We obtain the right-hand sides of (6) by matrix subtraction $[x_i] - [y_{m+1}^+] = [w]$ and matrix multiplication $[w][v] = [z]$. The rows of the matrix $[z]$ give the right-hand sides of equations in systems (6), e.g. the matrix element $z_m$ is the right-hand side of the nth equation in the mth system. The zeros in the last column of matrix $[z]$ are not considered here. Note that the matrix multiplication $[x][w]^T$ leads to the transposed matrix $[z]^T$, the columns of which are right-hand sides of the systems (6).

### Initial approximation

For the calculation of the initial approximation, Fiala (1980, 1982) suggested relations

$$c_{ij}^{(1)} = e_{ij}b_j \quad i = 1, \ldots, p; j = 1, \ldots, k$$

(7)

where $b_j$ are the solutions of the system of linear algebraic equations

$$\sum_{i=1}^{p} e_i c_{ij} b_j = \sum_{j=1}^{k} e_{ij} \quad j = 1, \ldots, k$$

(8)

and

$$e_{ij} = x_{ij} \left( \sum_{i=1}^{p} x_{ij}^2 \right)^{-1/2} \quad i = 1, \ldots, p; \quad j = 1, \ldots, k$$

(9)

$x_{ij}$ are the measured intensities of $k$ isolated diffraction lines in $p$ mixtures.

In concluding our considerations let us mention that the matrix formulation can be used also in the calculation of the initial approximation. It is easy to see that the matrix of system (8) is equal to the matrix product $[e_{ij}]^T[e_{ij}]$. However, this last statement is probably known in the theory of overestimated systems of linear algebraic equations. The system (8) is in fact a consequence of the system

$$\sum_{j=1}^{k} e_{ij} b_j = 1 \quad i = 1, \ldots, p,$$

(10)

which can generally have more equations than unknown quantities. The system (8) then determines the best estimates of the solution of the system (10) in the sense of least squares (Fiala, 1980, 1982).

### Concluding remarks

The matrix calculus allows the iterative process to be described in a lucid and compact form and enables at the same time the effective utilization of the matrix subroutines implemented practically in each computer. In cases where the mentioned systems of equations are unstable (Braun, 1986) it is possible to use the method for solution of ill-posed problems (e.g. Tikhonov & Arsenin, 1986). The matrix formulation is then extremely useful.

I thank Dr Jan Čermák, CSc for checking this manuscript and for stimulating discussions.

### References


### Computer Programs


**An automated full-symmetry Patterson search method.** By JORDI RIUS and CARLES MIRAVITLLES, Instituto de Ciencia de Materiales (CSIC), c/ Martí i Franqués, s/n, Apartado de Correos 30102, 08028 Barcelona, Spain

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**Abstract**

A full-symmetry Patterson search method is presented that performs a molecular coarse rotation search in vector space and orientation refinement using the $\sigma$ function. The oriented molecule is positioned using the fast translation function $\tau_0$, which is based on the automated interpretation of $\tau$ projections using the sum function. This strategy reduces the number of Patterson-function values to be stored in the rotation search, and the use of the $\tau_0$ function minimizes the required time for the development of all probable rotation search solutions. The application of this method to five representative test examples is shown.

**Introduction**

As is well known, the process of positioning a randomly oriented molecular fragment with rigid geometry in the unit cell can be split in the most general case into two three-dimensional searches, i.e. a rotation search followed by a translation search.

Most existing Patterson search methods execute the rotation search either in direct (vector) space, e.g. Braun, Hornstra & Leenhouts (1969), Nordman & Schilling (1970), Egert & Sheldrick (1985), or in reciprocal space, e.g. Rossmann & Blow (1962), Tollin & Cochran (1964), Crowther (1972), Tollin (1976), Langs (1986). Here, a rotation-search
strategy is discussed which performs the coarse angular scan
in vector space and the fragment orientation refinement in
reciprocal space by using the $\sigma$ function (Tollin, 1976).
Owing to the complementary properties of the rotation
functions in both spaces, a simple procedure results.

Traditionally, automated translation searches coupled to
rotation searches were performed using Patterson methods,
e.g. Braun et al. (1969), Nordman & Schilling (1970).
However, some vector-space translation searches are very
time consuming for complex structures (Doesburg & Beur-
skens, 1983). To overcome this problem, increasing attention
has been paid to alternative methods; for example, the
TRADIR procedure uses 'strengthened translation func-
tions' (Doesburg & Beurskens, 1983); the PATSEE program
(Egert & Sheldrick, 1985) maximizes the sum of the cosines
of a small number of strong translation-sensitive triple-
phase invariants. Here, the utility of the fast translation
function $r_0$, which is based on the automated interpretation
of $\tau$ projections using the sum function, is shown (Rius &
Miravitlles, 1986). The $\tau$ and $r_0$ functions also preserve in
the translation search the inherent advantages of all Patterson
methods, i.e. the reflections are handled independently and
not in an interrelated manner as in direct methods (Egert,
1983). This can be of particular importance when the number
of available reflections is small, e.g. when trying to
solve a crystal structure from a powder pattern.

### Rotation search

The rotation search for small rigid molecules is usually
executed in vector space, e.g. Hornstra (1970), Nordman
of vector-space methods is the compromise between the
storage of the whole Patterson function in core memory and
the accuracy of the stored Patterson values. The combi-
nation of the coarse rotation search in vector space, the
orientation refinement with the $\sigma$ function and the trans-
lation search with the $r_0$ function reduces the number of
Patterson values to be stored to a sphere of radius $5\lambda$ A
centred at the origin, i.e. 125 000 values for a uniform grid
with spacing 0.2 A. This allows the storage of each function
value in one byte of memory (a digit between 0 and 127),
even for relatively small computers.

The $\sigma$ function is used to refine previously found fragment
orientations. This strategy takes advantage of the sharp $\sigma$
peaks that are a consequence of the implicit consideration of
all intramolecular vectors, and minimizes the number of
$\sigma$ sampling points, thus reducing the incidence of its rather
slow computation.

The orientation of a fragment relative to a fixed co-
ordinate system can be described by three Eulerian angles,
or alternatively by a triplet of spherical polar angles ($\psi$, $\varphi$, $\chi$),
where $\psi$ = longitude and $\varphi$ = co-latitude define an axial
direction and $\chi$ is the spin about the axis. To minimize the
number of orientations to be tested in the coarse scan (mean
rotation increment of $7^\circ$), a network of points ($\psi$, $\varphi$) on
the sphere is defined (Beurkens, Beurskens, Strumpel & Nord-
man, 1984). For a molecular fragment without internal
symmetry the angular scan ranges for the rotation function
are: $0 \leq \psi \leq 360^\circ$, $0 \leq \varphi \leq 90^\circ$ and $0 \leq \chi \leq 360^\circ$. In the
evaluation of the rotation function, the time-consuming
computation of the coordinates of the rotated intramo-

### Translation search

From a practical standpoint, a translation search linked to a
rotation search must be fast enough to develop all probable
rotation-search solutions. The translation-search procedure
described here is based on the interpretation of the observed
cross-Patterson function using the fast full-symmetry trans-
lation function $r_0$ derived from the $\tau$ function (Rius &
Miravitlles, 1986), and is valid for the location of molecular
fragments as well as single heavy atoms. $r_0$ results from
considering in the expression of the $\tau$ function only those
Fourier terms having at least one component of $h_{ij} = h(R_i - R_j)$
equal to zero ($R_i$, $R_j$ = point-symmetry rotation
matrices). From a physical point of view, $r_0$ nearly
represents the automated interpretation of $\tau$ projections using the
sum function and is computed, in the most general case, with
three two-dimensional syntheses.

For most commonly occurring non-centrosymmetric space groups the $r_0$ calculation is very fast, since only one-
or two-dimensional Fourier syntheses are involved (Table 1).

### Table 1. Translation search for all non-cubic space groups

<table>
<thead>
<tr>
<th>Point symmetry of space group</th>
<th>$N$</th>
<th>$D$</th>
<th>$N_0$</th>
<th>$D_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>m</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2, mm2, 31m, 6, 6mm, 3,</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>3m1, 3m, 4, 4mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>222</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>$\frac{1}{2}$m, mmm, 4, 4/m, 422,</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>42m, 4m2, 4/mmm, 312.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6, 6m2, 3, 321, 31m, 3m1,</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>622, 62m, 6/m, 6/mmm, 32.3m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In these space groups, the matrix $R_k - R_j$ always has one zero column, so that at least one $h_{ij}$ component will always be zero. Since all Fourier terms are included in $\tau_0$, $\tau_0$ and $\tau$ are here equivalent, e.g. for space groups with 222 point symmetry.

For the remaining space groups, however, the $\tau$ function possesses a variable number of terms with all three $h_{ij}$ components different from zero, e.g. for all centrosymmetric space groups. In fact, for the extreme case of $P1$, the matrix $R_k - R_j$ always contains only non-zero columns, so that the only contributing reflections have are of the type $hk0$, $h0l$ and $0kl$.

$\tau_0$ is specially useful for high-symmetry space groups, i.e. those with 12 symmetry operations or more, since its computation, unlike the $\tau$ calculation, does not require the storage in core memory or in a data file of the real and imaginary coefficients of the $\tau$ terms.

All test examples so far performed indicate that the solution, i.e. the correct fragment translation, is always among the highest-ranked $\tau_0$ peaks.

### Test examples

This rotation/translation search procedure has been tested on about 25 structures. To show its usefulness, several representative test structures have been selected. These are the $\alpha$-D-mannoside BED, the three natural products AURO (auropolin), RAR (heliangolidin) and TURIO (a sesquiterpene), and a dimer of precocene II 3,4-epoxide PRECO. Relevant crystal and test data are in Table 2. The sizes of the search fragments are of the same order as those used by other authors, e.g. Egert & Sheldrick (1985), and were obtained from related compounds with the exception of TURIO. Owing to the difficulty of finding a suitable search model, a structure fragment consisting of a six-membered ring and two more C atoms was employed.

The rotation-search results in Table 2 confirm the observations of other authors; for instance, low-symmetry space groups are usually easier and rotation searches usually present fewer ambiguities than translation searches (Nordman & Hsu, 1982).

<table>
<thead>
<tr>
<th>Code name</th>
<th>BED$^a$</th>
<th>AURO$^b$</th>
<th>RAR$^c$</th>
<th>PRECO$^d$</th>
<th>TURIO$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>$C_{26}H_{24}NaO_4$</td>
<td>$C_{24}H_{34}O_9$</td>
<td>$C_{11}H_{22}O_5$</td>
<td>$C_{26}H_{32}O_8$</td>
<td>$C_{11}H_{24}O_2.H_2O$</td>
</tr>
<tr>
<td>Space group</td>
<td>$I4$</td>
<td>$P2_12_12_1$</td>
<td>$P2_12_12_1$</td>
<td>$Pc$</td>
<td>$P6_322$</td>
</tr>
<tr>
<td>$Z$</td>
<td>8</td>
<td>4</td>
<td>4</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td>Number of observed reflections $[F &gt; 3\sigma(F)]$</td>
<td>1693</td>
<td>766</td>
<td>1240</td>
<td>1933</td>
<td>1273</td>
</tr>
<tr>
<td>Model size</td>
<td>10</td>
<td>12</td>
<td>8</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>Scattering fraction</td>
<td>0.31</td>
<td>0.36</td>
<td>0.33</td>
<td>0.26</td>
<td>0.38</td>
</tr>
<tr>
<td>$\sigma_0/\sigma_w$</td>
<td>1.08</td>
<td>1.61</td>
<td>1.47</td>
<td>1.01</td>
<td>-</td>
</tr>
<tr>
<td>$\tau_0/\tau_{\text{sw}}$</td>
<td>0.93</td>
<td>0.90</td>
<td>0.89</td>
<td>0.89</td>
<td>0.93</td>
</tr>
<tr>
<td>Rank number of correct $\tau_0$ peak</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>R.m.s. deviation of translated model from final coordinates (Å)</td>
<td>0.21</td>
<td>0.10</td>
<td>0.12</td>
<td>0.31</td>
<td>0.38</td>
</tr>
</tbody>
</table>

References: (a) Sheldrick, Davison & Trotter (1978); (b) Camps, Coll, Dargallo, Rius & Miravitlles (1987); (c) Breton et al. (1985); (d) Camps, Coll, Conchillo, Meseguer, Molins & Miravitlles (1985); (e) Braekman, Dalouze, Dupont, Turch, Declercq, Germain & Van Meerssche (1981).

All rotation searches were calculated with the Patterson function sampled on a grid of 0.18–0.25 Å in a sphere of radius 5 Å and with sharpened $|F_\ell|^2$. The number of $(\psi, \varphi)$ points on the hemisphere is 466 and $\Delta \varphi = 5^\circ$. This represents 33 552 rotation trials in the coarse scan, although the computing effort, after the introduction of the simplification due to the sine–cosine symmetries, is approximately equivalent to only 11 000 trials (for the sum function). The $\sigma$ function is calculated with modified $|F_\ell|^2$ to remove the contributions of the origin of the Patterson function as suggested by Tollin (1976). Only 250 terms corresponding to the reflections with strongest absolute modified $|F_\ell|^2$ values were used in the $\sigma$ summation $|(\sin \theta / \lambda)_{\max} = 0.45 \, \text{Å}^{-1}|$.

The results of the application of $\tau_0$ to BED, AURO and RAR (here equivalent to $\tau$) are quite satisfactory (Table 2). PRECO has been selected to illustrate the behaviour of $\tau_0$ when applied to a centrosymmetric structure. The search fragment used is small, i.e. only a fraction of precocene II 3,4-epoxide, and less reliable, owing to the distortion introduced in precocene II by the dimer formation. Even in this unfavourable case, $\tau_0$ shows a maximum at the correct position (ranking number = 7).

Finally, TURIO is an example of a non-centrosymmetric high-symmetry structure. The application of $\tau_0$ here is also quite satisfactory.

For large fragments, the $R$ index alone, i.e. $R = \sum |F_\ell| - |F_\ell|/k|/\sum |F_\ell|$ where only positive contributions to the numerator are considered (Egert & Sheldrick, 1985) and with $k^2 = \sum |F_\ell|^2/\sum |F_\ell|^2$, is a good indication of the correct solution. For small fragments, however, the $R$ index is less reliable. To discriminate the correct solution in these cases, a phase refinement can be applied systematically to all probable solutions, so that the figures of merit employed in direct methods can be used. According to the authors' experience, 15 phase refinements are usually sufficient to ensure that the correct solution is found, i.e. three probable rotations corresponding to the three highest $\sigma$ peaks, and five translations for each rotation (five best $R$ values in the first ten $\tau_0$ peaks).

**ROTSEARCH** is a computer program which automatically executes the various procedures outlined. The program
needs the usual crystal data, the observed structure factors and the fragment coordinates, either Cartesian or crystallographic (up to 100 atoms). All default values can easily be changed by experienced users. The final output consists of a list of atom coordinates for the solution with the best $R$ value. The program also creates a file with the 15 most probable rotation–translation combinations, which can easily be introduced in a direct-methods system to calculate the respective figures of merit. All test calculations were performed with \textit{ROTSEARCH}.

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\textsc{Camps}, F., \textsc{Coll}, J., \textsc{Dargallo}, O., \textsc{Rius}, J. \& \textsc{Miravitlles}, C. (1987). \textit{Phytochemistry}. In the press.


\textbf{Computer derivation of the symmetry elements implied in a structure description.} By \textsc{Y. Le Page}, \textit{Chemistry Division, National Research Council of Canada, Ottawa, Canada K1A OR9}

\textbf{(Received 22 December 1986; accepted 10 February 1987)}

\textbf{Abstract}

The space-group symmetry implied in the atomic coordinates of a structure can be reconstructed by deriving the metric symmetry elements of the lattice from the cell data, and finding the location and the glide for corresponding space-group symmetry elements with the same orientation using the list of atomic coordinates. The \textit{MISSYM} computer program designed along these principles treated correctly the known examples of overlooked symmetry or quasi-symmetry that were submitted to it. As no computer program operating on refined atomic coordinates can prove the presence of extra symmetry in the crystal, the user should scrutinize the experimental evidence and report either a different space group or the existence of pseudo-symmetry whenever extra structural symmetry elements are disclosed by the program. The \textit{MISSYM} program is part of the \textit{NRCVAX} system of programs.

\textbf{Introduction}

Several recent articles (see \textsc{Marsh} \& \textsc{Herbsteen}, 1983; \textsc{Baur} \& \textsc{Tillmans}, 1986 and references therein) point out that a significant number of examples of ‘subgroup refinement’ can be found in the recent literature: the reported atomic architecture is essentially correct, but the space group used is a subgroup of the correct space group, a deficiency which is compensated by extra entries in the list of independent atoms.

The examples have been conveniently classified into three classes in \textsc{Baur} \& \textsc{Tillmans} (1986 and references therein) point out that a significant number of examples of ‘subgroup refinement’ can be found in the recent literature: the reported atomic architecture is essentially correct, but the space group used is a subgroup of the correct space group, a deficiency which is compensated by extra entries in the list of independent atoms.

The examples have been conveniently classified into three classes in \textsc{Baur} \& \textsc{Tillmans} (1986): (1) change of crystal system, (2) change of Laue class without change of system, and (3) addition of an inversion center. A cell-reduction program will flag the examples in class 1, those in class 3 can be suspected from the large correlations between refinement parameters, but no general method is known for tackling examples in class 2. \textsc{Herbsteen} \& \textsc{Marsh} (1982) tackle the three classes by...