COMPUTER PROGRAMS

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XABS2: an empirical absorption correction program.

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Abstract

The *XABS2* Fortran program calculates an empirical absorption correction based on minimization of the differences between F^2_{obs} and F^2_{calc}. The basic algorithm has been used in the crystallography laboratory at the University of California, Davis for over a decade, in the form of the program *XABS*. *XABS* relied upon an approximately linear relationship for spherical crystals between the transmission factor and $\sin^2\theta$ for $\theta \lesssim 30°$ when $\mu R \lesssim 5$. In *XABS2*, deviations from linearity are accounted for by a cubic equation in $\sin^2\theta$, which makes it applicable over the whole range of diffraction angle. The program needs no data in addition to the unique set but assumes a bisecting (symmetric) data-collection mode on a four-circle diffractometer. Since it does not require knowledge of the diffractometer setting angles, it can be applied even in cases where details of the original data collection are unknown.

Introduction

Despite the availability of several correction techniques, absorption remains a serious source of error in single-crystal X-ray crystallography. In many cases, rigorous analytical or numerical corrections, which rely on accurate face indexing (Busing & Levy, 1957; Coppens, Leiserowitz & Rabinovich, 1965) are not applicable due to crystal morphology. Semi-empirical techniques based on azimuthal (ψ) scans or equivalent reflexions (North, Phillips & Mathews, 1968; Flack, 1974, 1977) require a great deal of data in addition to the unique set. Full ψ scans can be impossible to record on diffractometers equipped with low-temperature machinery, or for unfavorable crystal orientations on κ-axis diffractometers (Walker & Stuart, 1983). Intensity variations about the diffraction vector can result from anisotropic primary (Seiler & Dunitz, 1978) or secondary extinction (Coppens & Hamilton, 1970). Such corrections can depend strongly on the reflections chosen for the ψ scans. The *DIFABS* method of Walker & Stuart (1983) provides an empirical correction based on minimization of $(|F_{obs}| - |F_{calc}|)^2$ whereby up to 46 coefficients are used to model the transmission factor as a truncated Fourier series in polar angles.

The basic assumption made in *XABS2* is similar to that used in *DIFABS*; both rely on the observation that errors caused by slightly misplaced atoms are evenly distributed throughout reciprocal space, whereas absorption effects are more localized. The algorithms, however, are quite different.

The starting point for *XABS* (and *XABS2*) was to establish an approximate relationship between the absorption correction factor, A^*, and the diffraction angle, θ, that could be substituted into the equation

$$F^2_{corrected} = A^* F^2_{obs}. \quad (1)$$

It was found that the transmission factor A ($A = 1/A^*$) varies almost linearly with $\sin^2\theta$ up to $\theta \simeq 30°$ for values of $\mu R \lesssim 5$. The approximation

$$A = a_1 \sin^2\theta + a_2 \quad (2)$$

formed the basis of the original *XABS* program (Moezzi, 1987). For Cu $K\alpha$ data, however, where $2\theta_{max}$ is often 120° or more, this linear approximation breaks down. The variation of A with $\sin^2\theta$ and μR (see Figs. 1*a*,*b*) suggests that a cubic equation in $\sin^2\theta$ would give an excellent fit over the whole range $0 < \theta < 90°$, providing a transmission factor of the form

$$A = a_1 \sin^6\theta + a_2 \sin^4\theta + a_3 \sin^2\theta + a_4. \quad (3)$$

The four experiment-dependent coefficients a_n can be obtained in a least-squares fit that minimizes $w_2(F^2_{obs} - kAF^2_{calc})^2$, where $w_2 = 1/\sigma(F^2_{obs})^2$ and k is an overall scale factor. To generalize the method to crystals of arbitrary shape, the four terms a_n are expanded to six terms each, analogous to the usual treatment of anisotropic thermal parameters. The program provides a fast correction for absorption effects in cases where accurate structural parameters are required, but analytical rigour is not critical. The original *XABS* program has been an option in the Siemens *SHELXTL* package for some years, and although it has been used in many hundreds of structure determinations a description of the algorithm has never been published.

Algorithm

The following section describes the algorithm used in *XABS2*. That used in *XABS* is the same apart from the approximation for the transmission factor. In the case of a spherical crystal, the function to be minimized is

$$R_2 = \sum_{data} w_2 \left[F^2_{obs} - \left(\sum_{n=1}^{4} a_n \sin^{2(4-n)}\theta \right) k F^2_{calc} \right]^2. \quad (4)$$

This function is a minimum when its derivative with respect to each a_1, a_2, a_3 and a_4 is zero, *i.e.*

$$\frac{\partial R_2}{\partial a_{n'}} = \sum_{data} w_2 \left[F^2_{obs} - \left(\sum_{n=1}^{4} a_n \sin^{2(4-n)}\theta \right) k F^2_{calc} \right] \times k F^2_{calc} \sin^{2(4-n')}\theta = 0, \quad (5)$$

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where $n' = 1, 2, 3, 4$. Equation (5) can be rearranged to give the normal equations

$$\sum_{\text{data}} w_2\left(\sum_{n=1}^{4} a_n \sin^{2(4-n')}\theta\right)kF^2_{\text{calc}} \sin^{2(4-n')}\theta = \sum_{\text{data}} w_2 F^2_{\text{obs}} F^2_{\text{calc}} \sin^{2(4-n')}\theta \quad (6)$$

for $n' = 1, 2, 3, 4$. These are solved to give a_1, a_2, a_3 and a_4 and a correction is obtained for each reflexion using (3) [or (2) in *XABS*]. To generalize the algorithm to accommodate non-spherical crystals, the absorption surface is approximated as an ellipsoid and each of the a_n coefficients is expanded to six terms,

$$a_n(h_1h_2h_3) = \left(\frac{\lambda^2}{4\sin^2\theta}\right)\sum_{i=1}^{3}\sum_{j=1}^{3}(a_{nij}h_ih_ja_i^*a_j^*), \quad (7)$$

where h_1, h_2, h_3, a_1^*, a_2^* and a_3^* represent h, k, l, a^*, b^* and c^*, respectively, and $a_{nij} = a_{nji}$. Equation (7) is substituted into (4) to give

$$R_2 = \sum_{hkl} w_2\left\{F^2_{\text{obs}} - \left[\sum_{n=1}^{4}\left(\frac{\lambda^2}{4\sin^2\theta}\right) \times \sum_{i=1}^{3}\sum_{j=1}^{3}(a_{nij}h_ih_ja_i^*a_j^*)\sin^{2(4-n)}\theta\right]kF^2_{\text{calc}}\right\}^2, \quad (8)$$

which is a minimum when its derivative with respect to all 24 a_{nij} is zero, *i.e.*

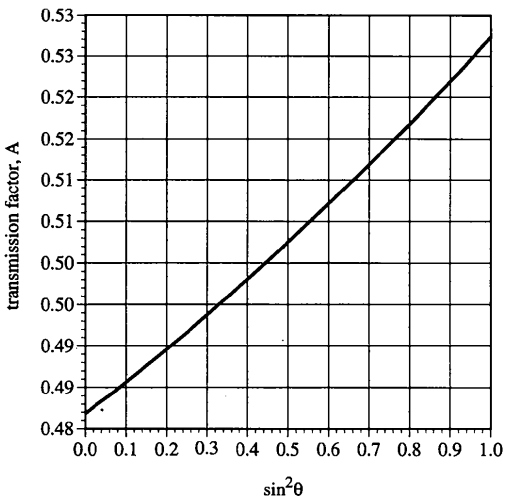
$$\frac{\partial R_2}{\partial a_{nij}} = \sum_{\text{data}} w_2\left[(F^2_{\text{obs}} - AkF^2_{\text{calc}})\left(kF^2_{\text{calc}}\frac{\partial A}{\partial a_{nij}}\right)\right] = 0. \quad (9)$$

The normal equations for the case of a non-spherical crystal are given by

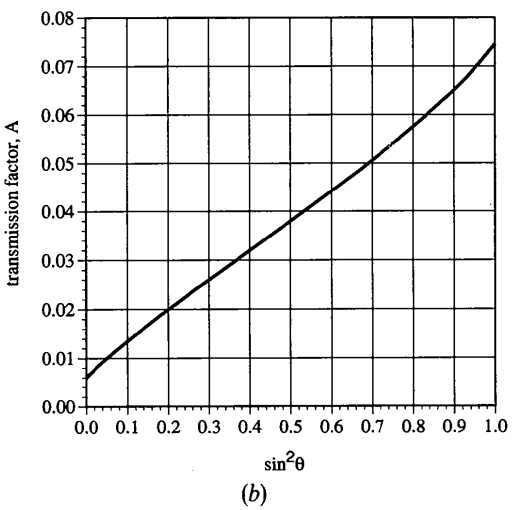
$$\sum_{\text{data}} w_2\left(\frac{\lambda^2}{4\sin^2\theta}\right)\left[\sum_{n=1}^{4}\sum_{i=1}^{3}\sum_{j=1}^{3}(a_{nij}h_ih_ja_i^*a_j^*)\sin^{2(4-n)}\theta\right] \times kF^4_{\text{calc}}(h_{i'}h_{j'}a_{i'}^*a_{j'}^*)\sin^{2(4-n')}\theta = \sum_{\text{data}} w_2F^2_{\text{obs}}F^2_{\text{calc}}(h_{i'}h_{j'}a_{i'}^*a_{j'}^*)\sin^{2(4-n')}\theta \quad (10)$$

for $n' = 1, 2, 3, 4$; $i' = 1, 2, 3$; $j' = 1, 2, 3$. These equations are solved to give the 24 coefficients a_{nij} needed to calculate a transmission factor for each reflexion, according to

$$A = \sum_{n=1}^{4}\left\{\frac{\lambda^2\sin^{2(3-n)}\theta}{4}\right\}\sum_{i=1}^{3}\sum_{j=1}^{3}a_{nij}h_ih_ja_i^*a_j^*. \quad (11)$$



(*a*)



(*b*)

Fig. 1. (*a*) Plot of transmission factor *versus* $\sin^2\theta$ for a spherical crystal with $\mu R = 0.1$. (*b*) Plot of transmission factor *versus* $\sin^2\theta$ for a spherical crystal with $\mu R = 5.0$.

Program

XABS2 is written in Fortran (standard Fortran77, except for use of the DO WHILE construct) to interface with the *SHELXL93* refinement program (Sheldrick, 1993), although adaptation to other refinement-package formats would be trivial. It requires input files filename.fcf containing h, k, l, F^2_{calc}, F^2_{obs} and $\sigma(F^2_{\text{obs}})$ and filename.res containing wavelength and unit-cell dimensions.

XABS2 depends strongly on the quality of the calculated data set. Since thermal parameters, and anisotropic thermal parameters in particular, are known to be adversely influenced by absorption effects, the correction should normally be performed with data from a model with isotropic thermal parameters. In addition, there are several classes of reflexion that should be excluded from the process in which the terms needed for absorption correction are calculated. Reasonable default values to identify such reflexions are built in but, if required, the user is free to specify various parameters used to bypass data points. $\sin\theta_{\text{min}}$ can be set to skip low-angle reflexions that are obscured by the beamstop, or it can be increased as a means of ensuring that no reflexions suffering from serious extinction are used. $\sin\theta_{\text{max}}$ can also be changed, its default is 1. A parameter can be set to exclude measurements with poor counting statistics, so that only those with F^2_{obs} greater than some multiple of $\sigma(F^2_{\text{obs}})$ are used. Other selection criteria include rejection if F^2_{obs} is less than some fraction of F^2_{calc} and rejection if F^2_{obs} is greater than some fraction of

$F(000)^2$. In the latter case, the general decrease of intensity with diffraction angle is taken into account.

Nature dictates that all crystals are different and, if extinction is to be treated properly, its effects should be analyzed independently for each structure. If all affected data are properly screened, an extinction correction may need to be incorporated in subsequent refinements. On the other hand, if no screening is applied, *XABS2* correction factors for all reflexions will be influenced by those suffering from extinction. There is a chance that this could introduce bias, but in practice it makes little difference to parameters derived in routine structure determinations.

In crystals containing a few strong absorbers and a number of light atoms, the diffraction pattern is often dominated by the heaviest atoms. The strong correlation between their thermal parameters and the scale factor may mean that neither the scale factor nor thermal parameters for any atom can be satisfactorily refined. In such cases, if the heavy-atom U's are fixed at some reasonable value prior to application of *XABS2*, the gross effects of absorption can be accounted for so that, in subsequent refinements, all parameters may be refined together.

Examples

The original *XABS* program has been used in many hundreds of small-molecule structure determinations in the past decade or so. Specific examples include the structures of $[Ni(CN)_2\{P(CH_2OH)Ph_2\}_3]$ (Hope, Olmstead, Power & Viggiano, 1984), in which H-atom positions (including the hydroxyl H atom) were only apparent after correction, and various 2,6-bis(diphenylphosphino)pyridine complexes of Pt^{II} and Pd^{II} (Wood, Hvoslef, Hope & Balch, 1984), in which unavoidable errors caused by poor crystal quality were largely eliminated. The changes made to the method that are incorporated in *XABS2* make it applicable to a wider range of problems, and also improve its performance. The most obvious effects of its use are reduced noise levels in difference Fourier maps, which makes H atoms easier to find and disorder easier to interpret. There is also usually a dramatic drop in R indices. The new program has been tested on a variety of structures (Velazquez, Baumann, Olmstead, Hope, Barrett & Hoffman, 1993; Brock, Hope & Kauzlarich, 1994; Rehr, Kuromoto, Kauzlarich, Del Castillo & Webb, 1994; Balch, Ginwalla, Lee, Noll & Olmstead, 1994). [Although the latter paper does not reference *XABS2*, it was actually used (Olmstead, 1994)].

Comparison tests with other methods of absorption correction have also been performed on two crystals: 2,2′-ethylenebis(η^5-indenyl)$TiCl_2$ (Parkin, Hitchcock, Hope & Nantz, 1994) and $Os[(en)_2Cl_2]Cl$ (en = ethylenediamine) (Parkin, 1993). In both cases, correction with *XABS2* compares favorably with those obtained by the more rigorous numerical face-indexed and semi-empirical techniques (programs *ABSC* and *XEMP*; Sheldrick, 1989). The actual correction factors obtained by each of the three methods are very similar.

For 2,2′-ethylenebis(η^5-indenyl)$TiCl_2$, absorption effects were apparent but not particularly pronounced. The structure was disordered across a mirror plane, which precluded the location of any H atoms in difference electron-density maps. In the final difference map, however, the largest feature was reduced after *XABS2* from 0.94 to 0.29 $eÅ^{-3}$ and the R index [based on $F > 4\sigma(F)$] fell from 5.78 to 3.47%. Corresponding values obtained after the numerical correction were 0.33 $eÅ^{-3}$ and 4.15% and, after semi-empirical correction based on equivalents from a full sphere of data, they were 0.58 $eÅ^{-3}$ and 4.42%.

Absorption was more of a problem in the crystal of $Os[(en)_2Cl_2]Cl$, whose irregular shape prevented application of the numerical correction. It had a linear absorption coefficient of 26.67 mm^{-1} for Cu $K\alpha$ radiation; although it was fairly small (0.12 × 0.10 × 0.08 mm), absorption effects were noticeable. Before correction, assignment of difference electron-density peaks as H atoms was not satisfactory and attempts to refine anisotropic thermal parameters did not yield meaningful results. After correction by *XABS2*, H atoms were readily assignable and the problems with non-positive-definite anisotropic thermal parameters were alleviated. The largest peak in a difference electron-density map decreased from 2.79 to 0.39 $eÅ^{-3}$ and the R index dropped from 4.15 to 1.96%. A semi-empirical correction (program *XEMP*; Sheldrick, 1989) based on all equivalent reflexions gave values of 0.54 $eÅ^{-3}$ and 2.43%.

XABS2 was also tested on two low-temperature protein structures, crambin and BPTI (Parkin, 1993). After correction, difference electron-density maps were cleaner, which facilitated the identification of water molecules. There were also large reductions in the R indices from about 10 to 7.3% for crambin and 16 to 12.7% for BPTI.

Concluding remarks

XABS2 provides a rapid, generally applicable, correction for absorption effects when accurate structural parameters are required but more rigorous techniques either cannot be used or are unavailable. Since the method relies on a calculated data set to formulate the correction, care should be taken to ensure as much validity as possible for the approximation. It should normally be applied when as many atoms as possible have been located and refined to convergence with isotropic thermal parameters and an appropriate weighting scheme. The way in which absorption can affect thermal parameters, particularly *via* the relative enhancement of intensity at high angle, means that the method should be used with caution for strong absorbers. In such cases, it may be advisable to perform a numerical semi-empirical or at least an equivalent-sphere correction prior to the application of *XABS2*. As a result of the difficulty of indexing and measuring crystal faces, and the assumptions implicit in correcting the purely θ-dependent part of the absorption surface in semi-empirical methods, it is likely that these techniques often leave some residual effects, which *XABS2* can reduce. In principle, *XABS2* can correct for any slowly varying change in scale factor, such as those created by truncated scans or a crystal longer than the beam cross section. These kinds of systematic error, however, should be identified and the appropriate action taken prior to data collection.

The program can be obtained from either the first or the third author by e-mail; the addresses are sp@oedipus.llnl.gov and hhope@ucdavis.edu, respectively. It is also available *via* anonymous ftp from oedipus.llnl.gov in the directory /pub/xabs.

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This program has been used successfully, without assistance from the authors, by Dr Jeff W. Kampf, Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, USA.

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