Mapping Parts of the Electron Density Distribution from X-Ray Bragg Scattering Intensities (Lambda Technique)

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Z. Naturforsch. **36a**, 1253—1254 (1981);
received October 8, 1981

By appropriate selection of two or three wavelengths, intensity differences can be used for obtaining directly the electron density distribution (i.e. the arrangement of atoms) for parts of a crystal structure. Application to macromolecules and amorphous binary substances appear feasible.

X-rays taken from a synchrotron source can be tuned over a wide range in λ. For using anomalous scattering effects [1] close to K or L absorption edges λ_c, special conditions for intensity collection can be met. The method briefly described below uses symmetry conditions imposed on the real (a) and imaginary part (b) of the x-ray atomic scattering factor defined by

$$a = (f_0 + f')\,T \quad \text{and} \quad b = f''\,T$$

with T = Debye-Waller "temperature factor".

A first possibility consists in selecting two wavelengths $\lambda_1 < \lambda_2$ on both sides of λ_c of one species of atoms (called "edge atoms") in a crystal structure such that

$$a_{e1} = a_{e2}\,, \quad b_{e1} \neq b_{e2} \tag{1a}$$

holds with

e denoting the edge atoms (of which k are assumed to be in the unit cell),

1, 2 denoting λ_1 and λ_2.

If $\lambda_2 - \lambda_1$ is small enough, the corresponding a and b for the "normal scatterers" ($m - k$ in the unit cell and denoted by the subscript n) follow

$$a_{n1} \cong a_{n2}\,, \quad b_{n1} \cong b_{n2} < b_{e1}\,. \tag{1b}$$

From the well-known general expression for $|F(\underline{h})|^2$

$$|F(\underline{h})|^2 = \sum_{\nu=1}^{m}\sum_{\mu=1}^{m}(a_\mu a_\nu + b_\mu b_\nu)\cos\underline{h}(\underline{r}_\nu - \underline{r}_\mu) + (a_\mu b_\nu - b_\mu a_\nu)\sin\underline{h}(\underline{r}_\nu - \underline{r}_\mu)$$

it follows via straight-forward arguments that the scaled intensity differences

$$\Lambda_{12}(\underline{h}) = \frac{|F_{\lambda1}(\underline{h})|^2 - |F_{\lambda2}(\underline{h})|^2}{b_{e1} - b_{e2}}\,, \tag{2}$$

permit computing a Fourier transform $\mathcal{F}$

$$L_{12}(\underline{u}) = \mathcal{F}[\Lambda_{12}(\underline{h})] = L_{12c}(\underline{u}) + i\,L_{12s}(\underline{u})\,. \tag{3}$$

The real part $L_{12c}(\underline{u})$ of (3) yields the vectors between the anomalous scatterers only [2]†. The imaginary part $L_{12s}(\underline{u})$ contains $k(m-k)$ vectors from each e-atom to all n-atoms. They represent k parallel "images" of the n-atom structure as "seen" from each e-atom [3]. These images are, however, disturbed by equivalent inverse and negative images caused by the anti-centrosymmetry of $L_{12s}(\underline{u})$. This will partly or (for centrosymmetric structures) completely erase these images.

In this case one can make use of a second symmetry condition by selecting a third wavelength λ_3 such that the role of b_e and a_e in (1a) is interchanged:

$$a_{e3} \neq a_{e2}\,, \quad b_{e3} \cong b_{e2}\,,$$
$$a_{n3} \cong a_{n2}\,, \quad b_{n3} \cong b_{n2}\,. \tag{4}$$

In full analogy to (2) and (3), the Fourier transform

$$L_{23}(\underline{u}) = L_{23c}(\underline{u}) + i\,L_{23s}(\underline{u}) \tag{5}$$

is computed. Addition of parts of (2) and (3) according to

$$L_{23c}(\underline{u}) + L_{12s}(\underline{u}) - L_{12c}(\underline{u}) = 2\sum_{\mu=1}^{k}\sum_{\nu=k+1}^{m}\varrho_{n\nu}(\underline{r}) * \beta_{e\mu}(\underline{r}) \tag{6}$$

compensates the anti-centrosymmetry mentioned above by the centrosymmetry of $L_{23c}(\underline{u})$ [4].

The right-hand side† of Eq. (6) with

$\varrho_n(\underline{r})$ electron density distribution (including thermal vibration) of the n-atoms,

$\beta_e(\underline{r})$ sharp, spherical density distribution for each of the e-atoms (smeared out by its thermal vibration), and

$*$ denoting convolution,

† These statements are exact if all $b_n = 0$ and $b_{e1} \neq f\,(\sin\theta)$ and $b_{e3} = b_{e2} \neq f\,(\sin\theta)$. They are close approximations under the conditions (1) and (4).

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provides undisturbed images (compared with $L_{12s}(\underline{y})$). It can be solved to obtain the n-atom arrangement (step 2) — either by deconvolution or by other techniques —, if the arrangement of the e-atoms has been found from $L_{12c}(\underline{y})$ (step 1). Step 2 (which can also be applied to $L_{12s}(\underline{y})$ alone) yields the true symmetry of the complete structure, including enantiomer or polarity. This step comprises a partial structure analysis without "knowing" phases. If only one e-atoms exists, step 1 is unnecessary and step 2 trivial, with results similar to [5]. In this case $\sum_{\nu=k+1}^{m} \varrho_n(\underline{r})$ follows directly from the diffraction intensity differences $\Lambda_{12}(\underline{h})$ and $\Lambda_{23}(\underline{h})$ (or $\Lambda_{12}(\underline{h})$ alone) without knowledge of phases†. A computer program has been implemented which performs step 2 (from Eq. (6) or from $L_{12s}(\underline{y})$).

Applications of this method (called "lambda technique" in our laboratory) may be envisaged for determination of crystal structures which cannot be solved by present routine methods, e.g. also pseudosymmetric and/or super-structures. Because the n-atoms need not be treated as individuals, a density map of unresolved (and perhaps not resolvable) n-atoms can be obtained. This may be helpful in the investigation of positionally disordered macromolecules (provided that collecting a double or triple data set appears possible). In amorphous binary substances, partial pair distribution functions [6] of the two constituents e and n can be separated in (e, e)- and (e, n)-distributions.

I wish to express cordial thanks to Mrs. A. Ribbens, Mr. J. Spilker, and Dr. G. Schäfer from our laboratory for a number of contributions to this topic which will be published in detail elsewhere.

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