d_{xy} , $d_{x^2-y^2}$ and d_{z^2} orbitals are taken as the basic functions. d wavefunctions in $1, \bar{1}, 2, m, 2/m, 3, \bar{3}, 32, 3m$ and $\bar{3}m$ crystal fields as well as those in the other crystal fields can

now be determined by the present method. It was derived for the point-charge model described by Kamimura, Sugano & Tanabe (1969) by taking the crystal-field potential energy ν_c as a perturbation and by expanding it with spherical harmonics. The secular equation was also calculated for each point-group symmetry. The relationship among c_{im} 's in Table 1 was derived from the relationship among the components of the secular equation. The restrictions of the coefficients of multipoles for d electrons were derived by Holladay, Leung & Coppens (1983). The transformation of a set of degenerate orbitals by a unitary matrix U changes neither the charge density nor the energy levels, that is,

$$\rho(\mathbf{r}) = (U\psi)^\dagger(U\psi) = \psi^\dagger(U^\dagger U)\psi = \psi^\dagger\psi. \quad (38)$$

Therefore the other choice of restrictions of c_{im} 's is also possible for degenerate orbitals. The restrictions in Table 1 are the limiting case to fix the relations to representative ones.

The scattering factor f_i of an electron in the i th orbital is expressed as

$$\begin{aligned} f_i(\mathbf{S}/\kappa_i) &= \int \psi_i(\kappa_i\mathbf{r}) \exp(2\pi i\mathbf{S}\cdot\mathbf{r})\psi_i(\kappa_i\mathbf{r}) \, d\mathbf{r} \\ &= \sum_m \sum_n c_{im}c_{in}f_{mn}(\mathbf{S}/\kappa_i), \end{aligned} \quad (39)$$

where

$$f_{mn}(\mathbf{S}/\kappa_i) = \int \varphi_m(\kappa_i\mathbf{r}) \exp(2\pi i\mathbf{S}\cdot\mathbf{r})\varphi_n(\kappa_i\mathbf{r}) \, d\mathbf{r}. \quad (40)$$

$f_{mn}(\mathbf{S})$ is calculated after Weiss & Freeman (1959) and Iwata (1977). The explicit form of $f_{mn}(\mathbf{S})$ is listed in Table 2. The scattering factor of all the d electrons of the transition metal is therefore

$$\begin{aligned} f_{3d}(\mathbf{S}) &= \sum_{i=1}^5 p_i f_i(\mathbf{S}/\kappa_i) \\ &= \sum_i p_i \sum_m \sum_n c_{im}c_{in}f_{mn}, \end{aligned} \quad (41)$$

where p_i is the occupation number of electrons in the i th orbital. Since the X-ray diffraction method cannot differentiate between the up and down spin orbitals unless the exchange effect is so significant that the electron density is deformed by the effect, and since the total wavefunction is assumed to be represented by the single Slater determinant, p_i is assumed to take integer values between 0 and 2. If all the values of κ_i are the same, this is further rewritten using the property of the unitary matrix C as

$$f_{3d}(\mathbf{S}) = p \sum_m f_{mm} + \sum_i \sum_m \sum_n (p_i - p) c_{im}c_{in}f_{mn}, \quad (42)$$

where p is an arbitrary number. The first term comes from spherical charge distribution and the second one from aspherical distribution. Equation (42) shows the possibility of reducing the number of the

Table 1. Allowed values and the relationship of the coefficients c_{im}

For definition of c_{im} , see equation (36). Basic functions φ_1 to φ_5 are those of d_{yz} , d_{zx} , d_{xy} , $d_{x^2-y^2}$, d_{z^2} orbitals, respectively. Coefficients c_{im} of each AO are summarized in parentheses and degenerate AO's are listed in braces. The quantization axis z_q is taken first along the main axis and then x_q and y_q are taken along twofold axes or perpendicular to mirror planes.

Point group	Allowed values of c_{im}	Restrictions of c_{im}	Restrictions of κ_i
$\bar{1}$	All c_{im}		
2	$(c_{11}, c_{12}), (c_{21}, c_{22}),$ $(c_{33}, c_{34}, c_{35}), (c_{43}, c_{44}, c_{45}),$ (c_{53}, c_{54}, c_{55})		
m			
$2/m$			
222	$(c_{11}), (c_{22}), (c_{33}),$ $(c_{44}, c_{45}),$ (c_{54}, c_{55})	$c_{54} = c_{45}, c_{55} = -c_{44}$	
$mm2$			
mmm			
3	$\{(c_{11}, c_{13}, c_{14}), (c_{22}, c_{23}, c_{24}),$ $\{(c_{31}, c_{33}, c_{34}), (c_{42}, c_{43}, c_{44}),$ $(c_{55})\}$	$c_{22} = c_{11}, c_{23} = c_{14}, c_{24} = -c_{13}$ $c_{42} = c_{31}, c_{43} = c_{34}, c_{44} = -c_{33}$	$\kappa_1 = \kappa_2$ $\kappa_3 = \kappa_4$
$\bar{3}$			
$32(x_q)^*$	$\{(c_{11}, c_{13}), (c_{22}, c_{24}),$ $\{(c_{31}, c_{33}), (c_{42}, c_{44}),$ $(c_{55})\}$	$c_{22} = -c_{11}, c_{24} = c_{13}$ $c_{31} = c_{13}, c_{33} = -c_{11}, c_{42} = c_{13}, c_{44} = c_{11}$	$\kappa_1 = \kappa_2$ $\kappa_3 = \kappa_4$
$3m(x_q)^*$			
$\bar{3}m(x_q)^*$			
4	$\{(c_{11}), (c_{22}),$ $(c_{33}, c_{34}),$ $(c_{43}, c_{44}),$ $(c_{55})\}$	$c_{43} = c_{34}, c_{44} = -c_{33}$	$\kappa_1 = \kappa_2$
$\bar{4}$			
$4/m$			
422	$\{(c_{11}), (c_{22}),$ $(c_{33}), (c_{44}),$ $(c_{55})\}$		$\kappa_1 = \kappa_2$
$4mm$			
$\bar{4}2m$			
$4/mmm$			
6	$\{(c_{11}), (c_{22}),$ $\{(c_{33}), (c_{44}),$ $(c_{55})\}$		$\kappa_1 = \kappa_2$ $\kappa_3 = \kappa_4$
$\bar{6}$			
$6/m$			
622			
$6mm$			
$\bar{6}m2$			
$6/mmm$			
23	$\{(c_{11}), (c_{22}), (c_{33}),$ $\{(c_{44}), (c_{55})\}$		$\kappa_1 = \kappa_2 = \kappa_3$ $\kappa_4 = \kappa_5$
$m\bar{3}$			
432			
$\bar{4}3m$			
$m\bar{3}m$			

* The twofold axis or the mirror is parallel or perpendicular to quantization axis x_q .

Table 2. Basic scattering factors for d electrons

f_{mn} is expressed by the polar coordinates (β, γ) of the scattering vector on the orthogonal quantum axis system,

$$f_{mn} = \langle j_0 \rangle + \{A_0(2 \cos^2 \beta - \sin^2 \beta) + A_1 \sin \beta \cos \beta + A_2 \sin^2 \beta\} \langle j_2 \rangle \\ + \{B_0(35 \cos^4 \beta - 30 \cos^2 \beta + 3) + B_1 \sin \beta \cos \beta (7 \cos^2 \beta - 3) + B_2 \sin^2 \beta (7 \cos^2 \beta - 1) \\ + B_3 \sin^3 \beta \cos \beta + B_4 \sin^4 \beta\} \langle j_4 \rangle.$$

c and s in the columns A_n and B_n represent $\cos(n\gamma)$ and $\sin(n\gamma)$, respectively.

f_{mn}	A_0	A_1	A_2	B_0	B_1	B_2	B_3	B_4
$f_{yz,yz}$	-5/14		15c/14	-3/14		-15c/14		
$f_{yz,zx}$			15s/14			-15s/14		
$f_{yz,xy}$		-15c/7			-15c/28		-15c/4	
f_{yz,x^2-y^2}		-15s/7			-15s/28		-15s/4	
f_{yz,z^2}		$75^{1/2}s/7$			$-675^{1/2}s/14$			
$f_{zx,zx}$	-5/14		-15c/14	-3/14		15c/14		
$f_{zx,xy}$		15s/7			15s/28		-15s/4	
f_{zx,x^2-y^2}		-15c/7			-15c/28		15c/4	
f_{zx,z^2}		$-75^{1/2}c/7$			$675^{1/2}c/14$			
$f_{xy,xy}$	5/7			3/56				-15c/8
f_{xy,x^2-y^2}								-15s/8
f_{xy,z^2}			$-75^{1/2}s/7$			$-675^{1/2}s/28$		
$f_{x^2-y^2,x^2-y^2}$	5/7			3/56				15c/8
$f_{x^2-y^2,z^2}$			$75^{1/2}c/7$			$675^{1/2}c/28$		
f_{z^2,z^2}	-5/7			9/28				

parameters to be determined. If for example we consider the Cu^{2+} ion (d^9) and if we can put $p_1 = 1$, $p = p_2 = p_3 = p_4 = p_5 = 2$, then (42) becomes

$$f_{3d}(\mathbf{S}) = 2 \sum_m f_{mm} - \sum_m \sum_n c_{1m} c_{1n} f_{mn}. \quad (43)$$

This means that only the coefficients of the hole orbital ψ_1 can be determined by X-ray diffraction. However, the values of κ_i are not the same unless the symmetry requires identical κ_i values or the orbitals are degenerate. Therefore (41) is to be used basically for the wavefunction analysis though the situation shown in (42) and (43) should be kept in mind. Naturally the orbitals which can be determined even if all the κ values are the same are expected to be determined more easily than the others. Re-orthogonalization of wavefunctions after each cycle of refinement was done using the Löwdin (1950) method in the present study, which treats all the orbitals with equal weight. The generalized method of orthogonalization by Kashiwagi & Sasaki (1973) which treats each orbital with proper weight can possibly be used for this case.

2. Scattering expression for molecular-orbital models

2.1. *Two-center scattering factors.* In MO models, basic functions φ_m in (1) are symmetry orbitals and may be conveniently expressed by a linear combination of atomic orbitals,

$$\varphi_m(\mathbf{r}) = \sum_j a_j(\mathbf{r}) \varphi_{mj}(\mathbf{r} - \mathbf{r}_j), \quad (44)$$

where \mathbf{r}_j is the atomic position of the j th atom. Hartree-Fock atomic orbitals expanded by Gaussian-type orbitals (GTO's) (see, for example, Huzinaga, 1984) may be employed for the following calculation:

$$\varphi_j(\mathbf{r}) = \sum_k b_{jk} \chi_{jk}(\alpha_k; \mathbf{r}), \quad (45)$$

where χ_{jk} is a GTO and the suffix m of φ_{mj} in (44) is dropped for the convenience of simplicity. Since the scattering factor for MO ψ_i is a Fourier transform of $\psi_i^* \psi_i$, it involves the Fourier transform of a product,

$$f_{jj'kk'}(\mathbf{S}) = \int_{-\infty}^{\infty} \chi_{jk}(\mathbf{r} - \mathbf{r}_j) \chi_{j'k'}(\mathbf{r} - \mathbf{r}_{j'}) \exp(2\pi i \mathbf{S} \cdot \mathbf{r}) d\mathbf{r}. \quad (46)$$

Two-center scattering factors $f_{jj'kk'}$ of second-row atoms were derived using GTO's by McWeeny (1953) and Stewart (1969). For a general case, the method of Taketa, Huzinaga & O-hata (1966) is used and we obtain

$$f_{jj'kk'}(\mathbf{S}) = N_{jk} N_{j'k'} G_1 G_2 \exp[2\pi i \mathbf{S} \cdot \mathbf{P}], \quad (47)$$

where N_{jk} and $N_{j'k'}$ are normalization constants of

χ_{jk} and $\chi_{j'k'}$, and

$$G_1 = \exp[-\alpha_k \alpha_{k'} (\overline{AB})^2 / \gamma] \\ \times \sum_{l=0}^{l_j+l_{j'}} \sum_{m=0}^{m_j+m_{j'}} \sum_{n=0}^{n_j+n_{j'}} f_l(l_j, l_{j'}, (\overline{AP})_x, (\overline{BP})_x) \\ \times f_m(m_j, m_{j'}, (\overline{AP})_y, (\overline{BP})_y) \\ \times f_n(n_j, n_{j'}, (\overline{AP})_z, (\overline{BP})_z) \quad (48a)$$

$$G_2 = \exp[-(2\pi S)^2 / 4\gamma] (\pi/\gamma)^{3/2} (i/2\gamma^{1/2})^{l+m+n} \\ \times H_l(\pi S_x / \gamma^{1/2}) H_m(\pi S_y / \gamma^{1/2}) H_n(\pi S_z / \gamma^{1/2}) \quad (48b)$$

where $\gamma = \alpha_k + \alpha_{k'}$. P is a point on the bond between j th and j' th atoms and is defined by

$$\overline{AP} = \alpha_{k'} \overline{AB} / (\alpha_k + \alpha_{k'}). \quad (49)$$

The relationships of these vectors are illustrated in Fig. 1. For the other notations readers should consult the paper by Taketa *et al.* (1966). It is to be noted that the term $\exp[2\pi i \mathbf{S} \cdot \mathbf{P}]$ in (47) is a phase factor for the product of χ_{jk} and $\chi_{j'k'}$.

2.2. *Temperature factors for two-center terms.* Since X-ray structure-factor formalism is based on the assumption of independent atoms in the crystal, the treatment of thermal smearing of the two-center terms has been a very serious problem. However, the temperature factor for the two-center terms can be derived approximately from the phase factor in (47). The point P vibrates as the atoms at the points A and B vibrate. Therefore the thermal smearing of the two-center term is introduced based on the assumptions: (a) that j and j' atoms vibrate independently, and (b) that the two-center term vibrates as the point P . The time average of the phase factor is calculated as

$$\langle \exp[2\pi i \mathbf{S} \cdot \mathbf{P}] \rangle = \langle \exp[2\pi i \mathbf{S} \cdot (\alpha_k \mathbf{r}_j + \alpha_{k'} \mathbf{r}_{j'}) / \gamma] \rangle \\ = \exp[2\pi i \mathbf{S} \cdot (\alpha_k \mathbf{r}_j^0 + \alpha_{k'} \mathbf{r}_{j'}^0) / \gamma] \\ \times T_j^{\alpha_k / \gamma} T_{j'}^{\alpha_{k'} / \gamma}, \quad (50)$$

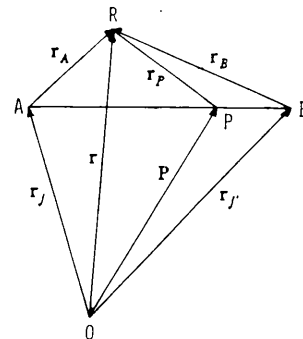


Fig. 1. Schematic drawing illustrating the relationships of vectors used in the calculation of the two-center scattering factor between the j th and the j' th atoms at A and B . Vectors \mathbf{r} , \mathbf{r}_j , $\mathbf{r}_{j'}$ and \mathbf{P} are those from the origin O to R , A , B and P , respectively. Vectors to R from A , B and P are \mathbf{r}_A , \mathbf{r}_B and \mathbf{r}_P , respectively.

where \mathbf{u}_j and $\mathbf{u}_{j'}$ are the displacement vectors of j th and j' th atoms from their equivalent positions \mathbf{r}_j^0 and $\mathbf{r}_{j'}^0$, respectively. $\langle \rangle$ means the average value. T_j and $T_{j'}$ are

$$T_j = \langle \exp [2\pi i \mathbf{S} \cdot \mathbf{u}_j] \rangle \quad (51a)$$

$$T_{j'} = \langle \exp [2\pi i \mathbf{S} \cdot \mathbf{u}_{j'}] \rangle, \quad (51b)$$

and T_j and $T_{j'}$ are by definition the temperature factors of the j th and j' th atoms. The temperature factor for the two-center term is derived on the two assumptions mentioned earlier. The independent-atom assumption is not a good assumption for the term of the GTO's with a bond between them. The assumption (b) is much more stringent than the Born-Oppenheimer approximation. Thus the present formalism of a two-center temperature factor needs experimental tests and may possibly be improved based on the detailed study of the interaction of the two atomic motions. However, the present equation is expected to be applicable to the actual analysis as a first approximation since the effect of the two-center terms on the structure factors is small.

The author thanks Professor F. Marumo for his continual encouragement during the entire period of this work. He is also grateful to Professor P. Coppens for his valuable discussions and hospitality during a stay in Buffalo, USA. The author is also grateful to Professor S. Iwata of Keio University and to Professor H. Kashiwagi of The Institute for Molecular Science for their valuable and helpful discussions. The author is indebted to Professor T. Ito of Kanagawa Institute of Technology for his discussion on two-center temperature factors. The computer center of the Institute of Molecular Science is gratefully acknowledged for permitting the author to use the computing facilities. The work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture, Japan. The work was also partly supported by the Japan-US cooperative program sponsored by the Japan Society of Promotion of Science.

APPENDIX

If the orthonormal condition in (8) is fulfilled, the idempotent matrix P can be obtained in the following way. Since S is a Hermitian matrix, it can be brought to the diagonal form \bar{S} by some unitary matrix U as

$$\bar{S} = U^\dagger S U. \quad (A1)$$

Therefore S is expressed as

$$S = U \bar{S} U^\dagger = U \bar{Q}_1 \bar{Q}_1 U^\dagger = S^{1/2} S^{\dagger 1/2}, \quad (A2)$$

where \bar{Q}_1 is a diagonal matrix so defined that the

square of each of the diagonal elements is equal to the corresponding diagonal element of \bar{S} . By replacing $CS^{1/2}$ with T , we get from (8) and (A2)

$$TT^\dagger = I. \quad (A3)$$

Then the matrix P is defined as

$$P = T^\dagger T. \quad (A4)$$

From the relation $(T^\dagger)_{ij} = (T)_{ji}^*$, P is easily shown to be a Hermitian matrix and from (A3)

$$P^2 = T^\dagger T (T^\dagger T) = T^\dagger I T = P. \quad (A5)$$

Therefore P is an idempotent matrix.

References

- CLINTON, W. L., FRISHBERG, C. A., MASSA, L. J. & OLDFIELD, P. A. (1973). *Int. J. Quantum Chem. Symp.* **7**, 505-514.
- CLINTON, W. L., GALLI, A. J. & MASSA, L. J. (1969). *Phys. Rev.* **177**, 7-13.
- COPPENS, P., GURU ROW, T. N., LEUNG, P., STEVENS, E. D., BECKER, P. J. & YANG, Y. W. (1979). *Acta Cryst.* **A35**, 63-72.
- COPPENS, P., WILLOUGHBY, T. V. & CSONKA, L. N. (1971). *Acta Cryst.* **A27**, 248-256.
- FRISHBERG, C. A. & MASSA, L. J. (1982). *Electron Distributions and the Chemical Bond*, edited by P. COPPENS & M. B. HALL, pp. 101-110. New York: Plenum Press.
- HAMILTON, W. C. (1964). *Statistics in Physical Science*. New York: Ronald Press.
- HANSEN, N. K. & COPPENS, P. (1978). *Acta Cryst.* **A34**, 909-921.
- HIRSHFELD, F. L. (1971). *Acta Cryst.* **B27**, 769-781.
- HOLLADAY, A., LEUNG, P. & COPPENS, P. (1983). *Acta Cryst.* **A29**, 377-387.
- HUZINAGA, S. (1984). *Gaussian Basis Sets for Molecular Calculations*. Amsterdam: Elsevier.
- ISHIGURO, T., ISHIZAWA, N., MIZUTANI, N., KATO, M., TANAKA, K. & MARUMO, F. (1983). *Acta Cryst.* **B39**, 564-569.
- IWATA, M. (1977). *Acta Cryst.* **B33**, 59-69.
- KAMIMURA, H., SUGANO, S. & TANABE, Y. (1969). *Ligand Field Theory and its Applications*. Tokyo: Syōkabō.
- KASHIWAGI, H. & SASAKI, F. (1973). *Int. J. Quantum Chem. Symp.* **7**, 515-520.
- KUJIMA, N., TANAKA, K. & MARUMO, F. (1982). *Acta Cryst.* **B38**, 545-548.
- KUJIMA, N., TANAKA, K. & MARUMO, F. (1983). *Acta Cryst.* **B39**, 557-561.
- KURKI-SUONIO, K. (1968). *Acta Cryst.* **A24**, 379-390.
- LÖWDIN, P. O. (1950). *J. Chem. Phys.* **18**, 365-375.
- LÖWDIN, P. O. (1955). *Phys. Rev.* **97**, 1474-1489.
- MCWEENEY, R. (1953). *Acta Cryst.* **6**, 631-637.
- MCWEENEY, R. (1960). *Rev. Mod. Phys.* **32**, 335-369.
- MIYATA, N., TANAKA, K. & MARUMO, F. (1983). *Acta Cryst.* **B39**, 561-564.
- STEWART, R. F. (1969). *J. Chem. Phys.* **51**, 4569-4577.
- STEWART, R. F. (1972). *J. Chem. Phys.* **57**, 1664-1668.
- TAKETA, H., HUZINAGA, S. & O-OHATA, K. (1966). *J. Phys. Soc. Jpn*, **21**, 2313-2324.
- TANAKA, K., KONISHI, M. & MARUMO, F. (1979). *Acta Cryst.* **B35**, 1303-1308.
- TANAKA, K. & MARUMO, F. (1988). In preparation.
- TSIREL'SON, V. G., MESTECHKIN, M. M. & OZEROV, R. P. (1977). *Dokl. Akad. Nauk SSSR*, **233**, 108-110.
- WEISS, R. J. & FREEMAN, A. J. (1959). *J. Chem. Phys. Solids*, **10**, 147-161.