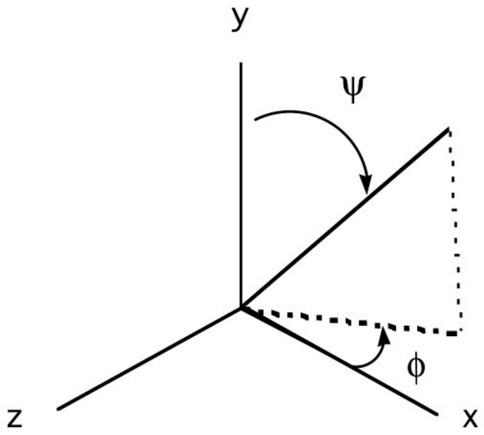
An Overview of Useful Mathematics for Crystallography



$$\begin{bmatrix} \cos\kappa+\sin^2\psi\cos^2\varphi(1-\cos\kappa) & \begin{matrix}\sin\psi\cos\psi\cos\varphi(1-\cos\kappa)\\ +\sin\psi\sin\varphi\sin\kappa\end{matrix} & \begin{matrix}-\sin^2\psi\cos\varphi\sin\varphi(1-\cos\kappa)\\ +\cos\psi\sin\kappa\end{matrix} \\ \begin{matrix}\sin\psi\cos\psi\cos\varphi(1-\cos\kappa)\\ -\sin\psi\sin\varphi\sin\kappa\end{matrix} & \cos\kappa+\cos^2\psi(1-\cos\kappa) & \begin{matrix}-\sin\psi\cos\psi\sin\varphi(1-\cos\kappa)\\ -\sin\psi\cos\varphi\sin\kappa\end{matrix} \\ \begin{matrix}-\sin^2\psi\cos\varphi\sin\varphi(1-\cos\kappa)\\ -\cos\psi\sin\kappa\end{matrix} & \begin{matrix}-\sin\psi\cos\psi\sin\varphi(1-\cos\kappa)\\ +\sin\psi\cos\varphi\sin\kappa\end{matrix} & \cos\kappa+\sin^2\psi\sin^2\varphi(1-\cos\kappa) \end{bmatrix}$$

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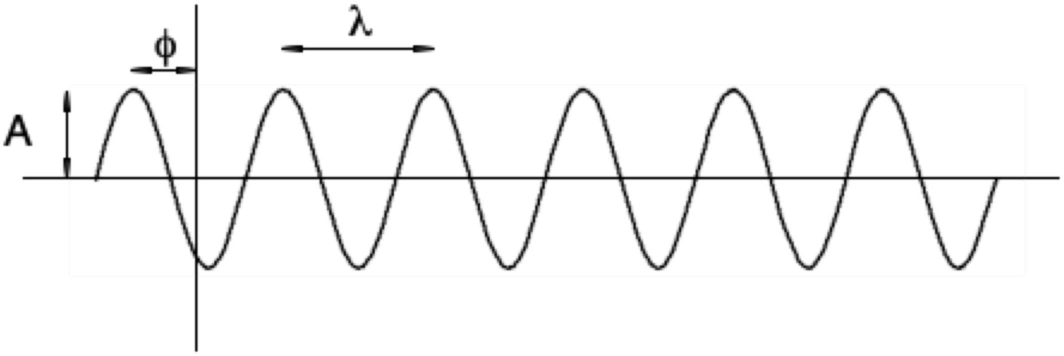
I. Waves and Complex Variables

The defining characteristics of a wave are the wavelength, amplitude and phase, as illustrated below



For fixed time, this can be written in terms of a cosine function of position as:

$$\psi(x) = A\cos\left(\frac{2\pi x}{\lambda} + \phi\right)$$

Or, for a fixed position, this can be written as a cosine function of time as:

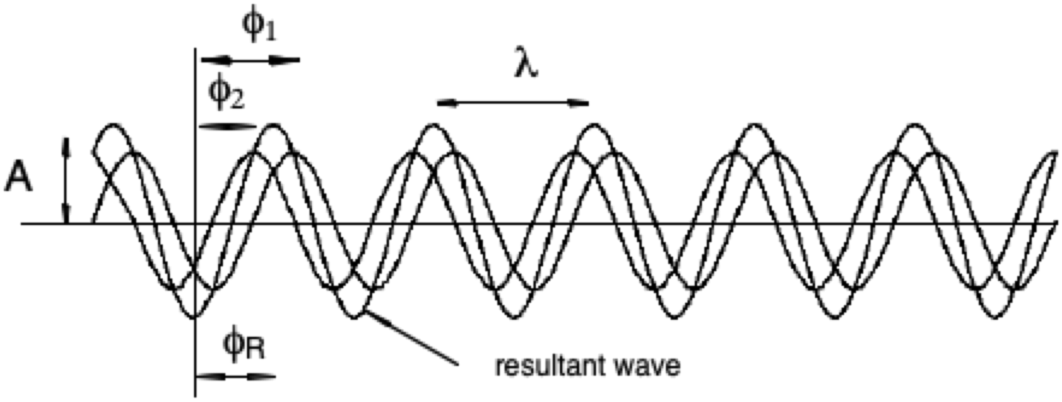
$$\psi(t) = A\cos(\omega t + \phi)$$

where ω is the angular frequency and is related to λ by the expression:

$$\omega = \frac{2\pi c}{\lambda}$$

The intensity of a plane wave (which is the average rate of energy flow in the wave) is related to the energy density of the radiation (which is energy/unit volume) which in turn depends on the amplitude squared of the wave (see Karplus and Porter, pg. 46, and Cantor and Schimmel, pg. 359). Therefore, $I \sim A^2$.

Now, imagine that there are two waves with the same amplitude and same wavelength, but different phases – how does the superposition of these look?



In this example, the phases of the two waves differ by 90°. The resultant wave has the same wavelength and a phase that is the average of the two input waves. This result can be shown mathematically through the use of trigonometric identities (Feynman I:29-5):

$$R = A\left[\cos\left(\omega t + \phi_1\right) + \cos\left(\omega t + \phi_2\right)\right]$$

with the trigonometric identity

$$\cos\alpha + \cos\beta = 2\cos\frac{1}{2}\left(\alpha + \beta\right)\cos\frac{1}{2}\left(\alpha - \beta\right)$$

this becomes

$$R = 2A\cos\frac{1}{2}\left(\phi_1 - \phi_2\right)\cos\left(\omega t + \frac{\phi_1 + \phi_2}{2}\right)$$

so that the resultant amplitude is

$$= 2A\cos\frac{1}{2}\left(\phi_1 - \phi_2\right)$$

and the resultant phase is the average of the two input phases

The intensity of the superimposed waves is given by the amplitude squared, or

$$I = 4A^2\cos^2\left(\frac{\varphi_1 - \varphi_2}{2}\right)$$

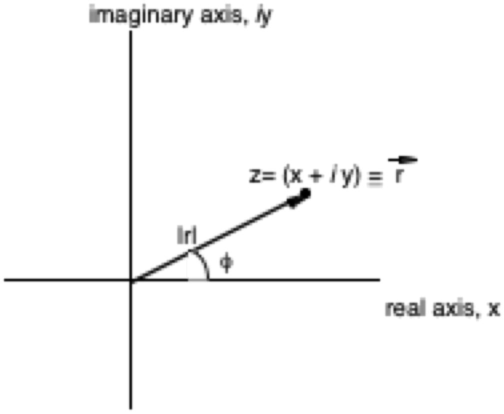
$$= 2A^2\left(1 + \cos\left(\varphi_1 - \varphi_2\right)\right)$$

using the above identity with $\beta = 0$ which becomes

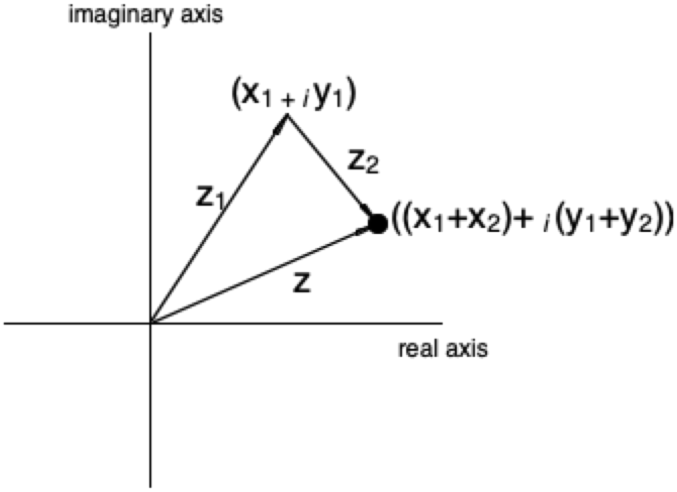
$$\cos^2\left(\frac{\alpha}{2}\right) = \frac{1 + \cos\alpha}{2}$$

Complex variables provide a convenient notation to simplify (believe it or not) calculations involving superposition of waves. First, some background. We can define the complex plane as having a real axis (by convention, the x axis) and an imaginary axis (by convention, the y axis). Components along the real axis are real numbers, while components along the imaginary axis are...

imaginary numbers, as indicated by a real number times the quantity i, where $i^2 = -1$. Hence, a complex number is represented as $x + iy \equiv z$.



A complex number can also be represented as a vector $\vec{r}$ with components $r \cos\phi + i\, r \sin\phi$, where $r^2 = x^2 + y^2$ and $\phi = \tan^{-1}(y/x)$. Complex numbers are added in an analogous fashion to adding vectors by independently summing the real and imaginary parts of the individual numbers:



A complex number can also be conveniently represented using an exponential notation:

$$\vec{r} = re^{i\phi}$$

where

$$e^{i\phi} = \cos\phi + i \sin\phi$$

[this relationship can be seen by expanding the exponential in terms of the appropriate power series expression for e^x, and factoring this into the cosine and sine series (see Box 13-1, Cantor and Schimmel]. The $\cos\phi$ and $\sin\phi$ terms are known as the real and imaginary components of a complex number, respectively, which are also designated Re and Im, respectively.

The exponential representation of complex variables is particularly useful because of the handy properties of exponentials, which can be used to derive trigonometric identities, etc. etc.

$$e^{ia}e^{ib} = \left[\cos a + i\sin a\right]\left[\cos b + i\sin b\right]$$

$$= \left(\cos a\cos b - \sin a\sin b\right) + i\left(\cos a\sin b + \sin a\cos b\right)$$

now, from the properties of exponentials

$$e^{ia}e^{ib} = e^{i(a+b)} = \cos\left(a+b\right) + i\sin\left(a+b\right)$$

equating the real and imaginary parts of these expressions gives

$$\cos\left(a+b\right) = \cos a\cos b - \sin a\sin b$$

$$\sin\left(a+b\right) = \cos a\sin b + \sin a\cos b$$

The conjugate of a complex number, z^*, is obtained by changing the sign of the imaginary component, ie $z^* = x - iy$. This is important, because the product zz^* is always real, and is equal to the length squared of a vector in the complex plane: $zz^* = (x + iy)(x - iy) = x^2 + y^2$.

Back to our wave example. Let's suppose that we have two waves that differ only in their phase term:

$$\psi_1 = \cos\left(\omega t + \varphi_1\right) = \mathrm{Re}\left[e^{i(\omega t + \varphi_1)}\right]$$

$$\psi_2 = \cos\left(\omega t + \varphi_2\right) = \mathrm{Re}\left[e^{i(\omega t + \varphi_2)}\right] = \mathrm{Re}\left[\psi_1 e^{i(\varphi_2 - \varphi_1)}\right]$$

Hence, the second wave is equal to the first wave times a factor that corrects for the phase difference between the two waves.

Now, lets look at the superposition of these two waves:

$$R = \psi_1 + \psi_2$$

The intensity (amplitude squared) may be calculated from the product of the exponentials times their complex conjugate

$$|R|^2 = \left(e^{i(\omega t + \varphi_1)} + e^{i(\omega t + \varphi_2)}\right)\left(e^{-i(\omega t + \varphi_1)} + e^{-i(\omega t + \varphi_2)}\right)$$

$$= 2 + e^{i(\varphi_1 - \varphi_2)} + e^{-i(\varphi_1 - \varphi_2)}$$

$$= 2 + 2\cos\left(\varphi_1 - \varphi_2\right)$$

Which equals the result derived in our initial trigonometric analysis of this problem, with A = 1.

Because of the convenience of working with the exponential/complex number representation of waves and phase shifts, this formalism is emphasized in crystallography, but it is certainly possible to work everything out explicitly and equivalently in terms of trigonometric functions.

II. Useful Properties of Fourier Transforms

The convolution and Parseval's theorem are described in most treatments of Fourier transforms, such as Titchmarsh, pp. 50-51.

Convolution Theorem

If the Fourier transforms of two functions g(x) and f(x) are given by G(h) and F(h), then:

$$\int g(x)f(x)e^{2\pi ihx}dx = \sum_k G(k)F(h-k)$$

ie the Fourier transform of the product of two functions is the convolution of the Fourier transforms of the two functions, and *vice-versa*. This result relates the Fourier transform of a crystal to the Fourier transforms of the molecule and the lattice, for example.

Parseval's Theorem:

$$\int\left|f(x)\right|^2 dx = \sum_h \left|F(h)\right|^2$$

This relationship is useful for calculating the mean square density over the entire unit cell from the structure factor amplitudes.

Generalizations to multiple functions are also possible; an extension to $\rho^3(x)$ is given by:

$$\begin{aligned}\int \rho^3(x)dx &= \int \sum_h \sum_p \sum_q F(h)F(p)F(q)e^{-2\pi i(h+p+q)x}dx \\ &= \sum_{hpq} F(h)F(p)F(q)\delta(h+p+q) \\ &= \sum_h F(-h)\sum_p F(p)F(h-p)\end{aligned}$$

To maximize this expression, the value of the second summation should be proportional to *F(h)*:

$$F(h) \approx \sum_p F(p)F(h-p)$$

since then the overall integral is given approximately by:

$$\int \rho^3(x)dx \approx \sum_h F(-h)F(h) = \sum_h I(h)$$

The relationship between Sayre's equation (*Acta Crystallogr.* **5**, 60-65 (1952)) and the maximization of ρ^3 has been noted by E. Stanley (*Acta Crystallogr.* **A35**, 966-970 (1979)). Another way in which maximization of ρ^3 may be accomplished is if all the structure factors have a phase angle of 0°; this corresponds to the Patterson solution (superatom at the origin) which does satisfy all these relationships, but which is (almost always, anyways) not the desired solution.

Sampling Theory

The molecular and crystal transforms of an object are given by:

$$F(S)=\int_{-1/2}^{1/2}\rho(x)e^{2\pi iSx}dx$$

$$F(h)=\int_{-1/2}^{1/2}\rho(x)e^{2\pi ihx}dx;\ h=\text{integer}$$

The crystal transform is given by the molecular transform sampled at reciprocal lattice points (convolution theorem).

By the inverse Fourier transform:

$$\rho(x)=\sum_{h}F(h)e^{-2\pi ihx}\quad\text{(neglecting the volume factor)}$$

$$\begin{aligned}F(S)&=\int_{-1/2}^{1/2}\sum_{h}F(h)e^{-2\pi ihx}e^{2\pi iSx}dx\\&=\sum_{h}F(h)\int_{-1/2}^{1/2}e^{2\pi i(S-h)}dx\\&=\sum_{h}F(h)\frac{\sin\pi(S-h)}{\pi(S-h)}\end{aligned}$$

This sampling theorem permits reconstruction of the continuous molecular transform from the discrete, sampled crystal transform.

Two and three-dimensional Fourier transforms (Intl. Tables II, 72-73; 322-323)

cylindrical coordinates

$$f\left(s,\varphi,z\right)=\int_{0}^{\infty}\int_{0}^{2\pi}\int_{-\infty}^{\infty}F(S,\Phi,Z)e^{-2\pi i\left[sS\cos\left(\Phi-\varphi\right)+zZ\right]}SdSd\Phi dZ$$

$$f\left(s\right)=2\pi\int_{0}^{\infty}F\left(S\right)J_{0}\left(2\pi S\right)SdS\qquad\text{(radial symmetry)}$$

polar coordinates

$$f\left(r,\vartheta,\varphi\right)=\int_{0}^{\infty}\int_{0}^{\pi}\int_{0}^{2\pi}F(R,\Theta,\Phi)e^{-2\pi irR\left[\cos\vartheta\cos\Theta+\sin\vartheta\sin\Theta\cos\left(\Phi-\varphi\right)\right]}R^{2}\sin\Theta dRd\Theta d\Phi$$

$$f\left(r\right)=4\pi\int_{0}^{\infty}F\left(R\right)\frac{\sin 2\pi\mathrm{rR}}{2\pi\mathrm{rR}}\mathrm{R}^{2}\mathrm{dR}\qquad\text{(radial symmetry)}$$

inverse transforms are given on pg. 322 of the Inter. Tables II; with unit scattering factor and an upper resolution s_0, the first two zeroes for the radial electron density in 3 and 2 dimensions occur at s_0r = 0.715, 1.230 and 0.610, 1.116, respectively (Table 6.3.2).

III. Matrices in Crystallography

The nxm matrix A may be represented by $\{A_{ij}\}$ where A_{ij} is the element of the ith row (of n) and jth column (of m), or more explicitly:

$$\begin{bmatrix} A_{11} & A_{12} & \cdots & A_{1m} \\ A_{21} & & & \\ \vdots & & & \\ A_{n1} & A_{n2} & & A_{nm} \end{bmatrix}$$

For coordinate transformations that we will be emphasizing in this discussion, n and m are typically both 3. For a full matrix least squares refinement, they would be equal to the number of parameters that are being refined.

Two matrices, A and B can be multiplied to give a new matrix C through the equation:

$$C_{ij} = \sum_k A_{ik} B_{kj}$$

So, the ijth element of C is given by the sum of the products between the elements of the ith row of A and the jth column of B. It is important to remember that, in general, $AB \neq BA$ (ie, matrices do not generally commute).

Column vectors, c, can be thought of as matrices consisting of just one column, while row vectors, r, can be thought of as matrices consisting of just one row. Matrices and vectors can also be multiplied together:

$$\left.\begin{aligned} y &= Ac \\ y_i &= \sum_k A_{ik} c_k \end{aligned}\right\rangle \text{ column vectors}$$

$$\left.\begin{aligned} u &= rA \\ u_j &= \sum_k r_k A_{kj} \end{aligned}\right\rangle \text{ row vectors}$$

A row vector and a column vector can be multipled together to give a scalar (number), which is also called the **dot product**:

$$r \bullet c = \sum_k r_k c_k = |r||c|\cos\vartheta$$

where θ is the angle between r and c. The dot product has the extremely useful property of representing the component of c in the direction of r, and *vice versa*.

The **identity** matrix, I, has 1's for the diagonal elements and 0's elsewhere:

$$\begin{bmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & & \\ \vdots & & \ddots & \\ 0 & & & 1 \end{bmatrix}$$

If the product of two matrices A and B equals I, then $A = B^{-1}$ and $B = A^{-1}$; ie, A and B are the inverse of each other.

The **transpose**, A^{T}, of a matrix A is formed by swapping the row and column elements:
$A_{ij}^{T} = A_{ji}$
Row vectors can be considered to be the transpose of column vectors, and *vice versa*. The transpose of the product of two matrices $\left(AB\right)^{T} = B^{T}A^{T}$.

A particularly useful class of matrices are **orthogonal** matrices, so named because if the rows (or columns) are considered to be vectors, then all the rows (or columns) are orthogonal to each other (ie, their dot product equals 0). **Rotation** matrices that correspond to rigid body rotations of various objects are orthogonal, because they transform one cartesian coordinate system to another (ie - the objects are not distorted by the transformation). For orthogonal matrices, the inverse is equal to the transpose:

$$A_{ij}^{-1} = A_{ij}^{T} = A_{ji}$$

If A is a rotation matrix that rotates object 1 to object 2, then $A^{-1} = A^{\mathrm{T}}$ is the rotation matrix that rotates object 2 to object 1

For **symmetric** matrices, the transpose of a matrix equals the matrix, and if this is an orthogonal matrix, then the inverse matrix also equals the original matrix:

$$A_{ij}^{T} = A_{ij}\left\{= A_{ij}^{-1} \text{ when } A \text{ is also orthogonal}\right\}$$

When A corresponds to a two fold rotation, then A is both orthogonal and symmetric, since applying two successive 180° rotations gets back to the starting structure, and this is the same as applying one 180° rotation, and then applying a -180° rotation (reverse rotation).

The **determinant** of a matrix can be calculated by various algorithms; for a 2x2 matrix:

$$\left\| \begin{matrix} a & b \\ c & d \end{matrix} \right\| = ad - bc$$

When the determinant is 0, then the rows (or columns) are not all linearly independent. This means that one or more of the rows (or columns) can be written as combinations of the other ones. This cannot happen for an orthogonal (rotation) matrix, except by error. If the determinant of a rotation matrix is negative, then it will convert a right handed coordinate system to a left handed coordinate system (this is generally bad).

The **eigenvalues**, λ, and **eigenvectors**, *x*, of a matrix *A* satisfy the equation:

$$Ax = \lambda x$$

where λ is a number (which can be complex). For cases where $\lambda=1$, then *x* defines a direction that is unaffected by application of the matrix *A*; for example if *A* is a rotation matrix, then the eigenvector *x* corresponding to $\lambda=1$ will be the rotation axis. Subroutines are generally available for these calculations, such as EIGEN or with Mathematica.

Examples

Relationships between Self-Rotation Function and Cross-Rotation Function Solutions:

Suppose two molecules, y_1 and y_2, are related by a rotation matrix *R*, determined, say, from a self rotation function:

$$y_2 = Ry_1$$

For the purposes of this problem, the translational components of the transformation are ignored.

Further suppose a known structure, x_1, can be rotated to y_1 and y_2 with the rotation matrices *P* and *Q*, perhaps determined from cross-rotation functions:

$$y_1 = Px_1$$
$$y_2 = Qx_1$$

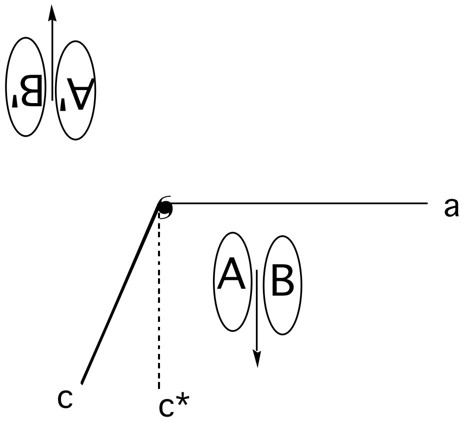
R, *P* and *Q* may be interconverted through the relationships:

$$y_2 = Qx_1 = Ry_1 = RPx_1$$
$$Q = RP$$
$$QP^T = RPP^T = R$$
$$R^T = \left(QP^T\right)^T = PQ^T$$

The orthogonal nature of these matrices (ie the inverse equals the transpose) was utilized in these derivations.

Analysis of non-crystallographic and crystallographic relationships in the MoFe-protein crystals.

The MoFe-protein from *A. vinelandii* crystallizes in space group $P2_1$ (a=108.4Å, b=130.5Å, c=81.5Å, β=110.8°), with one tetramer in the asymmetric unit. The tetramer consists of two αβ dimers that are related by a non-crystallographic twofold. **(NOTE: this is the old indexing and inconsistent with the crystallographic convention with a < c)**



The non-crystallographic rotation matrix and translation vector that relate dimers A and B are:

(a)
$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}_B = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}_A + \begin{pmatrix} 54.0 \\ -34.3 \\ -0.4 \end{pmatrix}$$

and the crystallographic operator that relates A, A' and B, B' is the 2_1 screw:

(b)
$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}_{A' \text{ or } A \text{ or } B \text{ or } B'} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}_{A \text{ or } A' \text{ or } B' \text{ or } B} + \begin{pmatrix} 0.0 \\ 65.2 \\ 0.0 \end{pmatrix}$$

With these operators, the transformation between A, B' (or A', B) may be determined:

(c)
$$\begin{aligned}
\begin{pmatrix} x \\ y \\ z \end{pmatrix}_{B'} &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}_B + \begin{pmatrix} 0.0 \\ 65.2 \\ 0.0 \end{pmatrix} \\
&= \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \left\{ \begin{bmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}_A + \begin{pmatrix} 54.0 \\ -34.3 \\ -0.4 \end{pmatrix} \end{bmatrix} \right\} + \begin{pmatrix} 0.0 \\ 65.2 \\ 0.0 \end{pmatrix} \\
&= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}_A + \begin{pmatrix} -54.0 \\ 30.9 \\ +0.4 \end{pmatrix}
\end{aligned}$$

The consequence of having a noncrystallographic two-fold axis perpendicular to a crystallographic 2_1 screw axis (which has a twofold rotational component) is to generate a third operator that has a twofold rotational component perpendicular to the other two. Hence, the rotation function gives three perpendicular two fold axes. Does this mean the structure has 222 symmetry?

NO! while some of these operations are true twofolds (such as the NCS twofold), others are screw operations that have translational components along the rotation axis (such as the crystallographic 2_1 screw). How can screw operations be distinguished from true rotations?

The key to this distinction is to determine whether the translational component of the transformation has any significant component in the direction of the rotation axis. Recall that the direction of the rotation axis can be identified with the eigenvector of the rotation matrix that has the unit eigenvalue (ie - application of the rotational operation to the point on the axis doesn't change that position). From this property, the rotation axis, *s*, can be identified, and the component of the translation vector, *d*, in this direction is given by the dot product $s*d$.

OP	rot. axis	translation	
	s	d(A)	$s \bullet d$(A)
(a)	$\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$	$\begin{pmatrix} 54.0 \\ -34.3 \\ -0.4 \end{pmatrix}$	-0.4
(b)	$\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0.0 \\ 65.2 \\ 0.0 \end{pmatrix}$	65.2
(c)	$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$	$\begin{pmatrix} -54.0 \\ 30.9 \\ 0.4 \end{pmatrix}$	-54.0

So, the only true twofold rotation axis is between the dimers in the tetramer (a), while the crystallographic operation (b), and the relationship between dimers in different tetramers (c) are screw operations. The translation in (b) necessarily equals b/2, while the translation in (c) nearly equals a/2.

Unit Cell Transformations

On occasion, it may be necessary to transform coordinates and reflection lists between different choices of unit cell. This could arise if the unit cell chosen by auto-indexing during data collection is not the cell that you would like, or if there is some relationship between different crystal forms that one wishes to emphasize. Here are some real-life examples

Example 1. It is possible to index cells such as $P3_121$ in two distinct, but correct, ways, that differ by rotation of the a and b axes by 60° about the c axis. What are the transformations that relate coordinates and reflections in these two indexings?

Example 2. Native CPA crystals grow in space group $P2_1$ with a=51.4Å, b=60.3Å, c=47.2Å and β=97.6°, with one molecule in the asymmetric unit. Addition of ligands to these crystals occasionally results in packing changes that increase the asymmetric unit volume by factors of 2 or 3. The new unit cell dimensions in these cases are a=74.4Å, b=60.4Å, c=65.6Å, β=97.72° for the doubled cell and a=100.7Å, b=60.4Å, c=74.4Å, β=104.6° for the tripled cell, respectively. All space groups are $P2_1$. What are the transformations that can be used to relate the native cell to these ligand-bound crystals, and what are the transformations that relate the native reflection indices to those measured from soaked crystals?

Example 3. MoFe-protein crystals (space group $P2_1$) can be indexed in two distinct fashions with cell dimensions a=108.4Å, b=130.5Å, c=81.5Å, β= 110.8°, and a=110.1Å, b=130.5Å, c=81.5Å, β=113.0°, respectively. What is the relationship between these two forms and what is the transformation that interconverts the reflection indices?

Unit cell and coordinate transformations can be easy to implement, with details on pages 70-72 of Volume A of the International Tables. Let **P** be the matrix that transforms the unit cell axes ($\mathbf{a_1}$) of crystal form 1 into the unit cell axes of crystal form 2 ($\mathbf{a_2}$):

$$\mathbf{a_2^T} = \mathbf{a_1^T}\ \mathbf{P}$$

where $\mathbf{a_1^T}$ is the row vector (a b c), etc. The determinant of **P** gives the unit cell volume of crystal 2 relative to crystal 1 (and will be positive if right-handed coordinate systems are used).

P also transforms the reflection indices from crystal 1 ($\mathbf{h_1}$) to the indices of crystal 2 ($\mathbf{h_2}$):

$$\mathbf{h_2^T} = \mathbf{h_1^T}\,\mathbf{P}$$

where $\mathbf{h_1^T}$ is the row vector (h k l). The inverse transform from crystal 2 to crystal 1 is given by the matrix $\mathbf{Q} = \mathbf{P^{-1}}$ (and usually, $\mathbf{P^{-1}}$ is not the same as $\mathbf{P^T}$). Q transforms the basis vectors:

$$\mathbf{a_2^*} = \mathbf{Q}\ \mathbf{a_1^*}$$

$$\mathbf{x_2} = \mathbf{Q}\,\mathbf{x_1}$$

where $\mathbf{a_1^*}$ is the column vector of the reciprocal space vectors, $\mathbf{x_1}$ is the column vector of the coordinates of a point in real space, etc. The eigenvectors of **Q** with unit eigenvalues correspond to directions (**x** vectors) that are unchanged by this transformation.

If the real space lattice is translated by a vector **p**, then the inverse shift is given by $\mathbf{q} = -\,\mathbf{Q}\,\mathbf{p}$.

The real space metric tensor, $G_{ij} = \mathbf{a_i}\cdot\mathbf{a_j}$, transforms as

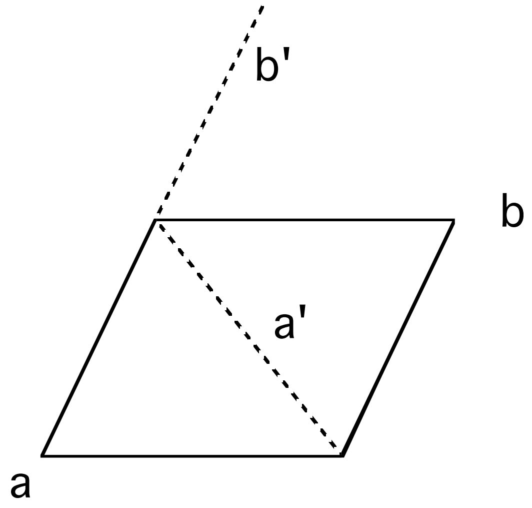
$$\mathbf{G_2} = \mathbf{P^T G_1 P}$$

and the reciprocal space metric tensor transforms as

$$\mathbf{G_2^*} = \mathbf{Q}\,\mathbf{G_1^*}\,\mathbf{Q^T}$$

Solutions to the introductory examples can be determined using these relationships

Example 1



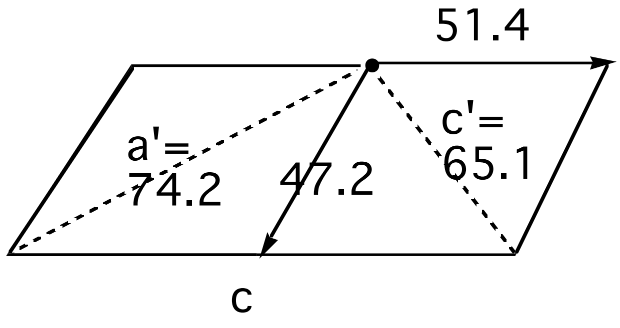
$$(a'b'c') = (abc)\begin{pmatrix} 1 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\left(h',k',l'\right) = \left(h+k,-h,l\right)$$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Example 2: Doubled Cell:

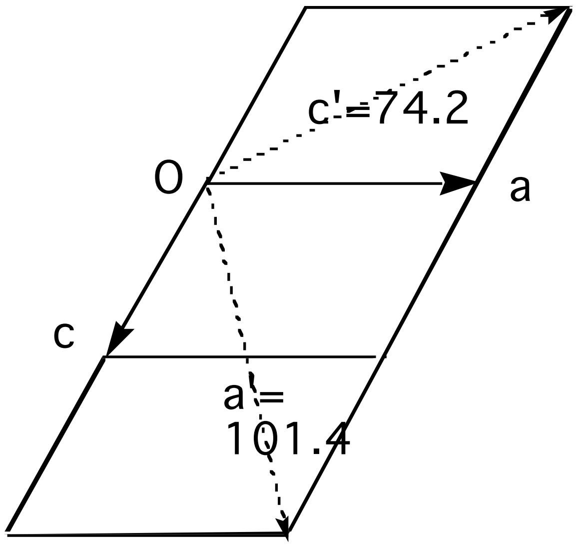
$$(a'b'c') = (abc)\begin{pmatrix} -1 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 1 \end{pmatrix}$$



(h' k' l') = (l-h, -k, h+l); This is a pseudo B-centered cell, since $h'+l' = 2l = \text{even}$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}' = \frac{1}{2}\begin{pmatrix} -1 & 0 & 1 \\ 0 & -2 & 0 \\ 1 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Tripled Cell:

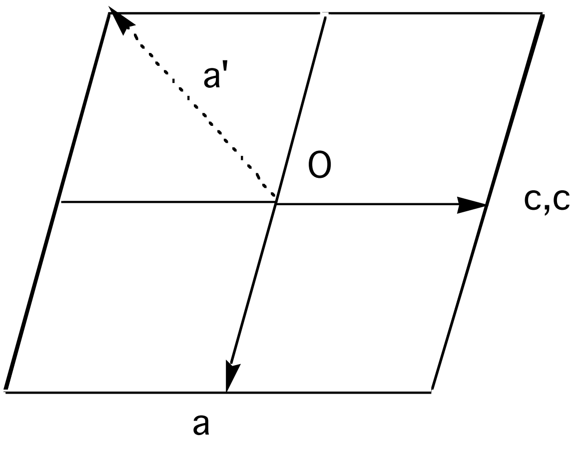


$$(a'b'c') = (abc)\begin{pmatrix} 1 & 0 & 1 \\ 0 & -1 & 0 \\ 2 & 0 & -1 \end{pmatrix}$$

$(h'k'l') = (h+2l, -k, h-l)$; In this case, $h' - l' \approx 3l$ for allowed reflections

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}' = \frac{1}{3}\begin{pmatrix} 1 & 0 & 1 \\ 0 & -3 & 0 \\ 2 & 0 & -1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Example 3



$$(a'b'c') = (abc)\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ -1 & 0 & 1 \end{pmatrix}$$

$$(h'k'l') = (-h-l, -k, l)$$

$a' = 110\text{Å}, b' = 130.5\text{Å}, c' = 81.5\text{Å}, \beta = 113.0^\circ$ (calculated either trigonometrically, or by transforming the metric tensor)

There many interesting applications of unit cell transformations involving rhombohedral cells:

Example 4: Transformation from primitive rhombohedral cell to triply primitive hexagonal cell

The standard obverse setting is used for the hexagonal cell, with origins at (0,0,0), (2/3,1/3,1/3), (1/3,2/3,2/3), and the reflection condition -h+k+l = 3n (see Table 5.1 and figure 5.7 of Vol A of the International Tables). For this transformation (see Table 5.1):

$$P = \begin{bmatrix} 1 & 0 & 1 \\ \bar{1} & 1 & 1 \\ 0 & \bar{1} & 1 \end{bmatrix} \qquad Q = P^{-1} = \begin{bmatrix} 2/3 & -1/3 & -1/3 \\ 1/3 & 1/3 & -2/3 \\ 1/3 & 1/3 & 1/3 \end{bmatrix}$$

$$G_R = a_R^2 \begin{bmatrix} 1 & \cos\alpha_R & \cos\alpha_R \\ \cos\alpha_R & 1 & \cos\alpha_R \\ \cos\alpha_R & \cos\alpha_R & 1 \end{bmatrix}$$

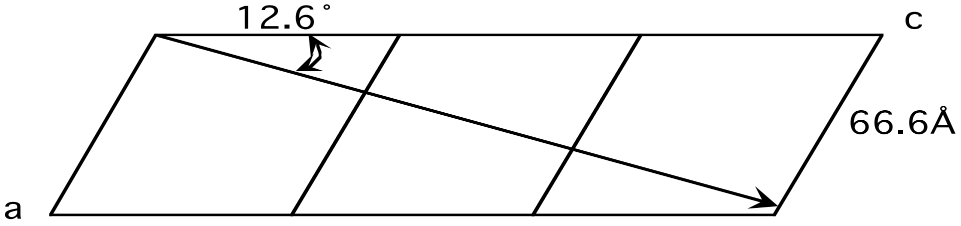
$$G_H = \begin{bmatrix} a_H^2 & a_H^2\cos\gamma_H & 0 \\ a_H^2\cos\gamma_H & a_H^2 & 0 \\ 0 & 0 & c_H^2 \end{bmatrix}$$

where γ_H=120°. Equating the relevant matrix elements in the relationship $G_H = P^T G_R P$ gives:

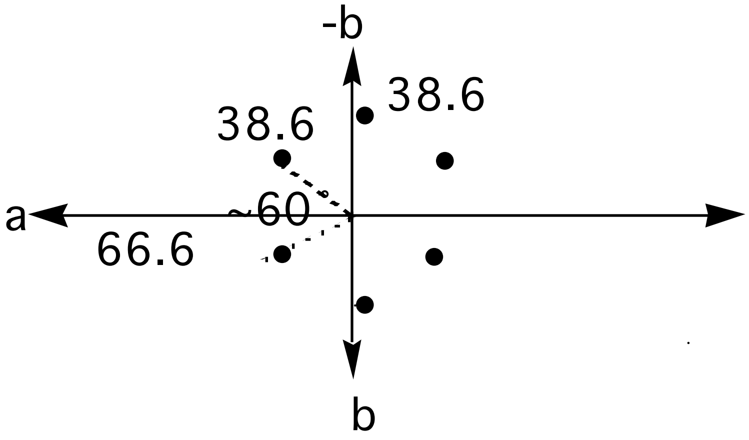
$$a_H = a_R\sqrt{2(1-\cos\alpha_R)}$$
$$c_H = a_R\sqrt{3(1+2\cos\alpha_R)}$$

$$\cos\alpha_R = \frac{2-3(a_H/c_H)^2}{6(a_H/c_H)^2+2}$$
$$a_R^2 = \frac{c_H^2(6(a_H/c_H)^2+2)}{18}$$

Example 5: A DNA crystal was collected in space group C2 with unit cell dimensions a=66.6Å, b=38.6Å, c=102.8Å, β=102.56°. Self rotation functions indicated that there were very strong two fold axes spaced every 60° in the ab plane, and a three fold axis perpendicular to this plane, suggesting that the crystals actually have higher symmetry. What might be the space group and unit cell dimensions of this higher symmetry form?



$$\frac{66.6}{\sin 12.6} \cong 305$$



Transform to R32:

$$\text{reindex}\,(a'b'c') = (abc)\begin{pmatrix} \frac{1}{2} & 0 & 1 \\ -\frac{1}{2} & 1 & 0 \\ 0 & 0 & 3 \end{pmatrix}$$

$$(h'k'l') = \frac{h-k}{2}, k, h+3l \qquad h'-k'+l' = 3n \qquad \text{reverse}$$

$$\text{reindex}\,(a'b'c') = (abc)\begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & 1 \\ \frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 3 \end{pmatrix}$$

$$(h'k'l') = \frac{h+k}{2}, \frac{-h+k}{2}, h+3l \qquad h'-k'-l' = 3n \qquad \text{obverse}$$

$$\text{reindex}\,(a'b'c') = (abc)\begin{pmatrix} 0 & -\frac{1}{2} & 1 \\ 1 & -\frac{1}{2} & 0 \\ 0 & 0 & 3 \end{pmatrix}$$

$$(h'k'l') = k, \frac{-h-k}{2}, h+3l \qquad h'-k'+l' = 3n \qquad \text{reverse}$$

$$\text{reindex}\,(a'b'c') - (abc)\begin{pmatrix} -\frac{1}{2} & 0 & 1 \\ \frac{1}{2} & -1 & 0 \\ 0 & 0 & 3 \end{pmatrix}$$

$$(h'k'l') = -h+k, -k, h+3l \qquad -h'+k'+l' = 3n \qquad \text{obverse}$$

Example 6

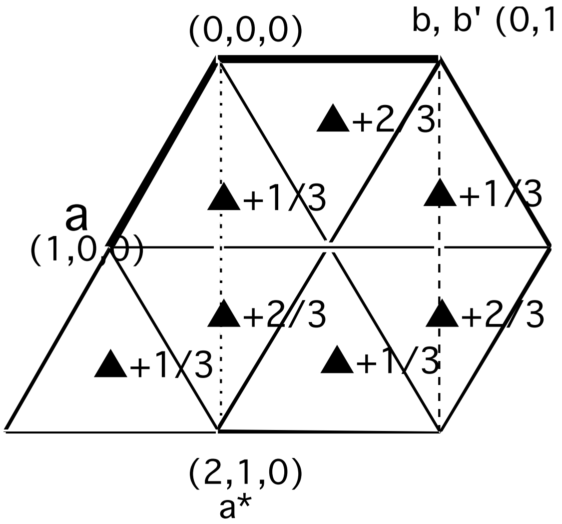
A crystal in space group R3 (a=148.0 Å, c=34.2 Å, hexagonal; a=85.2 Å, α=118.3°, rhombohedral) was originally indexed in space group C2 (a=87 Å, b=146 Å, c=33 Å, β=104.9°).

(a) Find the P matrix that converts the R3 cell to the C2 cell.

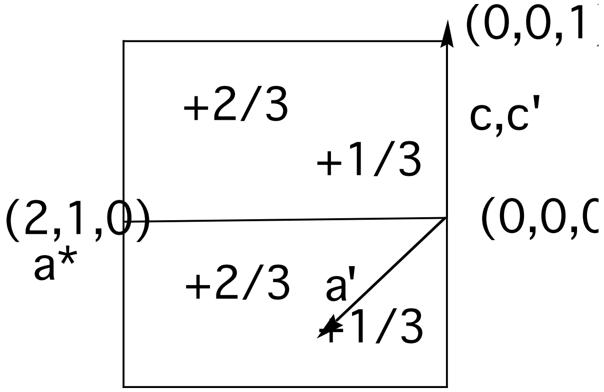
(b) From the hexagonal cell constants, calculate the monoclinic and primitive rhombohedral cell constants by transforming the metric tensor G.

(c) From the determinant of G, calculate the volume of the C2 cell relative to the R3 cell.

(d) Show that if the R3 cell indices obey -h+k+l=3n, then the C2 cell indices obey h+k=2n



projection in ab plane



projection in a*c plane

$$\begin{pmatrix} a' & b' & c' \end{pmatrix}_{\text{monoclinic}} = \begin{pmatrix} a & b & c \end{pmatrix}_{\text{hexagonal}} P$$

$$P = \begin{bmatrix} 2/3 & 0 & 0 \\ 1/3 & 1 & 0 \\ -2/3 & 0 & 1 \end{bmatrix}$$

$$G_{\text{monoclinic}} = P^T G_{\text{hexagonal}} P$$

$$= \begin{bmatrix} 2/3 & 1/3 & -2/3 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 21904. & -10950. & 0. \\ -10950. & 21904. & 0. \\ 0. & 0. & 1170. \end{bmatrix} \begin{bmatrix} 2/3 & 0 & 0 \\ 1/3 & 1 & 0 \\ -2/3 & 0 & 1 \end{bmatrix}$$

$$G_{\text{monoclinic}} = \begin{pmatrix} 7821. & 0 & -780. \\ 0 & 21904. & 0 \\ -780 & 0 & 1170. \end{pmatrix}$$

From the definition of the metric tensor, the cell constants can be extracted from the square roots of the diagonal elements, and the cell angles from the off-diagonal terms, to give for the C2 cell:
a=88.4Å, b=148.0Å, c=34.2Å, β=104.9°
The C2 cell volume is 2/3 that of the R3 cell, which equals the determinant of the P matrix.

The unit cell constants of the primitive rhombohedral cell can be calculated by similar methods, following the procedure of *Example 4*.

The C2 indices may be calculated from the R3 indices using the P matrix, to give:

$$\begin{aligned}
\begin{pmatrix} h & k & l \end{pmatrix}_{C2} &= \begin{pmatrix} \dfrac{2h+k-2l}{3} & k & l \end{pmatrix}_{R3} \\
\left(h+k\right)_{C2} &= \left(\frac{2h+k-2l}{3}+k\right)_{R3} \\
&= \left(\frac{2h+k-2l+(3k)}{3}\right)_{R3} \\
&= 2\left(\frac{h+2k-l}{3}\right) = 2\left(\frac{h-k-l+3k}{3}\right) = 2\left(\frac{3n+3k}{3}\right) = 2n'
\end{aligned}$$

so that the C centering extinctions are obeyed.

In the R3 cell, one of the rhombohedral origins contained within the C2 unit cell has coordinates (1/3, 2/3, -1/3). The corresponding coordinate in the C2 cell may be calculated using the Q matrix:

$$\begin{aligned}
\begin{pmatrix} x \\ y \\ z \end{pmatrix}_{\text{C2}} &= Q \begin{pmatrix} x \\ y \\ z \end{pmatrix}_{\text{R3}} \\
&= \begin{pmatrix} 3/2 & 0 & 0 \\ -1/2 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1/3 \\ 2/3 \\ -1/3 \end{pmatrix}_{\text{R3}} \\
&= \begin{pmatrix} 1/2 \\ 1/2 \\ 0 \end{pmatrix}_{\text{C2}}
\end{aligned}$$

This represents the C centering operation in the monoclinic cell.

Orthogonalization Convention

Our convention is that adopted by Brookhaven, TOM/FRODO, O, X-PLOR and CCP4 (ncode=1) - unit cells are orthogonalized onto a Cartesian coordinate system defined by **a**, **c*xa** and **c***. BEWARE: other programs, such as TNT use other orthogonalization conventions.

In matrix form, the general orthogonalization convention is given by:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix}_{\text{orthogonal}} = \begin{bmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & c\left\{\dfrac{\cos\alpha-\cos\beta\cos\gamma}{\sin\gamma}\right\} \\ 0 & 0 & \dfrac{\text{Volume}}{ab\sin\gamma} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}_{\text{fractional}}$$

where Vol = abc $(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha \cos\beta \cos\gamma)^{1/2}$ = sqrt(Det(**G**)).

Specific forms of this matrix for monoclinic and trigonal cells are given:

Monoclinic cells - orthogonal x and y superimpose with crystallographic a and b axes:

$$\begin{bmatrix} a & 0 & c\cos\beta \\ 0 & b & 0 \\ 0 & 0 & c\sin\beta \end{bmatrix}$$

Trigonal cells - orthogonal x and z superimpose with crystallographic a and c axes:

$$\begin{bmatrix} a & a\cos\gamma & 0 \\ 0 & a\sin\gamma & 0 \\ 0 & 0 & c \end{bmatrix}$$

Deorthogonalization: Deorthogonalization matrices are the **inverse** (**not transpose**) of the orthogonalization matrix. For monoclinic and trigonal cells, these matrices take the form:

Monoclinic:

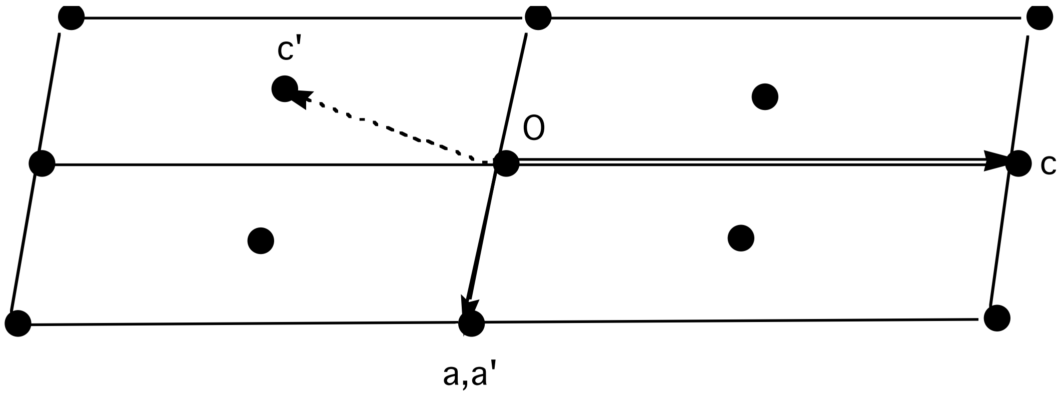
$$\begin{bmatrix} 1/a & 0 & \dfrac{-\cos\beta}{a\sin\beta} \\ 0 & 1/b & 0 \\ 0 & 0 & \dfrac{1}{c\sin\beta} \end{bmatrix}$$

Trigonal:

$$\begin{bmatrix} \dfrac{1}{a} & -\dfrac{\cos\gamma}{a\sin\gamma} \cong \dfrac{0.57735}{a} & 0 \\ 0 & \dfrac{1}{a\sin\gamma} \cong \dfrac{1.15470}{a} & 0 \\ 0 & 0 & \dfrac{1}{c} \end{bmatrix}$$

Example 7

Intensity data from RC-cytochrome c cocrystals were indexed in two separate $P2_1$ cells: a=77.5Å, b=82.3Å, c=130.0Å, β=101.6° (the "small" cell with one complex per asymmetric unit) and a=78.0, b=81.0, c=249.9, β=92.0° (the "large" cell with two complexes per asymmetric unit). Inspection of the native Patterson function of the large cell revealed a very large packing peak at (0.5, 0.06, 0.5) that relates two complexes in the asymmetric unit (ie - the two molecules in the asymmetric unit have the same orientation and differ only by a translation; at low resolution the crystal exhibits approximate B-center packing). Molecular replacement solutions were derived for both cells, and it was found that the RCs in the two crystal forms were almost exactly related by a twofold rotation about the **Z** axis. Are the RCs arranged similarly in the two crystal forms?



The large cell may be transformed to the small cell through the following relationship:

$$\begin{pmatrix} a' & b' & c' \end{pmatrix}_{\text{small cell}} = \begin{pmatrix} a & b & c \end{pmatrix}_{\text{large cell}} \begin{pmatrix} 1 & 0 & -1/2 \\ 0 & -1 & 0 \\ 0 & 0 & -1/2 \end{pmatrix}$$

By appropriate transformation of the metric G tensor, the cell constants of the small cell are calculated to be a=78.0Å, b=81.0Å, c=129.2Å, β=105.6˚ which are in reasonable agreement with the reported values. The determinant of the *P* matrix is 0.5, indicating that the small cell does have half the volume of the large cell. The fractional coordinates are transformed by the relationship:

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}_{\text{small cell}} = \begin{pmatrix} 1 & 0 & -1 \\ 0 & -1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}_{\text{large cell}}$$

Now, the PDB coordinates have been orthogonalized (designated by capital letters (XYZ)), and the relationship (given the rotation matrix R) between the MR solutions for the two crystal forms must take the orthogonalization convention into account.

$$\begin{pmatrix} X' \\ Y' \\ Z' \end{pmatrix}_{\text{small cell}} = R \begin{pmatrix} X \\ Y \\ Y \end{pmatrix}_{\text{large cell}}$$

$$\begin{pmatrix} 1/a' & & \dfrac{-\cos\beta'}{a'\sin\beta'} \\ 0 & 1/b' & 0 \\ 0 & 0 & \dfrac{1}{c'\sin\beta'} \end{pmatrix} \begin{pmatrix} X' \\ Y' \\ Z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & -1 \\ 0 & -1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \begin{pmatrix} 1/a & & \dfrac{-\cos\beta}{a\sin\beta} \\ 0 & 1/b & 0 \\ 0 & 0 & \dfrac{1}{c\sin\beta} \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$

$$\begin{pmatrix} X' \\ Y' \\ Z' \end{pmatrix} = \begin{pmatrix} a' & 0 & c'\cos\beta' \\ 0 & b' & 0 \\ 0 & 0 & c'\sin\beta' \end{pmatrix} \begin{pmatrix} 1 & 0 & -1 \\ 0 & -1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \begin{pmatrix} 1/a & & \dfrac{-\cos\beta}{a\sin\beta} \\ 0 & 1/b & 0 \\ 0 & 0 & \dfrac{1}{c\sin\beta} \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$

substituting the appropriate values for the cell constants and carrying out the matrix multiplication yields:

$$\begin{pmatrix} X' \\ Y' \\ Z' \end{pmatrix}_{\text{small cell}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \\ Y \end{pmatrix}_{\text{large cell}}$$

which is a twofold along X. However, in each cell there are crystallographically related molecules related by a twofold screw axis along y. If the transformation is calculated between the 2_1 screw related molecule in the large cell, and our original small cell molecule, then the transformation is:

$$\begin{pmatrix} X' \\ Y' \\ Z' \end{pmatrix}_{\text{small cell}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \\ Y \end{pmatrix}_{\text{large cell}} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} X \\ Y \\ Y \end{pmatrix}_{\text{large cell}}$$

so that molecules in the two cells are related by a twofold rotation about the orthogonal Z axis. This makes it likely that the RCs are packed similarly in the two crystal forms, although we haven't taken into account the translational component of the transformation.

Distances:

Distances between points can be calculated following orthogonalization of non-orthogonal coordinates if necessary; alternatively, distances can be calculated directly from fractional coordinates and the metric tensor G (real space) or G* (reciprocal space):

$$d^2 = d^t \cdot d = \begin{pmatrix} x & y & z \end{pmatrix}_{\text{fractional}} \begin{pmatrix} a \\ b \\ c \end{pmatrix} \begin{pmatrix} a & b & c \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}_{\text{fractional}}$$

$$= \begin{pmatrix} x & y & z \end{pmatrix} G \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$G = \begin{pmatrix} a\cdot a & a\cdot b & a\cdot c \\ a\cdot b & b\cdot b & b\cdot c \\ a\cdot c & b\cdot c & c\cdot c \end{pmatrix} = \begin{pmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{pmatrix}$$

$$d^2 = x^2a^2 + y^2b^2 + z^2c^2 + 2yzbc\cos\alpha + 2xzac\cos\beta + 2xyab\cos\gamma$$

$$V^2 = \det(G)$$

$$GG^* = I$$

The distance squared (d^{*2}) of a reflection with indices hkl from the origin of reciprocal space may be similarly calculated:

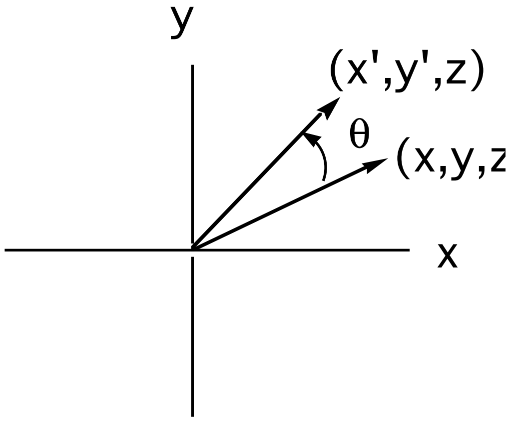
$$\left(d^*\right)^2 = \left(\frac{1}{d}\right)^2 = \begin{pmatrix} h & k & l \end{pmatrix} G^* \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

$$= h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2hk\cos\gamma^* + 2hl\cos\beta^* + 2kl\cos\alpha^*$$

$$= \left(\frac{2\sin\vartheta}{\lambda}\right)^2 \quad \text{(Bragg's Law)}$$

Rotation Angles

The basic rotation matrix can be illustrated for the case of a counterclockwise rotation about the z axis by the angle θ.



Rotation matrix about the z axis

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\vartheta & -\sin\vartheta & 0 \\ \sin\vartheta & \cos\vartheta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

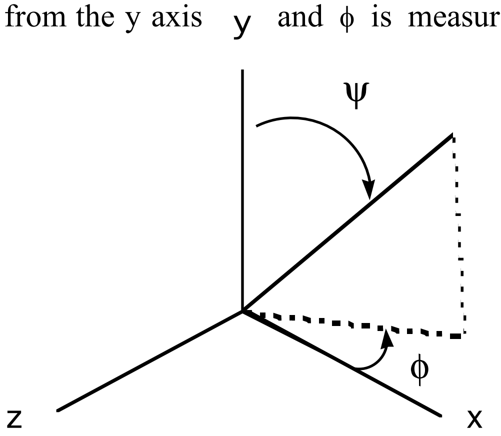
Rotation matrix about the y axis

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\vartheta & 0 & \sin\vartheta \\ 0 & 1 & 0 \\ -\sin\vartheta & 0 & \cos\vartheta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

By appropriate sequences of rotations about specified axes, it is possible to derive expressions for different types of rotation matrices by multiplication of matrices of the type illustrated above. There are numerous conventions; the main angle types are Euler (θ_1, θ_2, θ_3) and spherical polar (often ϕ, ψ, κ). The spherical polar angle convention used by XPLOR and in our group (at least traditionally) is given below; ψ is measured from the y axis and ϕ is measured in the xz plane from the x axis:

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} \equiv \begin{bmatrix} l \\ m \\ n \end{bmatrix} = \begin{bmatrix} \cos\varphi\sin\psi \\ \cos\psi \\ -\sin\varphi\sin\psi \end{bmatrix}$$

direction cosines in terms of (ϕ,ψ)



Using the convention that $x_{rot} = Ax$, where A is the rotation matrix, then the rotation matrix can be written in terms of spherical polar angles by the sequence of operations that first orients the rotation axis along y, then rotates about this axis by κ, and finally returns the rotation axis to the original direction:

$$R_y[\varphi]R_z[-\psi]R_y[\kappa]R_z[\psi]R_y[-\varphi]$$

to give:

$$\begin{bmatrix}
\cos\kappa+\sin^2\psi\cos^2\varphi\left(1-\cos\kappa\right) & \begin{array}{l}\sin\psi\cos\psi\cos\varphi\left(1-\cos\kappa\right)\\ +\sin\psi\sin\varphi\sin\kappa\end{array} & \begin{array}{l}-\sin^2\psi\cos\varphi\sin\varphi\left(1-\cos\kappa\right)\\ +\cos\psi\sin\kappa\end{array} \\
\begin{array}{l}\sin\psi\cos\psi\cos\varphi\left(1-\cos\kappa\right)\\ -\sin\psi\sin\varphi\sin\kappa\end{array} & \cos\kappa+\cos^2\psi\left(1-\cos\kappa\right) & \begin{array}{l}-\sin\psi\cos\psi\sin\varphi\left(1-\cos\kappa\right)\\ -\sin\psi\cos\varphi\sin\kappa\end{array} \\
\begin{array}{l}-\sin^2\psi\cos\varphi\sin\varphi\left(1-\cos\kappa\right)\\ -\cos\psi\sin\kappa\end{array} & \begin{array}{l}-\sin\psi\cos\psi\sin\varphi\left(1-\cos\kappa\right)\\ +\sin\psi\cos\varphi\sin\kappa\end{array} & \cos\kappa+\sin^2\psi\sin^2\varphi\left(1-\cos\kappa\right)
\end{bmatrix}$$

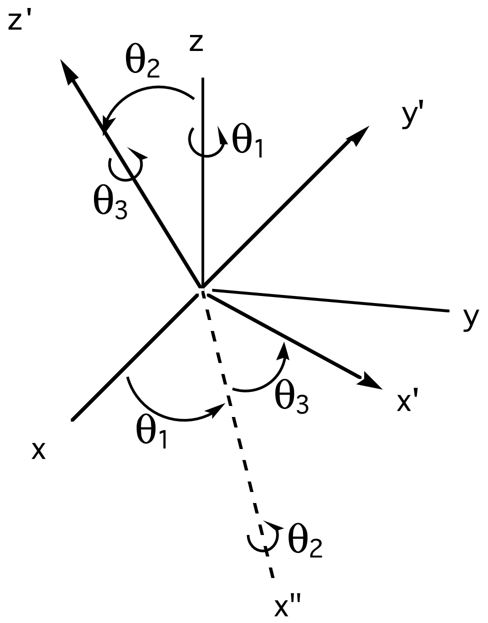
Another useful form writes the rotation matrix in terms of the direction cosines (*l,m,n*) of the rotation axis and the rotation angle κ:

$$\begin{bmatrix}
l^2+\left(m^2+n^2\right)\cos\kappa & lm\left(1-\cos\kappa\right)-n\sin\kappa & nl\left(1-\cos\kappa\right)+m\sin\kappa \\
lm\left(1-\cos\kappa\right)+n\sin\kappa & m^2+\left(l^2+n^2\right)\cos\kappa & mn\left(1-\cos\kappa\right)-l\sin\kappa \\
nl\left(1-\cos\kappa\right)-m\sin\kappa & mn\left(1-\cos\kappa\right)+l\sin\kappa & n^2+\left(l^2+m^2\right)\cos\kappa
\end{bmatrix}$$

The trace of the rotation matrix (sum of the diagonal elements) can be seen in this formulation to equal 1 + 2 cosκ (added 10/12/06).

Another set of commonly used rotation angles are the Euler angles. Again, there are many conventions, but a commonly used one (at least by X-PLOR and us!) is that (θ_1, θ_2, θ_3) correspond to rotations about the z, rotated x'' and rotated z' axes. The rotation matrix in terms of the Eulerian angles and the relationship between the unrotated x, y and z axes and the rotated x', y', and z' axes are depicted below (fixed (3,1) element on 10/11/06)

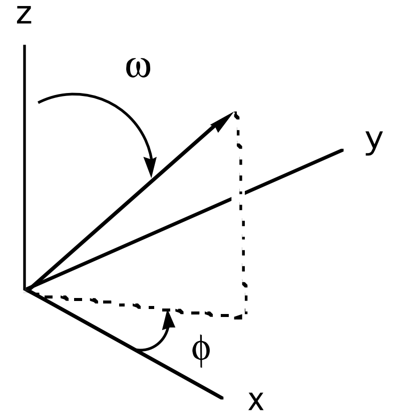
$$\begin{bmatrix}
\begin{array}{l}-\sin\vartheta_1\cos\vartheta_2\sin\vartheta_3\\ +\cos\vartheta_1\cos\vartheta_3\end{array} & \begin{array}{l}\cos\vartheta_1\cos\vartheta_2\sin\vartheta_3\\ +\sin\vartheta_1\cos\vartheta_3\end{array} & \sin\vartheta_2\sin\vartheta_3 \\
\begin{array}{l}-\sin\vartheta_1\cos\vartheta_2\cos\vartheta_3\\ -\cos\vartheta_1\sin\vartheta_3\end{array} & \begin{array}{l}\cos\vartheta_1\cos\vartheta_2\cos\vartheta_3\\ -\sin\vartheta_1\sin\vartheta_3\end{array} & \sin\vartheta_2\cos\vartheta_3 \\
\sin\vartheta_1\sin\vartheta_2 & -\cos\vartheta_1\sin\vartheta_2 & \cos\vartheta_2
\end{bmatrix}$$



CCP4 uses a different set of conventions; in this case, the Euler angle rotation matrix is the transpose of ours, so that our X-PLOR $(\theta_1, \theta_2, \theta_3)$ = CCP4 $(-\theta_3, -\theta_2, -\theta_1)$ = $(180-\theta_3, \theta_2, 180-\theta_1)$ (probably). In CCP4, the spherical polar angles are defined as φ, ω, κ, where ω is measured from the z axis (not y as in our convention) and φ is measured in the xy plane from the x axis.

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} \equiv \begin{bmatrix} l \\ m \\ n \end{bmatrix} = \begin{bmatrix} \cos\varphi\sin\omega \\ \sin\varphi\sin\omega \\ \cos\omega \end{bmatrix}$$

direction cosines in terms of (φ,ω)



Another Euler-type convention that is often used, particularly with Fast Rotation Functions, is designated αβγ, where the rotations are about axes in the order Z, new Y (not X!!) and new Z.

Useful matrix operations in Mathematica

Definition of a matrix, bigmat, giving the list of elements row by row

```
bigmat={{1,-1,0},{1,0,0},{0,0,1}}
```

MatrixForm produces a nicely formatted matrix

```
MatrixForm[bigmat]
```

Inverse calculates the matrix inverse

```
Inverse[bigmat]
```

Eigensystem will calculate the eigenvalues, followed by the eigenvectors in the same order

```
Eigensystem[bigmat]
```

```
Eigenvalues[bigmat]
Eigenvectors[bigmat]
```

Transpose calculates the matrix transpose

```
MatrixForm[Transpose[bigmat]]
```

The product of two matrices is specified by the "." (dot).

```
MatrixForm[Inverse[bigmat].bigmat]
```

Rotation matrix functions can also be defined:

```
rotz[α_] := {{Cos[α],-Sin[α],0},{Sin[α],Cos[α],0},{0,0,1}}
roty[β_] := {{Cos[β],0,Sin[β]},{0,1,0},{-Sin[β],0,Cos[β]}}
rotx[γ_] := {{1,0,0},{0,Cos[γ],-Sin[γ]},{0,Sin[γ],Cos[γ]}}
```

Arctan[x,y] = $\tan^{-1}$ (y/x)
Cross[x,y] = cross product of x and y
Trace[mat] = trace of matrix