

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

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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

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

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

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

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

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

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

$$A_{12}(\mathbf{h}) = \frac{|F_{\lambda_1}(\mathbf{h})|^2 - |F_{\lambda_2}(\mathbf{h})|^2}{b_{e1} - b_{e2}}, \quad (2)$$

permit computing a Fourier transform \mathcal{F}

$$L_{12}(\mathbf{y}) = \mathcal{F}[A_{12}(\mathbf{h})] = L_{12c}(\mathbf{y}) + iL_{12s}(\mathbf{y}). \quad (3)$$

The real part $L_{12c}(\mathbf{y})$ of (3) yields the vectors between the anomalous scatterers only [2]†. The imaginary part $L_{12s}(\mathbf{y})$ 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 $L_{12s}(\mathbf{y})$. 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:

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

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

$$L_{23}(\mathbf{y}) = L_{23c}(\mathbf{y}) + iL_{23s}(\mathbf{y}) \quad (5)$$

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

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

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

The right-hand side† of Eq. (6) with

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

$\beta_e(\mathbf{r})$ 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).

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-atom exists, step 1 is unnecessary and step 2 trivial, with results similar to [5]. In this case $\sum_{\nu=k+1}^m \rho_n(r)$ 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.

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