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A weighting scheme for least-squares structure refinement.

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Abstract

The truncated Chebyshev polynomial provides a reliable scheme for the automatic determination of empirical weights for least-squares structure refinement when the errors are a function of $|F_o|$.

The correct approach to least-squares refinement where the observations are not statistically independent of each other is through a properly determined weight matrix (Hamilton, 1964). In practice, however, the information needed to construct this matrix is not readily available and, even if it were, the cost of using it in least-squares refinement would be prohibitive. We therefore have to make approximations about the way our observations are weighted, and various approaches have been used. Early schemes to devise suitable weights included the use of simple analytic expressions that were believed to reflect the likely distribution of errors (Hughes, 1941), and this was quite adequate for photographic data. The use of quantum counters for measuring X-ray reflexions introduced the possibility of using weights based on counting statistics, but except in very favourable cases $w = 1/\sigma^2$ was not entirely satisfactory, so that additional correction terms were introduced (Cruickshank, 1970). The values of the coefficients for these terms, like those for the analytic expressions, were derived by examining $(|F_o| - |F_c|)^2$ for systematic trends.

Our approach to the problem was, like that of Nielson (1977), to confess that we did not know the source or form of all the errors in an experiment, but to believe that they could be represented by a smooth function in a suitable parameter space. We also hoped that, when we had included in our model all the variables needed to describe it to the accuracy of the experimental data, $\Delta^2 [= (|F_o| - |F_c|)^2]$ for groups of related reflexions indicated the weight to be associated with those reflexions. This means that the weight to be given to a particular reflexion at some stage in the refinement will reflect not only errors in the data, but shortcomings in the model being fitted. This is merely acknowledging the 'requirement that the average $w\Delta^2$ must be constant when the set of $w\Delta^2$ values for a given structure is analysed in any significant systematic fashion' (Cruickshank, 1961).

We therefore tried to fit Δ^2 to power series in $|F_o|$, $\sin\theta/\lambda$ and combinations of $|F_o|$ and $\sin\theta/\lambda$. This work (Hodder & Watkin, 1968) failed largely through ill-conditioning of the normal equations and unsuitable weighting of the observations used in the process. The analysis was stabilized by using Chebyshev polynomials fitted to $\langle\Delta^2\rangle$ with weights $w = 1/|F_o|^n$.

Results obtained over the last five years seem to have vindicated this process. The procedure we follow is to refine the structure with unit weights until all the necessary parameters have been included, and then look at the distribution of $\langle\Delta^2\rangle$ with $|F_o|$ and $\sin\theta/\lambda$. If, as is commonly the case, the distribution shows a smooth trend, we fit a number of Chebyshev polynomials in $|F_o|$, and look at the resulting $\langle w\Delta^2\rangle$ distributions. The polynomial with the least coefficients to give a satisfactory fit is accepted, a little more structure refinement done, weights recalculated for the new model, and the model then refined to convergence. It is rarely necessary to determine weights a third time.

Fig. 1 gives examples of weights determined by this process (Prout & Couldwell, 1977) for equal-times observations on a four-circle diffractomer. R at this stage, the end of unit weight refinement, was 7·74%. The curves are all smooth, and resemble Hughes's original scheme. Note however that maximum weight is given to medium size reflexions. Table 1 lists $\langle w\Delta^2\rangle$ as a function of $|F_o|$ and $(\sin\theta/\lambda)^2$, and in this case the three term scheme is adequate.

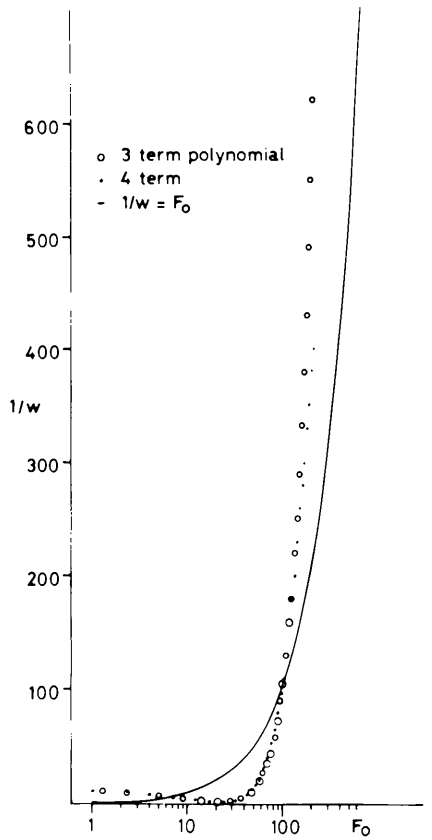

Fig. 1. Plot of $1/w$ *versus* $|F_o|$. Abscissa plotted on logarithmic scale.

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Table 1. *Mean values of Δ^2 and $w\Delta^2$ as a function of $|F_o|$ and $(\sin\theta/\lambda)^2$*

(1) $\langle\Delta^2\rangle$; (3), (4), (5) $\langle w\Delta^2\rangle$ for three, four and five term Chebyshev polynomials.

		(1)	(3)	(4)	(5)
Number of reflexions	$\langle\|F_o\|\rangle$	$\langle\Delta^2\rangle$			
78	8·7	7·54	1·53	1·45	1·46
1003	11·9	2·99	0·82	0·84	0·84
498	19·8	2·12	1·23	1·63	1·62
234	29·6	3·47	1·78	1·78	1·84
96	43·4	10·09	1·46	1·21	1·24
58	56·0	14·97	0·78	0·66	0·66
28	70·1	35·50	0·88	0·77	0·77
4	93·3	98·90	1·20	1·14	1·11
5	100·6	75·46	0·65	0·64	0·62
0	–	–	–	–	–
1	172·7	753·8	2·11	2·63	2·55
0	–	–	–	–	–
1	231·8	228·2	0·33	0·53	0·55
	$\langle(\sin\theta/\lambda)^2\rangle$				
91	0·2	29·44	1·94	1·89	1·91
163	0·28	11·93	1·47	1·51	1·52
196	0·35	4·24	1·19	1·27	1·28
216	0·40	2·77	1·21	1·35	1·35
250	0·45	2·39	1·07	1·19	1·20
247	0·49	2·16	0·89	1·01	1·01
251	0·53	2·46	0·93	1·04	1·04
243	0·57	2·54	0·75	0·80	0·80
158	0·60	3·95	1·03	1·05	1·05
109	0·63	4·49	1·09	1·08	1·08
82	0·66	6·18	1·52	1·51	1·51

This empirical weighting scheme is never used to mask correctable errors in the data, such as absorption, nor to evade the refinement of parameters, such as extinction, that could be resolved with the available data. It does however provide a reproducible method for obtaining weights satisfying Cruickshank's criterion from the available data for the parameters being refined.

The program is not readily available for other laboratories since it is part of the integrated crystallographic package, *CRYSTALS* (Carruthers, 1975). The Appendix outlines the computations involved.

APPENDIX

$F = |F_o|/|F_o|_{max}$.
$\Delta = |F_o| - |F_c|$, F_o and F_c on same scale.
w = weight used in model refinement.
$\Delta^\dagger = \Delta^2 - 1/w$.
$w^\dagger$ = weight used in determining Chebyshev coefficients.

We wish to make $\langle w\Delta^2\rangle$ constant as a function of $|F_o|$, and represent $1/w$ as a truncated Chebyshev polynomial, so that

$$1/\langle w\rangle = \langle\Delta^2\rangle = \sum_i a_i T_i^*(F). \quad (1)$$

If we let

$$G = 2^*F - 1,$$

$$T_0^*(F) = 1,$$

and

$$T_1^*(F) = G,$$

then

$$T_i^*(F) = [2^*G^*T_{i-1}^*(F)] - T_{i-2}^*(F) \quad \text{(Rollett, 1965).}$$

The Chebyshev coefficients, a_i, are to be determined, and are found by minimizing

$$M = \sum w^\dagger(\Delta^\dagger)^2$$
$$= \sum w^\dagger[\Delta^2 - \sum_i a_i T_i^*(F)]^2$$

over all reflexions. The weights used in this minimization are $w^\dagger = (1/F_{max})^P/(1 + F_o^P)$, in which P is usually 2. The elements of the normal matrix are given by

$$\sum w^\dagger T_i^*(F) T_l^*(F),$$

and the elements of the vector by

$$\sum w^\dagger T_i^*(F)\Delta^{\dagger 2},$$

where the summation is over all reflexions. The normal equations are solved for the Chebyshev coefficients, a_i, and the weights are then found from (1).

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