Non-orthogonal vector spaces

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Cartesian Coordinates

In general, a vector in any coordinate space can be represented as:

$\vec{x}_1 = x_1\,\vec{a} + y_1\,\vec{b} + z_1\,\vec{c}$ where $\vec{a}, \vec{b}$ and $\vec{c}$ are the basis vectors of that space.

The so-called Cartesian coordinate system is a very simple example, where $\vec{a}, \vec{b}$ and $\vec{c}$ are at mutual right angles to each other and are of unit length (Å, mm, inches, etc.). Such a system is also called an ortho-normal space, since the basis vectors are orthogonal and normalized. In such a system we can represent the dot product between two vectors as follows:

$\vec{x}_1 \bullet \vec{x}_2 = |\vec{x}_1||\vec{x}_2|\cos\vartheta = x_1x_2 + y_1y_2 + z_1z_2$ where ϑ is the angle between the vectors.

We can also write $\vec{x}_1$ as a column vector $\begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix}$ and its transpose $\vec{x}_1^T$ as a row vector $\begin{pmatrix} x_1 & y_1 & z_1 \end{pmatrix}$. The dot product in ortho-normal space can be written as the inner product $\vec{x}_1^T\,\vec{x}_2 = \begin{pmatrix} x_1 & y_1 & z_1 \end{pmatrix}\begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} = x_1x_2 + y_1y_2 + z_1z_2$.

In the special case of calculation of the length of $\vec{x}$ we have $|\vec{x}| = (\vec{x}^T\,\vec{x})^{1/2} = \sqrt{x^2 + y^2 + z^2}$, a result well known from high school.

Non-Ortho-normal Coordinates

However, the reason that this is so simple is that in an ortho-normal system, $\begin{matrix} \vec{a}\bullet\vec{a} = 1 & \vec{a}\bullet\vec{b} = 0 \\ \vec{b}\bullet\vec{b} = 1 & \vec{a}\bullet\vec{c} = 0 \\ \vec{c}\bullet\vec{c} = 1 & \vec{b}\bullet\vec{c} = 0 \end{matrix}$ therefore there are no cross-terms in the dot product. If we allow that the basis vectors can be of any length and may form arbitrary angles to each other (as, for instance, in a triclinic unit cell) then we need to take the full expansion of the dot product into account.

$$\begin{aligned}(x_1\vec{a} + y_1\vec{b} + z_1\vec{c}) \bullet (x_2\vec{a} + y_2\vec{b} + z_2\vec{c}) \;=\; & x_1x_2\vec{a}\bullet\vec{a} + x_1y_2\vec{a}\bullet\vec{b} + x_1z_2\vec{a}\bullet\vec{c} \\ & + y_1x_2\vec{b}\bullet\vec{a} + y_1y_2\vec{b}\bullet\vec{b} + y_1z_2\vec{b}\bullet\vec{c} \\ & + z_1x_2\vec{c}\bullet\vec{a} + z_1y_2\vec{c}\bullet\vec{b} + z_1z_2\vec{c}\bullet\vec{c}\end{aligned}$$

Well, that is a revolting state of affairs. However if we know the lengths of the vectors $\vec{a}, \vec{b}$ and $\vec{c}$ (expressed as the scalars a, b and c) and the angles between them, α, β and γ, (where α is the angle between $\vec{b}$ and $\vec{c}$, and β and γ are correspondingly defined) then the dot products between the basis vectors can easily be written out:

$$\begin{matrix} \vec{a}\bullet\vec{a} = a^2 & \vec{a}\bullet\vec{b} = \vec{b}\bullet\vec{a} = ab\cos\gamma \\ \vec{b}\bullet\vec{b} = b^2 & \vec{a}\bullet\vec{c} = \vec{c}\bullet\vec{a} = ac\cos\beta \\ \vec{c}\bullet\vec{c} = c^2 & \vec{b}\bullet\vec{c} = \vec{c}\bullet\vec{b} = bc\cos\alpha \end{matrix}$$

and the dot product of two vectors can be written as :

$$\vec{x}_1 \bullet \vec{x}_2 = \vec{x}_1^T\,\underline{M}\,\vec{x}_2 = \begin{pmatrix} x_1 & x_2 & x_3 \end{pmatrix}\begin{pmatrix} M_{11} & M_{12} & M_{13} \\ M_{21} & M_{22} & M_{23} \\ M_{31} & M_{32} & M_{33} \end{pmatrix}\begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix}$$

where the matrix elements are just the dot products of the basis vectors (comparing the above to the written-out dot product) and so $\underline{M}$ can be expressed in several ways:

$$\underline{M} \equiv \begin{pmatrix} \vec{a}\bullet\vec{a} & \vec{a}\bullet\vec{b} & \vec{a}\bullet\vec{c} \\ \vec{b}\bullet\vec{a} & \vec{b}\bullet\vec{b} & \vec{b}\bullet\vec{c} \\ \vec{c}\bullet\vec{a} & \vec{c}\bullet\vec{b} & \vec{c}\bullet\vec{c} \end{pmatrix} \equiv \begin{pmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{pmatrix} \equiv \begin{pmatrix} \vec{a} \\ \vec{b} \\ \vec{c} \end{pmatrix} \begin{pmatrix} \vec{a} & \vec{b} & \vec{c} \end{pmatrix}$$

where the last expression is the "outer product", producing a matrix from two vectors.

The obvious use of all this comes in calculating distances and angles between atoms in an arbitrary unit cell. The atomic positions of the atoms are just vectors from the origin to the atom. Two of them can be subtracted to get the vector from one atom to another:

$\begin{matrix} \vec{d}_{12} = \vec{x}_2 - \vec{x}_1 \\ \vec{d}_{13} = \vec{x}_3 - \vec{x}_1 \end{matrix}$. The distances are just $\begin{matrix} d_{12} = \left(\vec{d}_{12}^{\,T}\ \underline{M}\ \vec{d}_{12}\right)^{1/2} \\ d_{13} = \left(\vec{d}_{13}^{\,T}\ \underline{M}\ \vec{d}_{13}\right)^{1/2} \end{matrix}$ and the angle at atom 1 is defined by $\cos\vartheta = \dfrac{\vec{d}_{12}\bullet\vec{d}_{13}}{d_{12}d_{13}}$.

The critical place of $\underline{M}$ in these calculations is why it is called the "<u>metric</u> tensor".

<u>Relationships for a general unit cell and its reciprocal cell</u>.

The volume of a parallelepiped is easily expressed in vector terms as $V = \vec{a}\bullet\left(\vec{b}\times\vec{c}\right)$. It can also be written out as $V = abc\sqrt{1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma}$. (What does this look like if all the angles are 90°?) This expression is also equal to the square root of the determinant of the metric tensor, $V = (\det \underline{M})^{1/2}$. (Prove this to yourself)

In diffraction and other applications in solid state physics and chemistry, it is often convenient to use a coordinate system reciprocal to that of the lattice. That is:

$$\begin{matrix} \vec{a}\bullet\vec{a}^* = 1 & \vec{a}\bullet\vec{b}^* = 0 \\ \vec{b}\bullet\vec{b}^* = 1 & \vec{a}\bullet\vec{c}^* = 0 \\ \vec{c}\bullet\vec{c}^* = 1 & \vec{b}\bullet\vec{c}^* = 0 \end{matrix}$$

Thus, we construct the reciprocal cell with the reciprocal vectors normal to the plane of the other two real vectors. Since $V = \vec{a}\bullet(\vec{b}\times\vec{c}) = \vec{b}\bullet(\vec{c}\times\vec{a}) = \vec{c}\bullet(\vec{a}\times\vec{b})$, this gives

$$\vec{a}^* = \frac{\vec{b}\times\vec{c}}{V} \qquad \vec{b}^* = \frac{\vec{c}\times\vec{a}}{V} \qquad \vec{c}^* = \frac{\vec{a}\times\vec{b}}{V}$$ (remembering to keep the correct order in the cross-products).

It can also be easily shown that $V^* = 1/V$, and $\underline{M}^* = \underline{M}^{-1}$. Formulae for the magnitudes of a^* and α^*, etc. are as follows:

$$a^* = \frac{bc\sin\alpha}{V} \qquad \cos\alpha^* = \frac{\cos\beta\cos\gamma - \cos\alpha}{\sin\beta\sin\gamma}$$

$$b^* = \frac{ac\sin\beta}{V} \qquad \cos\beta^* = \frac{\cos\alpha\cos\gamma - \cos\beta}{\sin\alpha\sin\gamma}$$

$$c^* = \frac{ab\sin\gamma}{V} \qquad \cos\gamma^* = \frac{\cos\alpha\cos\beta - \cos\gamma}{\sin\alpha\sin\beta}$$

NOTE(1): Because of the reciprocal nature of the cells, the same equations work with all reciprocal quantities replaced by real values and all real values replaced by reciprocal values.

NOTE(2): Applying the above equations can be tedious at times. With a computer, you can use the fact that $\underline{M}^* = \underline{M}^{-1}$ to calculate the real values from reciprocal values and vice versa. The computer can invert the matrix, the cell edges are the square roots of the diagonal terms and once you have those you can use the off-diagonal terms to get the angles.

The Bragg condition tells us that diffraction will take place only when the crystal is so oriented that a vector $\underline{h}$ composed of the integers (h, k, ℓ) bisects the angle between the incident and diffracted beams, and that of the scattering angle 2θ must be related to the length of the vector by the Bragg equation $\lambda = 2d \sin\theta$. The length of the vector $\underline{h}$ is the reciprocal lattice distance d*, where d, the interplanar spacing, is equal to l/d*.

<u>Example</u>

The compound $NiBr_3 (P(CH_3)_2(C_6H_5))_2 \bullet 1/2\ NiBr_2(P(CH_3)_2 (C_6H_5))_2 \bullet C_6H_6$ crystallizes in the following (triclinic) cell:

a = 9.021 Å	α = 98°52'	cos α = -0.15414	sin α = 0.98805
b = 17.591 Å	β= 94°29'	cos β = -0.07817	sin β = 0.99694
c = 11.181 Å	γ = 90°44'	cos γ = -0.01280	sin γ = 0.99992

a) What is the volume of this cell?

$$\underline{M} = \begin{pmatrix} 81.3784 & -2.0728 & -7.8845 \\ -2.0728 & 322.2384 & -30.9375 \\ -7.8845 & -30.9375 & 125.0148 \end{pmatrix}$$

Det $\underline{M}$ = 3,1788 10^6 $Å^6$
$\underline{V}$ = 1782.9 $Å^3$

b) What are the reciprocal cell constants?

$$a^* = \frac{bc\sin\alpha}{V} = \frac{(17.951)(11.181)(\sin 98°52')}{1783.5} = 0.1123\ Å^{-1}$$

Similarly, $b^* = (ca \sin\beta)/V = 0.05640\ Å^{-1}$

$c^* = (ab \sin\gamma)/V = 0.09082\ Å^{-1}$

$$\cos a^* = \frac{\cos\beta\cos\gamma - \cos\alpha}{\sin\beta\sin\gamma} = 0.15562$$

Similarly, cos B* = 0.08112 and cos γ * = 0.02522 may be obtained from interchanging α for α*, etc. in the formulae given above. Note that in the same manner

$$V^* = a^*b^*c^* \sqrt{1-\cos^2\alpha^* - \cos^2\beta^* - \cos^2\gamma^* + 2\cos\alpha^*\cos\beta^*\cos\gamma^*} = 5.609 \times 10^{-4}\ Å^{-3}$$

and

VV* = 1

Note also that on a computer since $\underline{M}^* = \underline{M}^{-1}$

we could invert matrix $\underline{M}$ to obtain

$$\underline{M}^{-1} = \underline{M}^* = \begin{pmatrix} 0.012372 & 0.000158 & 0.000819 \\ 0.000158 & 0.003181 & 0.000797 \\ 0.000819 & 0.000797 & 0.008248 \end{pmatrix} = \left(\underline{a}^* \cdot \underline{a}^*\right)_{\text{etc.}}$$

and derive a* etc. from

$$a^* = \sqrt{\underline{M}^*(1,1)}$$

and cos γ*, etc. from

$$\cos \gamma^* = \frac{\underline{M}^*(1,2)}{\sqrt{\underline{M}^*(1,1)\cdot \underline{M}^*(2,2)}}$$

c) For the cell in the example compute d for the {2,1,1} parallel planes.

$$\underline{h} = h\underline{a}^* + k\underline{b}^* + \ell\underline{c}^* \text{ and } d^* = \frac{1}{d} = \frac{2\sin\theta}{\lambda} = |\underline{h}|$$

For a general coordinate system we have seen that the metric tensor for the vector space must be used. In the present case we have

$$d^{*2} = \frac{1}{d^2} = (hk\ell)\,(\underline{M}^*)\begin{pmatrix} h \\ k \\ \ell \end{pmatrix}$$

From the example we have M* and hence

$$\frac{1}{d_{211}^2} = d^{*2}_{211} = (2\ 1\ 1)\begin{pmatrix} 0.012372 & 0.00158 & 0.000819 \\ 0.000158 & 0.003181 & 0.000797 \\ 0.000819 & 0.000797 & 0.008248 \end{pmatrix}\begin{pmatrix} 2 \\ 1 \\ 1 \end{pmatrix} = 0.066422\ \text{Å}^{-2}$$

$d_{211} = 3.880$ Å

d) Given the wavelength of CuKα radiation of 1.542 Å at what Bragg θ does the 211 reflection occur?

$$\theta = \sin^{-1}(\lambda/2d) = \sin^{-1}\left(\frac{1.542}{(2)(3.880)}\right) = 11.46°$$

e) Suppose it is for some reason more convenient to use a body centered cell (make a sketch if you have trouble seeing this) defined by

$\underline{a}_{new} = \underline{a}_{old}$ $\underline{b}_{new} = \underline{b}_{old}$ $\underline{c}_{new} = 2\underline{c}_{old} - \underline{a}_{old} - \underline{b}_{old}$ or in matrix form

$$\underbrace{\begin{pmatrix} \underline{a} \\ \underline{b} \\ \underline{c} \end{pmatrix}}_{\text{I}} = \underbrace{\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -1 & -1 & 2 \end{pmatrix}}_{\text{matrix}}\underbrace{\begin{pmatrix} \underline{a} \\ \underline{b} \\ \underline{c} \end{pmatrix}}_{\text{P}}$$

body centered — $\underline{A}$ — primitive

note that the reverse transformation (centered cell to primitive) is given by

$$\underbrace{\begin{pmatrix} \underline{a} \\ \underline{b} \\ \underline{c} \end{pmatrix}}_{\text{P}} = \underline{A}^{-1}\underbrace{\begin{pmatrix} \underline{a} \\ \underline{b} \\ \underline{c} \end{pmatrix}}_{\text{I}} \quad \text{where } \underline{A}^{-1} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ ½ & ½ & ½ \end{pmatrix}$$

The determinant of such transformation matrices is the ratio of the related cell volumes. If the sign of the determinant is negative it indicates that the transformation is changing the handedness (right to left) of the coordinate system - which means the transformation should be changed to be a proper one. Note that

$$\mathrm{Det}(\underline{A}) = 2 = (\text{Vol I cell})/(\text{Vol P cell})$$

Coordinates in real space are vectors of the type $x\underline{a} + y\underline{b} + z\underline{c}$. This point in space must be invariant to the coordinate system chosen, so that for a new axis system $\underline{a}'$, $\underline{b}'$, $\underline{c}'$ the new coordinates x', y', z' must satisfy $x'\underline{a}' + y'\underline{b}' + z'\underline{c}' = x\underline{a} + y\underline{b} + z\underline{c}$.

This requires $\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}^T \bullet \begin{pmatrix} \underline{a}' \\ \underline{b}' \\ \underline{c}' \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}^T \bullet \begin{pmatrix} \underline{a} \\ \underline{b} \\ \underline{c} \end{pmatrix}$ which implies

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}_I = (\underline{A}^{-1})^T \begin{pmatrix} x \\ y \\ z \end{pmatrix}_P$$ (with the reverse transformation just $\underline{A}^T$)

Further note that, because of the reciprocal relation of the real and reciprocal lattices their product is also invariant, which requires

$$\begin{pmatrix} \underline{a}^* \\ \underline{b}^* \\ \underline{c}^* \end{pmatrix}_I = (\underline{A}^{-1})^T \begin{pmatrix} \underline{a}^* \\ \underline{b}^* \\ \underline{c}^* \end{pmatrix}_P = \begin{pmatrix} 1 & 0 & 1/2 \\ 0 & 1 & 1/2 \\ 0 & 0 & 1/2 \end{pmatrix} \begin{pmatrix} \underline{a}^* \\ \underline{b}^* \\ \underline{c}^* \end{pmatrix}_P$$

where $(\underline{A}^{-1})^T$ is the transpose of $\underline{A}$ inverse.

Similarly, the Miller indices, which are coordinates of reciprocal space, means that the vector for $h\underline{a}^* + k\underline{b}^* + \ell\underline{c}^*$ is invariant and so the Miller indices are related by the inverse transpose of the matrix that interrelates the reciprocal cells

$$\begin{pmatrix} h \\ k \\ \ell \end{pmatrix}_I = \left\{\left[(\underline{A}^{-1})^T\right]^{-1}\right\}^T \begin{pmatrix} h \\ k \\ \ell \end{pmatrix}_P$$ which means $$\begin{pmatrix} h \\ k \\ \ell \end{pmatrix}_I = \underline{A} \begin{pmatrix} h \\ k \\ \ell \end{pmatrix}_P$$ – the same relation as the unit cell vectors.

Thus, in our example

$h_I = h_P$
$k_I = k_P$
$\ell_I = 2\ell_P - h_P - k_P$

Note that this immediately gives the requirement $h_I + k_I + 2\ell_I = 2\ell_p$, i.e. the sum of h_I, k_I and ℓ_I must be an even integer. This is the extinction requirement of body centered cells.