MS44-P2 The use of your model to assess the features of a diffraction pattern

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The model for the diffraction pattern of a crystal structure tries to describe intensities at various points **h** in reciprocal space. Any particular quantum sees a phased quantity $\Sigma_m\ a_m(\mathbf{h})\ F_m(\mathbf{h})$ where the $a_m(\mathbf{h})$ are complex and the $F_m(\mathbf{h})$ are real. The observed intensity $I(\mathbf{h}) = Y_{obs}(\mathbf{h})^2$ is then an averaged quantity

$Y_{obs}(\mathbf{h})^2 = \Sigma_{m,n}\ F_m(\mathbf{h})F_m(\mathbf{h})\ \langle a_m(\mathbf{h})^* a_n(\mathbf{h}) + a_m(\mathbf{h}) a_n(\mathbf{h})^* \rangle/2 = \Sigma_{m,n}\ g_{mn}(\mathbf{h})F_m(\mathbf{h})F_n(\mathbf{h})$.

A count of $n(\mathbf{h}) \pm \sqrt{n}(\mathbf{h})$ associated with $Y_{obs}(\mathbf{h})^2$ corresponds to $\sqrt{n}(\mathbf{h}) \pm 1/2$ associated with $Y_{obs}(\mathbf{h})$. $Y_{obs}(\mathbf{h})$ can be described as a vector $\mathbf{Y}(\mathbf{h})$ in an M dimensional space with the same variance in any direction.

$\mathbf{Y}(\mathbf{h}) = \Sigma_m\ \sqrt{g_{mn}}(\mathbf{h})F_m(\mathbf{h})\ \mathbf{i}_m$ where $\mathbf{i}_m.\mathbf{i}_n = g_{mn}(\mathbf{h})/\sqrt{[g_{mm}(\mathbf{h})g_{nn}(\mathbf{h})]}$ so that $\mathbf{i}_m.\mathbf{i}_m = \mathbf{i}_n.\mathbf{i}_n = 1$.

The angle between $\mathbf{i}_m$ and $\mathbf{Y}(\mathbf{h})$ is given by $\cos(\varepsilon_m(\mathbf{h})) = \Sigma_n\ g_{mn}(\mathbf{h})F_n(\mathbf{h})/[\mathbf{Y}(\mathbf{h})\sqrt{g_{mm}}(\mathbf{h})]$.

Least squares refinement evaluates change in the direction of an initial model $\mathbf{Y}_{calc}(\mathbf{h})$ that is assumed to be the direction of $\mathbf{Y}_{obs}(\mathbf{h})$. The expressions for $g_{mn}(\mathbf{h})$ can be chosen so that stacking faults, twins and allo twins are simply special cases of a more general description, ie one where the crystal is not the same everywhere. The fraction of $Y_{obs}(\mathbf{h})^2$ associated with $\sqrt{g_{mm}}(\mathbf{h})\ F_m(\mathbf{h})$ is then $\cos^2(\varepsilon_m(\mathbf{h}))$ with an associated partial residual $\cos(\varepsilon_m(\mathbf{h}))[\mathbf{Y}_{obs}(\mathbf{h}) - \mathbf{Y}_{calc}(\mathbf{h})]\ .\mathbf{i}_m$.

The variance of $\mathbf{Y}_{calc}(\mathbf{h})$ can also be evaluated in terms of known or assumed variances and covariances of the parameters describing the model. Thus partial observations of variables can also be obtained [1]. The least squares refinement of the parameters describing the $g_{mn}(\mathbf{h})$ can be separated from the refinement of the parameters describing the $F_m(\mathbf{h})$. Peak positions and profiles are associated with changes in the $g_{mn}(\mathbf{h})$ for the same $F_m(\mathbf{h})$ and $F_n(\mathbf{h})$. There is thus an implicit merging of $F_m(\mathbf{h})$ values with an associated best least squares value, variance and effective partial observation coefficient $\langle\cos^2(\varepsilon_m(\mathbf{h}))\rangle$.

The background is part of the model of any intensity or linear combination of intensities and intensity data should have sufficient information for this to be known. The evaluation of the statistics for components of observations should assist the identification of sources of systematic error.

References

Rae. A.D., (2013) "*The use of partial observations, partial models, and partial residuals to improve the least squares refinement of crystal structures* ", Crystallography Reviews, Vol. 20, 155-229, Taylor & Francis.

Keywords: partial observations, least squares, error distribution

MS44-P3 Speeding up accurate scattering factors calculation for macromolecules. Algorithms for aspherical atom formalism and direct summation

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The most popular method of calculation of scattering factors (SF) for macromolecules is based on fast Fourier transform (FFT) of dynamic electron density of spherical atoms. With increasing number of high resolution data for large molecular systems a need for efficient implementation of more accurate methods of SF calculation emerges. We have developed a code combining improved description of atomic electron densities via aspherical atom model with accurate calculation of Fourier transform via direct summation. Such a combination can result in relatively slow calculation of SF. Therefore we have proposed few algorithms facilitating efficient calculation of SF. Some of them apply also for spherical atom model. The influence of the developments on execution time is discussed for model macromolecules. University at Buffalo Pseudoatom Databank (UBDB) [1] was used for parameterization of aspherical atom model.

[1] Jarzembska, K. N.&Dominiak, P. M. (2012) Acta Cryst. A68, 139-147.

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