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THE SELECTED-ELECTRON-SHELL METHOD PART I: THEORY

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ABSTRACT.—The representation of the electron density of atoms by Gaussian distribution was suggested by Ewald (1940). The analytical expression of the atomic scattering factor can then be given by a Gaussian polynomial, from which a new method, the selected-electron-shell (SES) method, is developed that allows one to analyze independently the role of the inner and outer electrons of an atom in a crystal from x-ray diffraction data. It is shown that it is also possible to study the thermal vibrations of a non-rigid atom. By comparing the electron density obtained by the SES method and the one calculated by convolution method, important details as the existence of mid-bond electrons, or polarization of the electron cloud can be investigated.

It is a well known fact that the electron density in a crystal can be studied via x-ray diffraction experiments. However, the electron density obtained by Fourier summation from experimental data is not accurate enough to allow the study of the true electron density distribution of atoms in the solid. This is due to several inaccuracies in the traditional method. Above all, the experimental method, which necessarily uses a given x-ray wavelength, introduces an important limitation resulting in what is known as the series termination effect. Moreover, in the calculations it is customary to use

the atomic scattering factor of atoms considered as rigid bodies with spherical symmetry, although several authors (see, for instance, McWeeney, 1951, 1952, 1953 and 1954) have pointed out that the atomic scattering function of a bonded atom is an anisotropic function. In order to overcome the restriction imposed by considering as spherical the atoms in the crystals, it is assumed that the departure from such spherical symmetry is caused by anisotropic thermal motion of the atoms in the solid, although serious doubts have been risen (Coppens, 1968) about the legitimacy of the procedure. Furthermore, difference Fourier syntheses have shown, time and again, that residual electron density in covalently bonded atoms occurs along the bonding direction, and consequently that the electron density of real atoms in crystals is far from being spherical.

There is no easy way however to overcome the limitations and inaccuracies of the traditional path. It is therefore necessary to seek a new solution of the problem. The present authors have shown in a previous paper (Amorós and Canut-Amorós, 1968) that it is possible to sepa-

rate the contributions to x-ray diffraction of the inner and outer electrons of atoms in molecular crystals. A simple description of the basic ideas has also been introduced in a recent book (J. L. and Marisa Amorós, 1968). The basic idea is to use Gaussian polynomials as the analytical representation of the atomic scattering function. The method is based on the separate treatment of such contributions by associating them with the traditionally accepted shell structure of the atoms, and the method can be called, appropriately, the selected-electron-shell (SES) method. In what follows, we shall describe the basic theory of the SES method. In order to implement the method, some computational aids have been developed in our Laboratory. A brief description of the programs and some results obtained by using such computational aids are included in the second part of this paper.

THE SELECTED-ELECTRON-SHELL APPROACH

The method assumes that the electron density of an atom can be given analytically by Gaussian polynomials. The representation of the electron density function of an atom by a Gaussian distribution was first introduced by Ewald (1940) in his Gaussian atom model. The use of Gaussian functions is very convenient, because the Fourier transform of a Gaussian function of width g is also a Gaussian function of width $1/\pi g$. Therefore the atomic scattering function of a Gaussian atom is also given by a Gaussian function. It was shown later (Vand, Eiland

and Pepinsky, 1957; Hosemann and Bagchi, 1962) that a better fit of the atomic scattering factor was obtained by using a Gaussian polynomial instead of a single Gaussian function. Along these lines, Moore (1963), Cromer and Waber (1964) and Kurki-Suonio, Meisalo, Merisalo and Peltola (1966) have given different sets of Gaussian polynomials that describe the scattering factor of different atoms. However, the use of Gaussian polynomials has physical meaning only when each Gaussian term of the polynomial is associated to the electron distribution of each main electron shell of the atom. In this case, the atomic-scattering amplitude can be expressed (Amorós and Canut-Amorós, 1968) by

$$f(\underline{r}^*) = \sum_{s=1}^S G_s \exp(-\pi^2 \underline{g}_s^2 \underline{r}^{*2}), \quad (1)$$

where G_s is the number of electrons in the s shell, g_s is the half width of the Gaussian function of the same shell, and r^* is the magnitude of the reciprocal vector. The summation extends to the S shells of the atom. Expression (1) is very convenient because it allows one to determine the Gaussian coefficients G_s and g_s from a semilogarithmic plot of the observed or theoretical scattering amplitude of the atom versus $|r^*|^2$.

Expression (1) corresponds to the scattering amplitude of an atom at rest. In real crystals, however, atoms are subject to thermal vibrations. For simplicity, let us assume that the atom vibrates isotropically in an harmonic potential field. The smearing function is given by a Gaussian probability $p(\underline{r})$ that is temperature dependent. Then the atomic scattering amplitude is modi-

fied by a temperature factor. The Fourier transform of $p(r)$ is

$$D_T(r^*) = \exp(-\pi^2 2\bar{u}_T^2 r^{*2}), \quad (2)$$

where u_T is the mean square amplitude of vibration of the atom. $D_T(r^*)$ is also a Gaussian function. The effective atomic-scattering amplitude at the temperature T is then corrected by the temperature factor, i.e.,

$$f_T(r^*) = f(r^*) \cdot D_T(r^*), \quad (3)$$

if the atom vibrates as a rigid body. The obvious consequence, long ago recognized in x-ray diffraction analysis, is that the effective atomic-scattering amplitude of the vibrating atom is temperature dependent. Equation (3) can be written explicitly in terms of the Gaussian components of the atomic scattering amplitude, i.e.,

$$f_T(r^*) = \sum_s \bar{g}_s \exp(-\pi^2 \bar{g}_{sT}^2 r^{*2}), \quad (4)$$

where the new Gaussian parameter g_{sT} is now given by

$$\bar{g}_{sT} = (\bar{g}_s^2 + 2\bar{u}_T^2)^{1/2}. \quad (5)$$

From (5) it follows that the only consequence on introducing an harmonic vibration on (1) is to vary the width of the Gaussian function. We have assumed the rigid-atom approximation to deduce (3). However, once the Gaussian components are explicitly introduced in the expression of the atomic-scattering amplitude (4), this restriction is no longer necessary, and the rigid atomic shell approximation can now be introduced, in which each atomic

shell can vibrate with a different amplitude u_{sT} . Under this assumption (5) becomes

$$\bar{g}_{sT}' = (\bar{g}_s^2 + 2\bar{u}_{sT}^2)^{1/2}, \quad (6)$$

and (4) accordingly can be rewritten as

$$f_T(r^*) = \sum_s \bar{g}_s \exp(-\pi^2 \bar{g}_{sT}'^2 r^{*2}). \quad (7)$$

The analytical approximation of the atomic scattering factor is therefore very convenient since it allows one to determine the temperature factor of the different shells independently. In the conventional method used in x-ray crystallography, only rigid atoms are assumed. Several hints exist, however, that this is not the case, and this method may prove useful in obtaining conclusive evidence on this matter.

In crystal-structure determination the temperature factor is usually expressed as

$$D_T([\sin \theta]/\lambda) = \exp(-B_T[\sin^2 \theta]/\lambda^2), \quad (8)$$

where B_T is related to the mean square vibrational amplitude by

$$B_T = 8\pi^2 \bar{u}_T^2, \quad (9)$$

for isotropic rigid body motion. The B_T factor can be introduced in the Gaussian width, which then takes the form

$$\bar{g}_{sT} = \bar{g}_s + \frac{B_T}{4\pi^2}^{1/2}, \quad (10)$$

where g_s is the form coefficient of the Gaussian describing the s electron shell at rest.

If we express the atomic-scattering

amplitude as a function of $(\sin \Theta)/\lambda$ instead of r^* , the following expression is obtained:

$$\underline{f}_T([\sin \Theta]/\lambda) = \sum_s \underline{G}_s \exp(-4\pi^2 \underline{g}_s^2 [\sin^2 \Theta]/\lambda^2) \left\{ \exp(-\underline{B}_T [\sin^2 \Theta]/\lambda^2), \quad (11) \right.$$

or else

$$\underline{f}_T([\sin \Theta]/\lambda) = \sum_s \underline{G}_s \exp(-\underline{B}_{sT}'' [\sin^2 \Theta]/\lambda^2), \quad (12)$$

with the same temperature factor B_T for each s shell

$$\underline{B}_{sT}'' = 4\pi^2 \underline{g}_s^2 + \underline{B}_T, \quad (13)$$

i.e., in the rigid body atom approach.

¶ In the rigid atomic shell approach, one can introduce temperature factors B_{sT} associated to each shell s , and define

$$\underline{B}_{sT}' = 4\pi^2 \underline{g}_s^2 + \underline{B}_{sT}, \quad (14)$$

where

$$\underline{B}_{sT} = 8\pi^2 \underline{u}_{sT}^2. \quad (15)$$

B_{sT}' can be deduced from x-ray diffraction experiments, in terms of

$$\underline{f}_T([\sin \Theta]/\lambda) = \sum_s \underline{G}_s \exp(-\underline{B}_{sT}' [\sin^2 \Theta]/\lambda^2). \quad (16)$$

Let us remember that the coefficients B_{sT}' contain both the form and tem-

perature factor of the Gaussian describing the rigid electron shell s .

X-ray crystal-structure analysis is done by means of finding the best fit between observed and calculated structure factors. The conventional structure-factor equation is well known. In the isotropic case, we have

$$\underline{F}(\underline{r}^*) = \sum_j \sum_s \underline{G}_{js}' \exp(-\underline{B}_{js}'' [\sin^2 \Theta]/\lambda^2) \exp(-2\pi i \underline{r}_j \cdot \underline{r}_h^*), \quad (17)$$

when the Gaussian components of the atomic scattering amplitude are explicitly introduced. The new summation extends to the S electron shells of the atom j , and B_{js}'' has the meaning defined by (13).

If we deal with a structure that has been well-refined by the conventional method, it is reasonable to assume that the coordinates r_j of the atoms are well determined. We may then accept those coordinates as known constants. But even in the case where conventional thermal analysis is assumed to be satisfactory, i.e., that we know the exponents B_{jT} for the different atoms in the structure, we are forced to determine the new B_{js}' as they now contain the as they now contain the temperature and the Gaussian parameters of a rigid shell. These values can be obtained through a least squares refinement, by using the B_{js}'' as starting values. The new parameters B_{js}' contain information about the average electron density of the given shell of the atom at the temperature at which the observations have been made.

We know (Slater, 1965) that in molecular structures a bond depends on the overlapping of charge in the outer shells of the two bonded atoms. This overlapping is expected to be at a maximum when the maximum charge densities of the outer shells of the two atoms coincide. The anisotropy in the electron density of the atoms of a molecule depends, then, on the contribution of the outer electrons alone and this anisotropy will be modified to some extent by thermal motion. The distribution of the inner electrons however is expected to be spherically symmetric. Then any anisotropy observed in the distribution of the inner electrons must come from the distortion produced by the anisotropy of the thermal motion alone. This gives a good way to determine with high accuracy the thermal motion of the atomic nuclei and the inner electrons tightly bonded to them. In molecular crystals with C, N, O and H, the region outside a limiting sphere of r^* about $0.9 \text{ \AA}^{-1}$ contains the contribution of the inner electrons alone. In this case, it is possible to deduce for the shell K the best values of B'_{jk} using only experimental data obtained from high diffraction angles. The structure factor for reflections in this region is then given by

$$\begin{aligned} \underline{F}(\underline{r}_h^*) &= \underline{F}_K(\underline{r}_h^*) = \sum_j \underline{G}_{jK} \\ &\exp(-\underline{B}'_{jK} [\sin^2 \theta]/\lambda^2) \\ &\exp(-2\pi i \underline{r}_{j-} \cdot \underline{r}_h^*), \\ (|\underline{r}_h^*| &\geq \underline{R}_{L \text{ lim}}), \end{aligned} \quad (18)$$

where $\underline{R}_{L \text{ lim}}$ corresponds to the region where the outer electrons no longer contribute.

Up to now, we have considered isotropic thermal motion, however atoms in real crystals are in general subjected to anisotropic thermal vibrations. The simplest case of this kind of thermal motion is represented by a second rank symmetric tensor $\underline{U}$. In this case the temperature factor B is transformed into another tensor $\underline{B}$ related to $\underline{U}$ by

$$\underline{B} = \frac{\underline{U}}{8\pi^2}. \quad (19)$$

We can then write

$$\underline{D}(\underline{r}^*) = \exp[-(\sum \underline{B}_{ij} \underline{m}_i \underline{m}_j) (\sin^2 \theta)/\lambda^2]. \quad (20)$$

In this expression, $\underline{m}$ is a unit vector in reciprocal space and $\sum \underline{B}_{ij} \underline{m}_i \underline{m}_j$ can be considered as the value of $\underline{B}$ in the direction of $\underline{m}$. For the sake of computation, the temperature factor D in (20) is usually expressed in terms of dimensionless quantities β_{ij} as follows:

$$\begin{aligned} \underline{D} &= \exp[-(\beta_{11} \underline{h}^2 + \beta_{22} \underline{k}^2 \\ &+ \beta_{33} \underline{l}^2 + 2\beta_{12} \underline{h}\underline{k} + 2\beta_{13} \underline{h}\underline{l} \\ &+ 2\beta_{23} \underline{k}\underline{l})]. \end{aligned} \quad (21)$$

The following known relations exist between β_{ij} and B_{ij} :

$$\begin{aligned} B_{11} &= \frac{4\beta_{11}}{a^{*2}} & B_{22} &= \frac{4\beta_{22}}{b^{*2}} \\ B_{33} &= \frac{4\beta_{33}}{c^{*2}} & B_{12} &= \frac{4\beta_{12}}{a^*b^*} \\ B_{13} &= \frac{4\beta_{13}}{a^*c^*} & B_{23} &= \frac{4\beta_{23}}{b^*c^*} \end{aligned} \quad (22)$$

Assuming anisotropic thermal vibrations, B'_{jk} in (18) must be substituted for B'_{jk} the tensor that includes both the spherically symmetric form factor and the anisotropic temperature factor of the K shell.

Once the best values of the Gaussian parameters of the shell describing the inner electrons have been determined by least squares refinement using high order diffraction data, it is just a matter of routine to calculate the contribution F_k of these electrons to every observed x-ray diffraction data. The observed amplitudes F_{obs} contain the contribution of all the electrons in the crystal. We can calculate a Fourier series of the form

$$\begin{aligned} \rho_{outer}(\mathbf{r}) &= \sum_{\mathbf{h}} (F_{obs} - F_K) \\ &\quad \exp(2\pi i \mathbf{r} \cdot \mathbf{r}_{\mathbf{h}}^*), \\ &\quad (|\mathbf{r}_{\mathbf{h}}^*| < R_{L \text{ lim}}), \end{aligned} \quad (23)$$

that has important properties. First, it is free from series termination effects, because the coefficients in (23) are zero outside $R_{L \text{ lim}}$. Second, it contains the information of the most important electrons, the outer electrons, in the bonding system of a molecule. It contains also the contribution of the hydrogen atoms if they are present in the structure. The $(F_{obs} - F_k)$ Fourier summation is fundamental in the analysis of the electron distribution in a molecule and it is the basic equation in the SES method.

CALCULATION OF THE ELECTRON DENSITY BY CONVOLUTION METHOD

The purpose of the method outlined in this paper is not only to get the best fitting atomic scattering amplitude of the atoms in a given crystal structure, and to obtain a display of the experimental density function of the outer electrons, but also to compare this electron density distribution with the calculated one in terms of the different Gaussian atoms, considered as a whole or as individual contributions of the shells. Consequently the last step of the SES method is the theoretical calculation of the electron density of a crystal. We shall deal now with this problem.

The electron density of an atom is the inverse Fourier transform of its atomic scattering amplitude. It follows from what has been said at the beginning of our discussion that the electron density in the Gaussian approximation is given by the Gaussian polynomial

$$\rho(\underline{r}) = \sum_{\underline{s}=1}^S \frac{G_{\underline{s}}}{(\pi g_{\underline{s}}^2)^{3/2}} \exp\left(-\frac{1}{2} \underline{r}^2\right), \quad (24)$$

that is readily obtained from (1). In a similar way, by applying a Fourier transformation to (7), one obtains,

$$\rho_T(\underline{r}) = \sum_{\underline{s}=1}^S \frac{G_{\underline{s}}}{(\pi g_{\underline{s}}'^2)^{3/2}} \exp\left(-\frac{1}{2} \underline{r}^2\right). \quad (25)$$

From least squares refinement, the B'_{sT} values are obtained rather than g'_{sT} . However those can be readily obtained because

$$g'_{sT} = \frac{\sqrt{B'_{sT}}}{2\pi} = 0.1591 \sqrt{B'_{sT}}. \quad (26)$$

The new equation (25) gives the averaged electron-density of the Gaussian atom spread by the thermal motion.

The electron density inside a unit cell of the crystal can be calculated by convolving the Gaussian functions (25) describing the different atoms with the atomic peak functions $z_j(\underline{r})$ that define the coordinates of the atoms in the unit cell,

$$\rho_{\text{cell}}(\underline{r}) = \sum_{j=1}^J \sum_{\underline{s}=1}^S \rho_{jST}(\underline{r}) * z_j(\underline{r}). \quad (27)$$

The electron density calculated from (27) represents the assumption of a spherically symmetric Gaussian distribution of the electrons in the different shells of the atom. To introduce a non-spherical symmetry, the coefficient g'_{sT} must be substituted for a second rank tensor.

The electron density maps obtained by convolution are very convenient for the analysis of the experimental SES maps. Differences between the two maps will appear if the observed electron density is not only due to the overlap of the outer electrons, but also to the presence of mid-bond extra electrons or the existence of polarization of the electron cloud. These are basic questions of interest to chemists and physicists alike, and the SES method may prove fruitful in such cases. The SES method is basically an experimental method and, as in any experimental approach, the results obtained depend largely upon the accuracy of the experimental data and of the corrections applied to them. The observed $F_o(hkl)$ values should be corrected for Compton and thermal diffuse scattering, and extinction must be taken care of. Preliminary research on organic compounds (Amorós and Canut-Amorós, 1968a, b), inorganic covalent crystals (Amorós, Canut-Amorós, and Montoto, 1968) and ionic compounds (Savanonda, 1968) has shown the validity of the theory and the plausibility of the method.

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