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An Improvement in the Algorithm for Absorption Correction by the Analytical Method

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The most time-consuming step in the analytical method for absorption correction is the examination for each Howells polyhedron of the large number of tetrahedra formed from all possible sets of one auxiliary point with the faces of previously found tetrahedra. In the present method, a formula is presented for the absorption of a polyhedron (a slice) with two parallel faces, which are planes of constant absorption. With this formula, the absorption of a Howells polyhedron can be calculated, with much less effort, by systematically dividing it into slices.

Introduction

Absorption correction by the analytical method has the immense advantage over numerical integration of being exact, but it suffers from being slower in most circumstances. This paper presents an alternative method of calculation that increases the speed; it may also be of value in other problems concerned with absorption and extinction.

The nomenclature used is that of De Meulenaer & Tompa (1965) and Alcock (1970), and a sample calculation is presented based on the example of the latter.

The analytical calculation has several sections for each reflexion. These are, with the relative times taken (by the Fortran program *ABSCOR* running within the X-Ray 63 system):

- | | |
|---|----|
| (i) calculation of the diffraction angles and general overheads, | 9% |
| (ii) finding the auxiliary points, | 29 |
| (iii) selecting those points which are the vertices of each Howells polyhedron, | 11 |

- | | |
|--|----|
| (iv) calculating the transmission for each Howells polyhedron, | 51 |
|--|----|

Stages (iii) and (iv) are considered here. Stage (iii) can be reduced by storing for each point a list of the Howells polyhedra it can contribute to, once the point is found. This leaves stage (iv) as the most important.

A Howells polyhedron is defined as the portion of a crystal which is reached by rays entering the crystal through one particular face and leaving through one particular face (possibly the same one). This means (De Meulenaer & Tompa, 1965) that within the polyhedron, the loci of points of constant absorption are a series of parallel planes on which the rays have constant path length in the crystal. These planes may be arbitrarily oriented in relation to the polyhedron vertices and faces. In the original method, the explicit formula for the transmission of a general tetrahedron is used. The polyhedron is split up into its component tetrahedra by considering all combinations of a face and a vertex, and discarding those not producing genuine tetrahedra.

In the present approach, the total transmission of a polyhedron is obtained differently. The polyhedron is divided into slices by planes parallel to the loci of constant absorption, so that each vertex lies on a plane (such as the shaded plane of Fig. 1). Each slice is then considered separately. It is bounded by two parallel planes and its own vertices are either vertices of the original Howells polyhedron, or lie on an edge between two such vertices (Fig. 1). A transformation (a pure rotation) is applied so that the z axis is perpendicular to the parallel planes, and the contribution to the absorption of this slice can then be readily calculated.

Contribution of a slice

The area of a convex polygon in a plane (A) perpendicular to the z axis, whose vertices have coordinates x_i, y_i, z_A is:

$$D_A = \frac{1}{2} \sum_{i=1}^N (x_i y_{i+1} - y_i x_{i+1}) = \frac{1}{2} E \quad (1)$$

(with a cyclic indexing). To obtain the volume of a slice, the vertices of the top and bottom planes must be made to correspond by introducing extra dummy vertices wherever two edges from vertices on one bounding plane meet at one vertex on the other plane (as at 3 in Fig. 1).

Then, the coordinates of a point on an edge of the slice between the i th vertices on planes A and B are $(x_i + t\delta x_i); (y_i + t\delta y_i); (z_A + t\delta z)$ where $\delta x_i, \delta y_i, \delta z$ are the differences in x, y and z coordinates for the i th vertices on planes A and B , and t is the fractional distance of the point from plane A to plane B . The area of the polyhedron at level T (fractional coordinate t) is:

$$D_t = \frac{1}{2} \sum_{i=1}^N (x_i + t\delta x_i) (y_{i+1} + t\delta y_{i+1}) - (x_{i+1} + t\delta x_{i+1}) (y_i + t\delta y_i) \quad (2)$$

$$= \frac{1}{2} (E + tF + t^2G) \quad (3)$$

with E as given in equation (1),

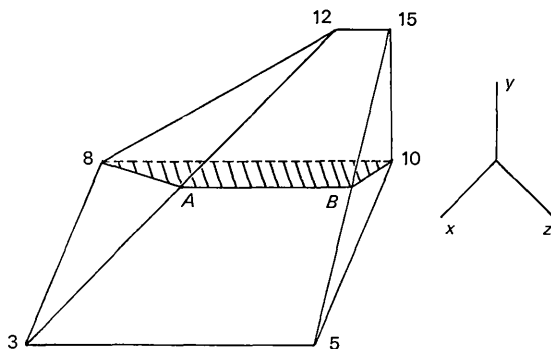


Fig. 1. A perspective view of the Howells polyhedron from the crystal (Fig. 2) of Alcock (1970) lit through faces 7 and 11. The shaded plane is one of constant absorption, passing through points 8 and 10 and the interpolated points A and B . The axes shown are the original and not the rotated ones.

$$F = \sum_{i=1}^N \delta x_i y_{i+1} + \delta y_{i+1} x_i - \delta x_{i+1} y_i - \delta y_i x_{i+1}$$

and

$$G = \sum_{i=1}^N \delta x_i \delta y_{i+1} - \delta y_i \delta x_{i+1}.$$

The total volume of the slice is:

$$V_S = \int_{z_A}^{z_B} D_t dz \quad (4)$$

or, substituting from $t = (z_i - z_A)/(z_B - z_A)$, i.e.

$$dt = dz/(z_B - z_A),$$

$$V_S = \frac{1}{2} (z_B - z_A) \int_0^1 (E + tF + t^2G) dt = \frac{1}{2} (z_B - z_A) (E + F/2 + G/3). \quad (5)$$

In the absence of absorption, the diffracted power is proportional to this volume, but when absorption is present, the diffraction from a plane of the slice is given by

$$D_t \exp(-\mu P_t) dz$$

where P_t is the path length (incoming and outgoing) of rays diffracted in this plane. Because of the definition of the Howells polyhedron, P_t is given by

$$P_t = P_A + t\delta P$$

where P_A is the path length to plane A , and δP the difference between planes A and B ,

$$\delta P = P_B - P_A.$$

The total diffracted power is

$$R_S = \int_{z_A}^{z_B} D_t \exp(-\mu P_t) dz$$

or,

$$R_S = \frac{1}{2} (z_B - z_A) \exp(-\mu P_A) \times \int_0^1 (E + tF + t^2G) \exp(-\mu t\delta P) dt \quad (6)$$

$$= \frac{1}{2} (z_B - z_A) \exp(-\mu P_A) \times [\exp(-\mu t\delta P) \{ -E/\mu\delta P - F(\mu t\delta P + 1)/\mu^2(\delta P)^2 - G[\mu^2 t^2(\delta P)^2 + 2\mu t\delta P + 2]/\mu^3(\delta P)^3 \}]_0^1 \quad (7)$$

$$= \frac{1}{2} (z_B - z_A) \exp(-\mu P_A) \exp(-\mu\delta P) \times \{ -E/\mu\delta P - F(\mu\delta P + 1)/\mu^2(\delta P)^2 - G[\mu^2(\delta P)^2 + 2\mu\delta P + 2]/\mu^3(\delta P)^3 \} - \frac{1}{2} (z_B - z_A) \exp(-\mu P_A) \times [-E/\mu\delta P - F/\mu^2(\delta P)^2 - 2G/\mu^3(\delta P)^3] \quad (8)$$

which can be used more conveniently by substituting in the first term:

$$\exp(-\mu P_B) = \exp(-\mu P_A) \exp(-\mu\delta P).$$

The transmission of the Howells polyhedron is given by the sum of the R_S values for each slice, and that for the whole crystal, R_T , by summing the transmission of each polyhedron. The transmission factor is then

simply $A=R_T/V_T$ (V_T =total crystal volume). To determine $dA/d\mu$ for the extinction correction, R_S for each slice can readily be differentiated with respect to μ , and these derivatives summed and divided by V_T in the same way. This is an improvement on the numerical method used in *ABSCOR* which suffers from rounding errors if μ is small or if the computer has a short word length, although analytical differentiation may also be possible there.

Application to a polyhedron

A Howells polyhedron is defined by the coordinates of its vertices relative to the standard orthogonal axes on which the crystal is defined. These vertices are arranged in order of increasing path length (P_i , of the rays through the crystal) and they must be converted to the axis set with z normal to the planes of constant path length. This can always be achieved by two rotations, about the x axis by θ and about the y axis by φ , *i.e.* by a matrix of form

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & \sin \theta \\ 0 & -\sin \theta & \cos \theta \end{bmatrix} \begin{bmatrix} \cos \varphi & 0 & -\sin \varphi \\ 0 & 1 & 0 \\ \sin \varphi & 0 & \cos \varphi \end{bmatrix} \\ = \begin{bmatrix} \cos \varphi & 0 & -\sin \varphi \\ \sin \theta \sin \varphi & \cos \theta & \sin \theta \cos \varphi \\ \cos \theta \sin \varphi & -\sin \theta & \cos \theta \cos \varphi \end{bmatrix}. \quad (9)$$

A convenient method of obtaining such a matrix is given in the Appendix.

With the vertices arranged in order of increasing path length, the polyhedron can be divided into slices by planes through the vertices corresponding to each different path length found. To achieve the necessary correspondence between the vertices on the top and bottom of each slice, these have to be in sequence, and the edges joining each vertex to vertices on the next slice must be identified, so that any dummy vertices can be inserted.

This identification of corresponding points on the top and bottom of a slice would be very difficult just from the vertices of the Howells polyhedron, but fortunately the edges of the polyhedron obey definite rules, and when each auxiliary point is found [stage (ii)] a list can be made of all the possible edges joining it to auxiliary points already known. The rules for these connexions are in Table 1.* For a particular Howells polyhedron the edges can then be extracted from the complete list.

The ordering of the points bounding one slice so that they form a convex polyhedron has proved to be the trickiest aspect of these calculations. These points may be either vertices of the Howells polyhedron, or points interpolated between two vertices. The general procedure is as follows. Starting with one of the points at one level (already ordered), the edges that descend from it are examined. Each such edge will correspond to a

Table 1. *Rules for joining edges in the polyhedron*

Point	Connected to preceding points
Vertex	<i>A</i> To another vertex by an edge of the original crystal.
<i>SP0</i>	<i>B</i> To the vertex generating it (V_1). <i>C</i> To the second vertex of any edge from V_1 that lies in the face containing the <i>SP0</i> . <i>D</i> To another <i>SP0</i> in the same face, generated by a vertex connected to V_1 by a crystal edge.
<i>SPQ</i>	<i>E</i> To the <i>SP0</i> generating it. <i>F</i> To the vertex (V_1) generating this <i>SP0</i> . <i>G</i> To the vertices (V_2 , and/or V_3) of the edge which generates the <i>SPQ</i> if they are joined to the <i>SP0</i> or to V_1 . <i>H</i> An <i>S21</i> is connected to an <i>S12</i> if the V_1 of the <i>S21</i> is the same as the V_2 or V_3 of the <i>S12</i> and the V_1 of the <i>S12</i> is the same as the V_2 or V_3 of the <i>S21</i> .
<i>S0P</i>	<i>I</i> To the vertices at the ends of the edge containing it. <i>J</i> To any other <i>S0P</i> or <i>S0Q</i> in the same edge. <i>K</i> To an <i>S0P</i> in the same face that is generated by the same edge. <i>L</i> To an <i>SP0</i> in the same face that is generated by a vertex of the generating edge. <i>M</i> To a vertex of the generating edge, if it and the <i>S0P</i> lie in the same face. <i>N</i> To an <i>SQP</i> if the V_1 of the <i>SQP</i> lies in the edge containing the <i>S0P</i> and the <i>SQP</i> is generated by the edge generating the <i>S0P</i> . <i>O</i> An <i>S02</i> in edge <i>B</i> , generated by edge <i>A</i> , is linked to an <i>S01</i> in edge <i>A</i> , generated by edge <i>B</i> .
<i>S00</i>	<i>P</i> To the 4 points in the same face that produce it. <i>Q</i> To an <i>SPQ</i> if its vertex V_1 lies on the edge (<i>P</i>) generating the <i>S00</i> and the edge of the <i>SPQ</i> is the edge (<i>Q</i>) generating the <i>S00</i> . <i>R</i> To a vertex common to both the edges generating the <i>S00</i> . <i>S</i> To another <i>S00</i> in the same face with either the same edge (<i>P</i>) or the same edge (<i>Q</i>).

point in the next level. The edge may terminate in this next level at a vertex of the polyhedron, but if it descends further, a point must be interpolated. If each point on the upper level generated only one point on the lower level, these would automatically be ordered. Therefore an ordered list can be built up of the first points generated, plus an unordered list from any further points (with a note of which of the ordered points it relates to); all the points on the bottom of a slice that are generated by *one* point on the top of the slice must be adjacent. The procedure for ordering the points on the topmost level is similar. The first two points encountered form the ordered list and any further points form the unordered list.

For the insertion of the unordered points into the ordered list, a property of a convex polyhedron is used. The centre of gravity of any selection of its vertices lies within (or on the edge of) the polyhedron formed by the selected points and of polyhedra formed by these and other points. A new origin is chosen at the centre of gravity of the ordered points. Then, if point 3 is to be inserted either between points 1 and 2 or after

* These rules have not been deduced systematically and further connexions may possibly occur in complex cases.

point 2, a decision can be made by examining the line 1-2. If 3 is on the opposite side of the line from the origin, *i.e.* its distance from the line is positive, then to retain a *convex* polygon it must be inserted between points 1 and 2. In the special case of the origin falling on the line 1-2, a positive distance corresponds to an order 1-3-2. If point 3 coincides with points 1 or 2 then its position is decided by considering which point on the previous level it is connected to.

Example

Fig. 2 shows a crystal with the auxiliary points that are found in stage (ii) of the absorption calculation (Alcock, 1970). At the same time the edges, which will be the edges of the Howells polyhedra, are obtained. These are given in Table 2. The Howells polyhedron lit through faces 7 and 1 can be used to illustrate the rest of the calculation, and is shown in Fig. 1. Its coordinates and path lengths are given in Table 3. A rotation matrix calculated as in the Appendix is:

$$\begin{bmatrix} -0.8988 & 0.00 & 0.4383 \\ -0.2930 & 0.7437 & -0.6009 \\ -0.3260 & -0.6685 & -0.6685 \end{bmatrix}$$

and this gives the rotated coordinates in Table 3. There are two points with minimum path length, 3 and 5, arbitrarily taken to be in this order. One edge joins 3 to 5 at the same level, and two edges descend from 3. The first goes to 8 at the next level. This therefore starts the list of ordered points at level 2. The second edge goes to 12 at level 3 and so point *A* must be interpolated at level 2. Its order relative to point 8 is unknown. Similarly, considering 5, point 10 is added to the ordered list and an interpolated point *B* to the unordered list.

The centre of gravity of the ordered points lies midway between 8 and 10, and the distance of the point *A* from line 8-10 is calculated positive. *A* is

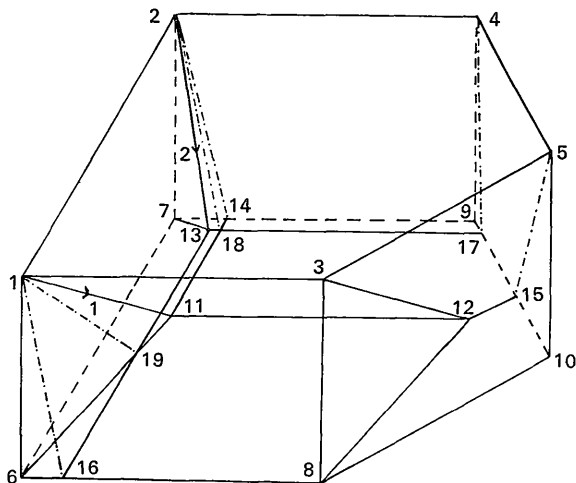


Fig. 2. The crystal of Alcock (1970) showing the vertices and the auxiliary points. For clarity, this crystal was chosen to avoid any points of type *SPQ*. Face 7 is bounded by vertices 3, 5, 8, 10 and face 1 by vertices 1, 2, 3, 4, 5.

Table 2. Edges of the Howells polyhedra for the example given in the text

Point	Type	Connexions
11	S10	1 by B; 6 by C
12	S10	3 by B; 8 by C; 11 by D
13	S20	2 by B; 7 by C
14	S01	2 by M; 7 by I; 9 by I; 11 by L
15	S01	5 by M; 9 by I; 10 by I; 12 by L
16	S02	1 by M; 6 by I; 8 by I; 13 by L
17	S02	4 by M; 9 by I; 10 by I; 13 by L; 15 by J
18	S00	2 by R; 11 by P; 13 by P; 14 by P; 17 by P
19	S00	1 by R; 6 by P; 11 by P; 13 by P; 16 by P

therefore inserted to give the order 8-A-10 (*i.e.* 10-8-A by cyclic permutation). *B* is then examined in relation to point 10, and specifically the line A-10; it has a positive distance from this line and so is inserted before 10, giving a final order 8-A-B-10. The calculations for the first slice can now be made using these points and points 3 and 5 (both doubled) to give *E*, *F* and *G* of equation (3) as in Table 3, a volume of 11.71 and a diffracting power of 3.48. For the second slice, the order of points 12 and 15 follows automatically, and the calculations give a volume of 11.17 and a diffracting power of 0.78.

Results

After incorporating the algorithm described here, and after combining the selection of points for Howells polyhedra with their finding, the times taken for the various parts of the program are (in arbitrary units):

	New	
Finding and selecting points	32	42%
Transmission of polyhedra	34	45
Angle and other calculations	9	12
	<hr/> 75	
	Old	
Finding points	29	
Selecting points	11	
Transmission of polyhedra	51	
Angle and other calculations	9	
	<hr/> 100	

Thus there has been an overall saving of 25%. The test crystal is a simple one with only seven faces and for more complex cases the saving should be greater. There is a penalty, the increased storage needed for the array containing the edges of the Howells polyhedra.

Further gains in speed must come from improvements in stage (ii). One suggestion has been made by Dr H. Tompa (private communication) but has not been tested in a program. This is to speed up the calculation of intersections of rays and faces, and hence of the coordinates of the auxiliary points by transforming the crystal for each reflexion to a set of non-orthogonal axes with *x* as the incoming ray direction, *y* as the outgoing ray direction and *z* chosen conveniently. The

Table 3. *Statistics for the example given in the text*

Point	Optical path length	Original coordinates			Rotated coordinates		
		x	y	z	x	y	z
3	0.0	2.5	3.75	-2.5	-3.34	3.56	-1.65
5	0.0	2.5	0.0	1.25	-1.70	-1.48	-1.65
8	2.04	-2.5	3.75	-2.5	1.15	5.02	-0.02
10	2.04	-2.5	0.0	1.25	2.79	-0.02	-0.02
12	4.83	-2.5	0.92	-1.15	1.74	0.74	2.21
15	4.83	-2.5	-1.67	-0.42	2.06	-0.26	2.21
Interpolated points							
A	2.04				-1.20	2.37	-0.02
B	2.04				-0.11	-0.97	-0.02

For slice 1: the vertices are paired and ordered

8	A	B	10
3	3	5	5

and $E=26.90$, $F=-21.41$, $G=-5.49$.

For slice 2: the vertices are paired and ordered

12	12	15	15
8	A	B	10

and $E=0.0$, $F=6.37$, $G=20.53$.

return to orthogonal coordinates could be made at the same stage as the rotation of individual polyhedra described above.

Another place for improvement may be the treatment of coincident sets of auxiliary points. These may occasionally arise by chance, but appear systematically when ray 1 through one vertex (A) intersects ray 2 through another vertex (B). This happens when the plane containing ray 1 and ray 2 is parallel to the edge joining vertices (A) and (B). The result is that two S_{12} and two S_{21} points all coincide. At present coincident points are tested for and eliminated during stage (iv) but it would probably be better to eliminate the coincident points during stage (ii), naming a new type of point (SAB) formed by the intersection of a ray 1 through vertex (A) with a ray 2 through vertex (B), combining the properties of the original S_{12} and S_{21} points.

APPENDIX

BY M. R. LEVINE

Work first presented by Levine (1965) has been incorporated in a method of obtaining the rotation matrix to make the planes of constant absorption correspond to constant z coordinate. Consider a reflecting point x', y', z' whose incident ray passes through face 1

$$a_1x + b_1y + c_1z = d_1$$

and whose diffracted ray passes through face 2

$$a_2x + b_2y + c_2z = d_2.$$

The path length, p , through the crystal of a ray diffracted at x', y', z' is then

$$p = \frac{d_1 - a_1x' - b_1y' - c_1z'}{\cos \alpha_1 \sqrt{a_1^2 + b_1^2 + c_1^2}} + \frac{d_2 - a_2x' - b_2y' - c_2z'}{\cos \alpha_2 \sqrt{a_2^2 + b_2^2 + c_2^2}} \quad (10)$$

where α_1 and α_2 are the angles between ray 1 and the normal to face 1, and ray 2 and the normal to face 2. For a particular value of p , equation (10) is the equation of the plane for which the path length has this value. If a_1, b_1, c_1 and a_2, b_2, c_2 are already normalized, then the direction cosines of the normal to the plane of constant absorption are proportional to

$$\left(\frac{a_1}{\cos \alpha_1} + \frac{a_2}{\cos \alpha_2}, \frac{b_1}{\cos \alpha_1} + \frac{b_2}{\cos \alpha_2}, \frac{c_1}{\cos \alpha_1} + \frac{c_2}{\cos \alpha_2} \right)$$

and these can be normalized to give the actual cosines a_3, b_3, c_3 . For the one special case, where the path length is constant through the whole volume of the polyhedron, all three cosines are zero, and this can easily be detected. This arises if the rays are entering and leaving the crystal through parallel faces and make equal angles with the normals of these two faces.

The required rotation matrix must convert

$$(a_3, b_3, c_3) \text{ to } (0, 0, 1)$$

and a matrix of the form given above, (9), is suitable. The equations of the form

$$a_3 \cos \varphi - c_3 \sin \varphi = 0$$

etc. can readily be solved for suitable (not necessarily unique) values of $\sin \varphi$, $\cos \varphi$, $\sin \theta$ and $\cos \theta$.

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