# Supplementary material on unit cell parameters, the spacing of lattice planes, interplanar angles and angles involving lattice directions

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## Derivation of the general formula for unit cell volume

In the coordinate transformation essay we showed that fractional coordinates (*x*, *y*, *z*) measured relative to the crystallographic unit cell vectors (**a**, **b**, **c**) can be converted to orthogonal coordinates (*X*, *Y*, *Z*) by the following expression:

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & -c\sin\beta\cos\alpha^* \\ 0 & 0 & c\sin\beta\sin\alpha^* \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

We can refer to the orthogonal *X*, *Y* and *Z* coordinates in the context of unit vectors **i**, **j** and **k** which are described in Chapter 2 of *Crystals, X-rays and Proteins* by D. Sherwood and J. Cooper (OUP, 2010, 2015), hereafter referred to as CXP.

Considering the tip of the **a** vector at fractional coordinate (1, 0, 0), by matrix multiplication we obtain **a** = *a* **i**, and likewise for **b** at (0, 1, 0) and **c** at (0, 0, 1) we get:

$$\mathbf{b} = b\cos\gamma\,\mathbf{i} + b\sin\gamma\,\mathbf{j} \quad \text{and}$$

$$\mathbf{c} = c\cos\beta\,\mathbf{i} - c\sin\beta\cos\alpha^*\,\mathbf{j} + c\sin\beta\sin\alpha^*\,\mathbf{k}$$

In Chapter 8 of CXP, we showed that the volume of the unit cell is given by $V = \mathbf{a}\cdot\mathbf{b}\wedge\mathbf{c}$. From the properties of the vector triple scalar product (*e.g.* see Wikipedia), the formula can also be expressed as $V = \mathbf{a}\wedge\mathbf{b}\cdot\mathbf{c}$ . The volume *V* is therefore given by:

$$V = a\,\mathbf{i}\wedge(b\cos\gamma\,\mathbf{i} + b\sin\gamma\,\mathbf{j})\cdot(c\cos\beta\,\mathbf{i} - c\sin\beta\cos\alpha^*\,\mathbf{j} + c\sin\beta\sin\alpha^*\,\mathbf{k})$$

and remembering that $\mathbf{i}\wedge\mathbf{i}=0$ and $\mathbf{i}\wedge\mathbf{j}=\mathbf{k}$, etc, gives:

$$V = abc\sin\gamma\,\mathbf{k}\cdot(\cos\beta\,\mathbf{i} - \sin\beta\cos\alpha^*\,\mathbf{j} + \sin\beta\sin\alpha^*\,\mathbf{k})$$

From the properties of the dot product, *e.g.* $\mathbf{k}\cdot\mathbf{i} = \mathbf{k}\cdot\mathbf{j} = 0$ and $\mathbf{k}\cdot\mathbf{k} = 1$, *etc*, we can say:

$$V = abc\sin\alpha^*\sin\beta\sin\gamma$$

In the coordinate transformations essay we showed that $\cos\alpha^* = \dfrac{\cos\beta\cos\gamma - \cos\alpha}{\sin\beta\sin\gamma}$ and since $\sin\alpha^* = \sqrt{1-\cos^2\alpha^*}$ we can state:

$$\sin\alpha^* = \sqrt{1 - \left(\frac{\cos\beta\cos\gamma - \cos\alpha}{\sin\beta\sin\gamma}\right)^2}$$

$$=\sqrt{\frac{\sin^2\beta\sin^2\gamma-(\cos^2\beta\cos^2\gamma+\cos^2\alpha-2\cos\alpha\cos\beta\cos\gamma)}{\sin^2\beta\sin^2\gamma}}$$

$$=\sqrt{\frac{\sin^2\beta\sin^2\gamma-((1-\sin^2\beta)(1-\sin^2\gamma)+1-\sin^2\alpha-2\cos\alpha\cos\beta\cos\gamma)}{\sin^2\beta\sin^2\gamma}}$$

$$=\sqrt{\frac{\sin^2\beta\sin^2\gamma-(1-\sin^2\gamma-\sin^2\beta+\sin^2\beta\sin^2\gamma)-1+\sin^2\alpha+2\cos\alpha\cos\beta\cos\gamma}{\sin^2\beta\sin^2\gamma}}$$

$$=\sqrt{\frac{\sin^2\beta\sin^2\gamma-1+\sin^2\gamma+\sin^2\beta-\sin^2\beta\sin^2\gamma-1+\sin^2\alpha+2\cos\alpha\cos\beta\cos\gamma}{\sin^2\beta\sin^2\gamma}}$$

$$=\sqrt{\frac{-1+\sin^2\gamma+\sin^2\beta-1+\sin^2\alpha+2\cos\alpha\cos\beta\cos\gamma}{\sin^2\beta\sin^2\gamma}}$$

$$=\frac{\sqrt{\sin^2\alpha+\sin^2\beta+\sin^2\gamma+2\cos\alpha\cos\beta\cos\gamma-2}}{\sin\beta\sin\gamma}$$

Substituting this into the formula for the unit cell volume gives:

$$V=abc\sqrt{\sin^2\alpha+\sin^2\beta+\sin^2\gamma+2\cos\alpha\cos\beta\cos\gamma-2}$$

## Determining the *d*-spacing of lattice planes (resolution)

The scattering or reciprocal lattice vector, **S**, has amplitude $|\mathbf{S}| = \frac{1}{d}$ , as described in Chapter 8 of CXP. The following well-known formula: $\mathbf{S} = h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*$ suggests that if we can orthogonalise the reciprocal lattice coordinates (*h*, *k*, *l*) we could then use 3D Pythagoras to determine $|\mathbf{S}|$ or $\frac{1}{d}$ . A simple way to orthogonalise the reciprocal lattice coordinates is to use the same convention for aligning the orthogonal axes with **a***, **b*** and **c*** as that used for the real lattice vectors in the coordinate transformations essay. The orthogonal reciprocal lattice coordinates (*H*, *K*, *L*) are immediately given by:

$$\begin{pmatrix}H\\K\\L\end{pmatrix}=\begin{pmatrix}a^* & b^*\cos\gamma^* & c^*\cos\beta^*\\ 0 & b^*\sin\gamma^* & -c^*\sin\beta^*\cos\alpha\\ 0 & 0 & c^*\sin\beta^*\sin\alpha\end{pmatrix}\begin{pmatrix}h\\k\\l\end{pmatrix}$$

$$H=ha^*+kb^*\cos\gamma^*+lc^*\cos\beta^*$$

$$K=kb^*\sin\gamma^*-lc^*\sin\beta^*\cos\alpha$$

$$L=lc^*\sin\beta^*\sin\alpha$$

Squaring each term gives:

$$H^2 = (ha^* + kb^* \cos\gamma^* + lc^* \cos\beta^*)^2$$

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

$$K^2 = (kb^* \sin\gamma^* - lc^* \sin\beta^* \cos\alpha)^2 = k^2 b^{*2} \sin^2\gamma^* + l^2 c^{*2} \sin^2\beta^* \cos^2\alpha - 2kl\, b^* c^* \cos\alpha\ \sin\beta^* \sin\gamma^*$$

$$L^2 = l^2 c^{*2} \sin^2\beta^* \sin^2\alpha$$

Making use of the relationship $\sin^2\theta + \cos^2\theta = 1$ gives:

$$K^2 + L^2 = k^2 b^{*2} \sin^2\gamma^* + l^2 c^{*2} \sin^2\beta^* - 2kl\, b^* c^* \cos\alpha\ \sin\beta^* \sin\gamma^*$$

and

$$\begin{aligned} H^2 + K^2 + L^2 = {} & h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hk\, a^* b^* \cos\gamma^* + 2hl\, a^* c^* \cos\beta^* \\ & + 2kl\, b^* c^* (\cos\beta^* \cos\gamma^* - \cos\alpha\ \sin\beta^* \sin\gamma^*) \end{aligned}$$

$$\begin{aligned} & = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hk\, a^* b^* \cos\gamma^* + 2hl\, a^* c^* \cos\beta^* \\ & + 2kl\, b^* c^* (\cos\beta^* \cos\gamma^* + \sin\beta^* \sin\gamma^* \cos(180° - \alpha)) \end{aligned}$$

From Fig. 2 of the coordinate transformations essay, we can simplify this expression to:

$$\frac{1}{d^2} = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hk\, a^* b^* \cos\gamma^* + 2hl\, a^* c^* \cos\beta^* + 2kl\, b^* c^* \cos\alpha^*$$

A more elegant approach is to use the properties of the vector dot product as follows:

$$|\mathbf{S}|^2 = \frac{1}{d^2} = \mathbf{S}\cdot\mathbf{S} = (h\,\mathbf{a}^* + k\,\mathbf{b}^* + l\,\mathbf{c}^*)\cdot(h\,\mathbf{a}^* + k\,\mathbf{b}^* + l\,\mathbf{c}^*)$$

$$= h^2\, \mathbf{a}^*\cdot\mathbf{a}^* + k^2\, \mathbf{b}^*\cdot\mathbf{b}^* + l^2\, \mathbf{c}^*\cdot\mathbf{c}^* + 2hk\, \mathbf{a}^*\cdot\mathbf{b}^* + 2hl\, \mathbf{a}^*\cdot\mathbf{c}^* + 2kl\, \mathbf{b}^*\cdot\mathbf{c}^*$$

since the dot product is distributive and commutative. Substituting other formulae derived in Chapter 8 of CXP, we get exactly the same formula as that derived from using 3D Pythagoras on the orthogonalised reciprocal lattice coordinates:

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

We can express this equation in terms of the real lattice parameters as follows:

$$\begin{aligned} |\mathbf{S}|^2 = {} & h^2\left(\frac{bc\sin\alpha}{V}\right)^2 + k^2\left(\frac{ac\sin\beta}{V}\right)^2 + l^2\left(\frac{ab\sin\gamma}{V}\right)^2 + 2hk\left(\frac{bc\sin\alpha}{V}\right)\left(\frac{ac\sin\beta}{V}\right)\cos\gamma^* \\ & + 2hl\left(\frac{bc\sin\alpha}{V}\right)\left(\frac{ab\sin\gamma}{V}\right)\cos\beta^* + 2kl\left(\frac{ac\sin\beta}{V}\right)\left(\frac{ab\sin\gamma}{V}\right)\cos\alpha^* \end{aligned}$$

Given $\cos\alpha^* = \dfrac{\cos\beta\cos\gamma - \cos\alpha}{\sin\beta\sin\gamma}$ , $\cos\beta^* = \dfrac{\cos\alpha\cos\gamma - \cos\beta}{\sin\alpha\sin\gamma}$ and $\cos\gamma^* = \dfrac{\cos\alpha\cos\beta - \cos\gamma}{\sin\alpha\sin\beta}$

from the coordinate transformations essay, we get:

$$\frac{1}{d^2} = h^2\left(\frac{bc\sin\alpha}{V}\right)^2 + k^2\left(\frac{ac\sin\beta}{V}\right)^2 + l^2\left(\frac{ab\sin\gamma}{V}\right)^2 + 2hk\left(\frac{bc}{V}\right)\left(\frac{ac}{V}\right)(\cos\alpha\cos\beta - \cos\gamma)$$
$$+ 2hl\left(\frac{bc}{V}\right)\left(\frac{ab}{V}\right)(\cos\alpha\cos\gamma - \cos\beta) + 2kl\left(\frac{ac}{V}\right)\left(\frac{ab}{V}\right)(\cos\beta\cos\gamma - \cos\alpha)$$

$$= \frac{1}{V^2}\Big[h^2b^2c^2\sin^2\alpha + k^2a^2c^2\sin^2\beta + l^2a^2b^2\sin^2\gamma + 2hkabc^2(\cos\alpha\cos\beta - \cos\gamma)$$
$$+ 2hlab^2c(\cos\alpha\cos\gamma - \cos\beta) + 2kla^2bc(\cos\beta\cos\gamma - \cos\alpha)\Big]$$

$$= \frac{1}{V^2}\Big[h^2b^2c^2(1-\cos^2\alpha) + k^2a^2c^2(1-\cos^2\beta) + l^2a^2b^2(1-\cos^2\gamma) + 2hkabc^2(\cos\alpha\cos\beta - \cos\gamma)$$
$$+ 2hlab^2c(\cos\alpha\cos\gamma - \cos\beta) + 2kla^2bc(\cos\beta\cos\gamma - \cos\alpha)\Big]$$

In Chapter 3 of the book *Crystals and X-rays* by Kathleen Lonsdale (Bell, 1948) on page 54 an interesting determinant version of this formula "*which is easy to remember, because of its symmetry*" is given:

$$\frac{1}{d^2} = \frac{\dfrac{h}{a}\begin{vmatrix} \frac{h}{a} & \cos\gamma & \cos\beta \\ \frac{k}{b} & 1 & \cos\alpha \\ \frac{l}{c} & \cos\alpha & 1 \end{vmatrix} + \dfrac{k}{b}\begin{vmatrix} 1 & \frac{h}{a} & \cos\beta \\ \cos\gamma & \frac{k}{b} & \cos\alpha \\ \cos\beta & \frac{l}{c} & 1 \end{vmatrix} + \dfrac{l}{c}\begin{vmatrix} 1 & \cos\gamma & \frac{h}{a} \\ \cos\gamma & 1 & \frac{k}{b} \\ \cos\beta & \cos\alpha & \frac{l}{c} \end{vmatrix}}{\begin{vmatrix} 1 & \cos\gamma & \cos\beta \\ \cos\gamma & 1 & \cos\alpha \\ \cos\beta & \cos\alpha & 1 \end{vmatrix}}$$

To check that these formulae are consistent, expanding the first term of the numerator as described in the Appendix of Chapter 2 of CXP, gives:

$$\left(\frac{h}{a}\right)^2(1-\cos^2\alpha) + \frac{h}{a}\cos\gamma\left(\frac{l}{c}\cos\alpha - \frac{k}{b}\right) + \frac{h}{a}\cos\beta\left(\frac{k}{b}\cos\alpha - \frac{l}{c}\right)$$

the second:

$$\left(\frac{k}{b}\right)\left(\frac{k}{b} - \frac{l}{c}\cos\alpha\right) + \frac{hk}{ab}(\cos\alpha\cos\beta - \cos\gamma) + \frac{k}{b}\cos\beta\left(\frac{l}{c}\cos\gamma - \frac{k}{b}\cos\beta\right)$$

and the third:

$$\left(\frac{l}{c}\right)\left(\frac{l}{c}-\frac{k}{b}\cos\alpha\right)+\frac{l}{c}\cos\gamma\left(\frac{k}{b}\cos\beta-\frac{l}{c}\cos\gamma\right)+\frac{hl}{ac}(\cos\alpha\cos\gamma-\cos\beta)$$

Expanding the denominator gives:

$$1-\cos^2\alpha+\cos\gamma(\cos\alpha\cos\beta-\cos\gamma)+\cos\beta(\cos\alpha\cos\gamma-\cos\beta)$$

$$=\ \sin^2\alpha+\cos\gamma\cos\alpha\cos\beta-\cos^2\gamma+\cos\beta\cos\alpha\cos\gamma-\cos^2\beta$$

$$=\ \sin^2\alpha+\cos\gamma\cos\alpha\cos\beta+\sin^2\gamma\ -1+\cos\beta\cos\alpha\cos\gamma+\sin^2\beta\ -1$$

$$=\ \sin^2\alpha+\sin^2\beta+\sin^2\gamma+2\cos\alpha\cos\beta\cos\gamma-2\quad\text{and we showed earlier that this equals}\quad\left(\frac{V}{abc}\right)^2\ .$$

The determinant formula therefore becomes:

$$\frac{1}{d^2}=\left(\frac{abc}{V}\right)^2\left[\left(\frac{h}{a}\right)^2(1-\cos^2\alpha)+\frac{h}{a}\cos\gamma\left(\frac{l}{c}\cos\alpha-\frac{k}{b}\right)+\frac{h}{a}\cos\beta\left(\frac{k}{b}\cos\alpha-\frac{l}{c}\right)\right.$$
$$+\left(\frac{k}{b}\right)\left(\frac{k}{b}-\frac{l}{c}\cos\alpha\right)+\frac{hk}{ab}(\cos\alpha\cos\beta-\cos\gamma)+\frac{k}{b}\cos\beta\left(\frac{l}{c}\cos\gamma-\frac{k}{b}\cos\beta\right)$$
$$\left.+\left(\frac{l}{c}\right)\left(\frac{l}{c}-\frac{k}{b}\cos\alpha\right)+\frac{l}{c}\cos\gamma\left(\frac{k}{b}\cos\beta-\frac{l}{c}\cos\gamma\right)+\frac{hl}{ac}(\cos\alpha\cos\gamma-\cos\beta)\right]$$

$$=\frac{1}{V^2}\left[h^2b^2c^2(1-\cos^2\alpha)+hab^2c^2\cos\gamma\left(\frac{l}{c}\cos\alpha-\frac{k}{b}\right)+hab^2c^2\cos\beta\left(\frac{k}{b}\cos\alpha-\frac{l}{c}\right)\right.$$
$$+(ka^2bc^2)\left(\frac{k}{b}-\frac{l}{c}\cos\alpha\right)+hkabc^2(\cos\alpha\cos\beta-\cos\gamma)+ka^2bc^2\cos\beta\left(\frac{l}{c}\cos\gamma-\frac{k}{b}\cos\beta\right)$$
$$\left.+la^2b^2c\left(\frac{l}{c}-\frac{k}{b}\cos\alpha\right)+la^2b^2c\cos\gamma\left(\frac{k}{b}\cos\beta-\frac{l}{c}\cos\gamma\right)+hlab^2c(\cos\alpha\cos\gamma-\cos\beta)\right]$$

$$=\frac{1}{V^2}\left[h^2b^2c^2(1-\cos^2\alpha)+hlab^2c\cos\gamma\cos\alpha-hkabc^2\cos\gamma+hkabc^2\cos\beta\cos\alpha-hlab^2c\cos\beta\right.$$
$$+k^2a^2c^2-kla^2bc\cos\alpha+hkabc^2(\cos\alpha\cos\beta-\cos\gamma)+kla^2bc\cos\beta\cos\gamma-k^2a^2c^2\cos^2\beta$$
$$\left.+l^2a^2b^2-kla^2bc\cos\alpha+kla^2bc\cos\beta\cos\gamma-l^2a^2b^2\cos^2\gamma+hlab^2c(\cos\alpha\cos\gamma-\cos\beta)\right]$$

$$=\frac{1}{V^2}\left[h^2b^2c^2(1-\cos^2\alpha)+k^2a^2c^2(1-\cos^2\beta)+l^2a^2b^2(1-\cos^2\gamma)+2hkabc^2(\cos\alpha\cos\beta-\cos\gamma)\right.$$
$$\left.+2hlab^2c(\cos\alpha\cos\gamma-\cos\beta)+2kla^2bc(\cos\beta\cos\gamma-\cos\alpha)\right]$$

and, with some grouping of terms by colour for clarity, the equivalence is demonstrated.

The determinant formula is given again below:

$$\frac{1}{d^2}=\frac{\frac{h}{a}\begin{vmatrix}\frac{h}{a} & \cos\gamma & \cos\beta\\ \frac{k}{b} & 1 & \cos\alpha\\ \frac{l}{c} & \cos\alpha & 1\end{vmatrix}+\frac{k}{b}\begin{vmatrix}1 & \frac{h}{a} & \cos\beta\\ \cos\gamma & \frac{k}{b} & \cos\alpha\\ \cos\beta & \frac{l}{c} & 1\end{vmatrix}+\frac{l}{c}\begin{vmatrix}1 & \cos\gamma & \frac{h}{a}\\ \cos\gamma & 1 & \frac{k}{b}\\ \cos\beta & \cos\alpha & \frac{l}{c}\end{vmatrix}}{\begin{vmatrix}1 & \cos\gamma & \cos\beta\\ \cos\gamma & 1 & \cos\alpha\\ \cos\beta & \cos\alpha & 1\end{vmatrix}}$$

One rule-of-thumb for remembering it must be to start with the denominator, which has diagonal mirror symmetry, and imagine that the top 3 determinants are empty. We can simply drop all of the denominator terms into each empty determinant and replace one column with *h/a*, *k/b* and *l/c* depending on whether it is the first, second or third term of the numerator, as shown in cyan.

## The metric tensor

In the above notes we have converted our coordinates from fractional to the **ijk** orthogonal system but it is possible to do the same mathematics with fractional coordinates. Consider a point at ($x_1$, $y_1$, $z_1$), its position vector with respect to the crystallographic axis vectors **a**, **b** and **c** is given by the matrix product:

$$\mathbf{r_1} = \begin{pmatrix}x_1 & y_1 & z_1\end{pmatrix}\begin{pmatrix}\mathbf{a}\\ \mathbf{b}\\ \mathbf{c}\end{pmatrix} \quad \text{or } \mathbf{r}_1=x_1\mathbf{a}+y_1\mathbf{b}+z_1\mathbf{c}$$

and another point at ($x_2$, $y_2$, $z_2$) will have position vector:

$$\mathbf{r_2} = \begin{pmatrix}x_2 & y_2 & z_2\end{pmatrix}\begin{pmatrix}\mathbf{a}\\ \mathbf{b}\\ \mathbf{c}\end{pmatrix} \quad \text{or } \mathbf{r}_2=x_2\mathbf{a}+y_2\mathbf{b}+z_2\mathbf{c}$$

The dot product of $\mathbf{r_1}$ and $\mathbf{r_2}$ is as follows:

$$\mathbf{r_1}\cdot\mathbf{r_2}=(x_1\mathbf{a}+y_1\mathbf{b}+z_1\mathbf{c})\cdot(x_2\mathbf{a}+y_2\mathbf{b}+z_2\mathbf{c})$$

$$=x_1x_2\mathbf{a}\cdot\mathbf{a}+x_1y_2\mathbf{a}\cdot\mathbf{b}+x_1z_2\mathbf{a}\cdot\mathbf{c}+y_1x_2\mathbf{b}\cdot\mathbf{a}+y_1y_2\mathbf{b}\cdot\mathbf{b}+y_1z_2\mathbf{b}\cdot\mathbf{c}+z_1x_2\mathbf{c}\cdot\mathbf{a}+z_1y_2\mathbf{c}\cdot\mathbf{b}+z_1z_2\mathbf{c}\cdot\mathbf{c}$$

$$=\begin{pmatrix}x_1 & y_1 & z_1\end{pmatrix}\begin{pmatrix}x_2\mathbf{a}\cdot\mathbf{a} & y_2\mathbf{a}\cdot\mathbf{b} & z_2\mathbf{a}\cdot\mathbf{c}\\ x_2\mathbf{b}\cdot\mathbf{a} & y_2\mathbf{b}\cdot\mathbf{b} & z_2\mathbf{b}\cdot\mathbf{c}\\ x_2\mathbf{c}\cdot\mathbf{a} & y_2\mathbf{c}\cdot\mathbf{b} & z_2\mathbf{c}\cdot\mathbf{c}\end{pmatrix}$$

$$=\begin{pmatrix}x_1 & y_1 & z_1\end{pmatrix}\begin{pmatrix}\mathbf{a}\cdot\mathbf{a} & \mathbf{a}\cdot\mathbf{b} & \mathbf{a}\cdot\mathbf{c}\\ \mathbf{b}\cdot\mathbf{a} & \mathbf{b}\cdot\mathbf{b} & \mathbf{b}\cdot\mathbf{c}\\ \mathbf{c}\cdot\mathbf{a} & \mathbf{c}\cdot\mathbf{b} & \mathbf{c}\cdot\mathbf{c}\end{pmatrix}\begin{pmatrix}x_2\\ y_2\\ z_2\end{pmatrix}$$

The 3x3 matrix is called the ***metric tensor*** G and it has diagonal symmetry since **a·b**=**b·a**, etc. In the **ijk** system, the metric tensor is a 3x3 identity matrix since **i·i**=1, **i·j**=0, etc. Expanding the terms of G for the general case gives:

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

One practical application of the metric tensor is to calculate interatomic distances directly from fractional coordinates without first orthogonalising them and then using 3D Pythagoras. Consider two atoms differing in $x$, $y$ and $z$ by $\Delta x$, $\Delta y$ and $\Delta z$, the interatomic distance, $d$, can be determined from:

$$d^2 = (\Delta x \;\; \Delta y \;\; \Delta z)\,\mathrm{G}\begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix}$$

Another, quite often-quoted application is in calculating the angle (say $\theta$) between two vectors *e.g.* $\mathbf{r_1}$ and $\mathbf{r_2}$ which can be given as $\cos\theta = \mathbf{r_1}\cdot\mathbf{r_2}/r_1 r_2$ . However, although the numerator of this formula can be expressed in terms of G, as shown previously, it hides the calculation of the amplitudes in the denominator, which requires orthogonalising the fractional coordinates, to the point where I do not think it is very useful.

Expanding G as a determinant gives:

$$a^2b^2c^2 - a^2b^2c^2\cos^2\alpha + ab\cos\gamma\left(abc^2\cos\alpha\cos\beta - abc^2\cos\gamma\right) + ac\cos\beta\left(ab^2c\cos\alpha\cos\gamma - ab^2c\cos\beta\right)$$

$$= \; a^2b^2c^2(1-\cos^2\alpha) + a^2b^2c^2\cos\alpha\cos\beta\cos\gamma - a^2b^2c^2\cos^2\gamma + a^2b^2c^2\cos\alpha\cos\beta\cos\gamma - a^2b^2c^2\cos^2\beta$$

$$= \; a^2b^2c^2\left(\sin^2\alpha + \cos\alpha\cos\beta\cos\gamma - \cos^2\gamma + \cos\alpha\cos\beta\cos\gamma - \cos^2\beta\right)$$

$$= \; a^2b^2c^2\left(\sin^2\alpha + \sin^2\beta + \sin^2\gamma + 2\cos\alpha\cos\beta\cos\gamma - 2\right) \; = \; V^2$$

The latter follows from the expression for the unit cell volume derived in the first section, namely:

$$V = abc\sqrt{\sin^2\alpha + \sin^2\beta + \sin^2\gamma + 2\cos\alpha\cos\beta\cos\gamma - 2}$$

and gives us the important result that the determinant of the metric tensor is the volume of the unit cell squared.

Given the general 3x3 matrix:

$$A = \begin{pmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{pmatrix}$$

the formula for its inversion is:

$$A^{-1}=\frac{1}{\Delta}\begin{pmatrix} y_2 z_3 - z_2 y_3 & z_1 y_3 - y_1 z_3 & y_1 z_2 - z_1 y_2 \\ z_2 x_3 - x_2 z_3 & x_1 z_3 - x_3 z_1 & z_1 x_2 - x_1 z_2 \\ x_2 y_3 - y_2 x_3 & x_3 y_1 - x_1 y_3 & x_1 y_2 - x_2 y_1 \end{pmatrix}$$

where Δ is the determinant of A. The inverse of G is therefore given by:

$$\mathrm{G}^{-1}=\frac{1}{V^2}\begin{pmatrix} b^2c^2-b^2c^2\cos^2\alpha & abc^2\cos\alpha\cos\beta-abc^2\cos\gamma & ab^2c\cos\alpha\cos\gamma-ab^2c\cos\beta \\ abc^2\cos\alpha\cos\beta-abc^2\cos\gamma & a^2c^2-a^2c^2\cos^2\beta & a^2bc\cos\beta\cos\gamma-a^2bc\cos\alpha \\ ab^2c\cos\alpha\cos\gamma-ab^2c\cos\beta & a^2bc\cos\beta\cos\gamma-a^2bc\cos\alpha & a^2b^2-a^2b^2\cos^2\gamma \end{pmatrix}$$

$$=\frac{1}{V^2}\begin{pmatrix} b^2c^2(1-\cos^2\alpha) & abc^2(\cos\alpha\cos\beta-\cos\gamma) & ab^2c(\cos\alpha\cos\gamma-\cos\beta) \\ abc^2(\cos\alpha\cos\beta-\cos\gamma) & a^2c^2(1-\cos^2\beta) & a^2bc(\cos\beta\cos\gamma-\cos\alpha) \\ ab^2c(\cos\alpha\cos\gamma-\cos\beta) & a^2bc(\cos\beta\cos\gamma-\cos\alpha) & a^2b^2(1-\cos^2\gamma) \end{pmatrix}$$

$$=\frac{1}{V^2}\begin{pmatrix} b^2c^2\sin^2\alpha & abc^2\sin\alpha\sin\beta\cos\gamma^* & ab^2c\sin\alpha\sin\gamma\cos\beta^* \\ abc^2\sin\alpha\sin\beta\cos\gamma^* & a^2c^2\sin^2\beta & a^2bc\sin\beta\sin\gamma\cos\alpha^* \\ ab^2c\sin\alpha\sin\gamma\cos\beta^* & a^2bc\sin\beta\sin\gamma\cos\alpha^* & a^2b^2\sin^2\gamma \end{pmatrix}$$

The latter follows from the formulae derived in the coordinate transformations essay using the spherical cosine rule. Using the equations for the reciprocal cell dimensions derived in Chapter 8 of CXP, we get:

$$\mathrm{G}^{-1}=\begin{pmatrix} \mathbf{a}^*\cdot\mathbf{a}^* & \mathbf{a}^*\cdot\mathbf{b}^* & \mathbf{a}^*\cdot\mathbf{c}^* \\ \mathbf{b}^*\cdot\mathbf{a}^* & \mathbf{b}^*\cdot\mathbf{b}^* & \mathbf{b}^*\cdot\mathbf{c}^* \\ \mathbf{c}^*\cdot\mathbf{a}^* & \mathbf{c}^*\cdot\mathbf{b}^* & \mathbf{c}^*\cdot\mathbf{c}^* \end{pmatrix}$$

The last step demonstrates that the inverse of the metric tensor for the real lattice is in fact the metric tensor of the reciprocal lattice, although that will probably be very obvious anyway to someone with a decent understanding of matrices.

There is a theorem in Mathematical Crystallography by M. B. Boisen and G. V. Gibbs (Ed. P. H. Ribbe) *Reviews in Minerology* **15** (1985) which states in effect that:

$$\frac{1}{d^2}=\begin{pmatrix} h & k & l \end{pmatrix}\mathrm{G}^{-1}\begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

This can be seen by substituting for $\mathrm{G}^{-1}$ as below:

$$\frac{1}{d^2}=\begin{pmatrix} h & k & l \end{pmatrix}\begin{pmatrix} \mathbf{a}^*\cdot\mathbf{a}^* & \mathbf{a}^*\cdot\mathbf{b}^* & \mathbf{a}^*\cdot\mathbf{c}^* \\ \mathbf{b}^*\cdot\mathbf{a}^* & \mathbf{b}^*\cdot\mathbf{b}^* & \mathbf{b}^*\cdot\mathbf{c}^* \\ \mathbf{c}^*\cdot\mathbf{a}^* & \mathbf{c}^*\cdot\mathbf{b}^* & \mathbf{c}^*\cdot\mathbf{c}^* \end{pmatrix}\begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

and expanding this gives:

$$\frac{1}{d^2}=\begin{pmatrix} h & k & l \end{pmatrix}\begin{pmatrix} h\,\mathbf{a}^*\cdot\mathbf{a}^*+k\,\mathbf{a}^*\cdot\mathbf{b}^*+l\,\mathbf{a}^*\cdot\mathbf{c}^* \\ h\,\mathbf{b}^*\cdot\mathbf{a}^*+k\,\mathbf{b}^*\cdot\mathbf{b}^*+l\,\mathbf{b}^*\cdot\mathbf{c}^* \\ h\,\mathbf{c}^*\cdot\mathbf{a}^*+k\,\mathbf{c}^*\cdot\mathbf{b}^*+l\,\mathbf{c}^*\cdot\mathbf{c}^* \end{pmatrix}$$

$$=h^2\,\mathbf{a}^*\cdot\mathbf{a}^*+k^2\,\mathbf{b}^*\cdot\mathbf{b}^*+l^2\mathbf{c}^*\cdot\mathbf{c}^*+2hk\,\mathbf{a}^*\cdot\mathbf{b}^*+2hl\,\mathbf{a}^*\cdot\mathbf{c}^*+2kl\,\mathbf{b}^*\cdot\mathbf{c}^*$$

which we showed earlier follows from the definition of **S**, thus proving the theorem.

## Angles between lattice planes

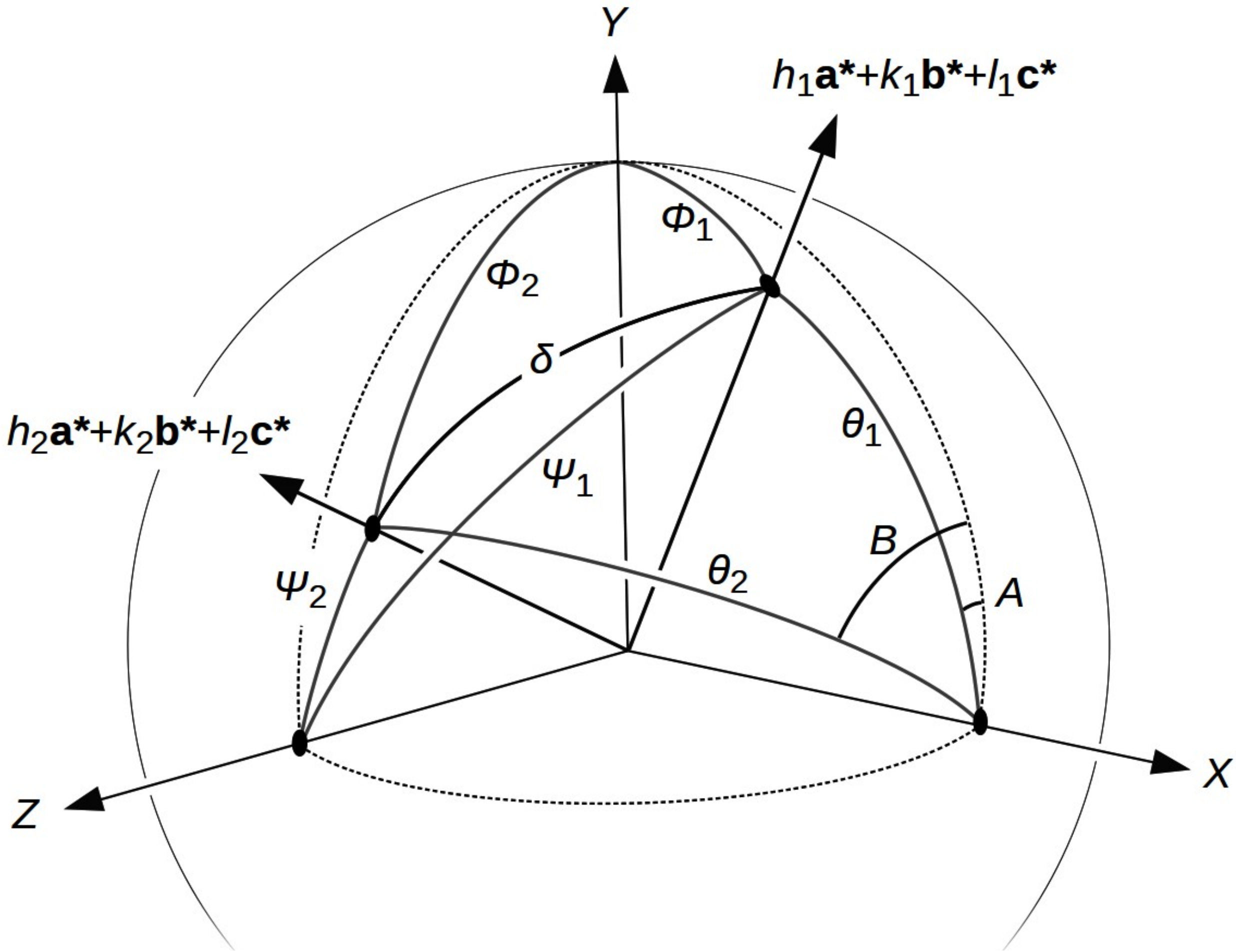
We showed earlier that the coordinates of a reciprocal lattice vector can be orthogonalised as follows:

$$H=ha^*+kb^*\cos\gamma^*+lc^*\cos\beta^*$$

$$K=kb^*\sin\gamma^*-lc^*\sin\beta^*\cos\alpha$$

$$L=lc^*\sin\beta^*\sin\alpha$$

and these can be converted to directions cosines. Considering the angles which the vector makes with the orthogonal *X*, *Y* and *Z* axes as $\theta$, $\Phi$ and $\Psi$, respectively, we get direction cosines: $\cos\theta=\frac{H}{|\mathbf{S}|}=Hd$ , $\cos\phi=Kd$ and $\cos\psi=Ld$ . The following figure shows two reciprocal lattice vectors ($h_1$, $k_1$, $l_1$) and ($h_2$, $k_2$, $l_2$) which make angles $\theta_1$, $\Phi_1$, $\Psi_1$ and $\theta_2$, $\Phi_2$, $\Psi_2$ with the Cartesian axes, respectively. These angles can be considered as arcs of great circles making the system amenable to spherical trigonometry.




The arcs shown as dashed lines are 90° in length since they represent the angles between the orthogonal axes. The arc of length $\delta$ represents the angle between the two reciprocal lattice vectors and since these are normal to the corresponding lattice planes, $\delta$ is also the interplanar angle. From the spherical cosine rule, looking at the triangle formed by arcs $\theta_1$, $\theta_2$ and $\delta$ we can see that:

$$\cos\delta = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(B-A)$$

which demonstrates that we need to determine the angles A and B before $\delta$ can be calculated. Considering the triangle formed by the right hand 90° arc along with arcs $\theta_1$ and $\Phi_1$ we can see that:

$$\cos\phi_1 = \cos\theta_1 \cos 90° + \sin\theta_1 \sin 90° \cos A$$

and this simplifies to $\cos\phi_1 = \sin\theta_1 \cos A$ . Likewise for the spherical triangle formed by the same 90° arc with $\theta_2$ and $\Phi_2$ we get $\cos\phi_2 = \sin\theta_2 \cos B$ and this gives us the following formulae:

$$A = \arccos\left(\frac{\cos\phi_1}{\sin\theta_1}\right) \quad \text{and} \quad B = \arccos\left(\frac{\cos\phi_2}{\sin\theta_2}\right) \quad .$$

We can now calculate the interplanar angle from the formula we gave earlier:

$$\cos\delta = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(B-A)$$

However, we need to be aware that none of the formulae above considered the angular distance from the *Z*-axis. This is important since one of the reciprocal lattice vectors may be in the adjacent octant with a *Z* coordinate of opposite sign to the other. In this case the formula becomes:

$$\cos\delta = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(B+A)$$

and determining which equation to use involves a simple check on the signs of the *Z* coordinates of the two vectors.

## Angles between crystal direction vectors

Given the orthogonalisation matrix derived in the coordinate transformations essay,

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & -c\sin\beta\cos\alpha^* \\ 0 & 0 & c\sin\beta\sin\alpha^* \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

any direction vector in the crystal lattice $\mathbf{r} = p\,\mathbf{a} + q\,\mathbf{b} + r\,\mathbf{c}$ where *p*, *q* and *r* are integers, will have components on orthogonal axes as follows:

$$X = pa + qb\cos\gamma + rc\cos\beta$$

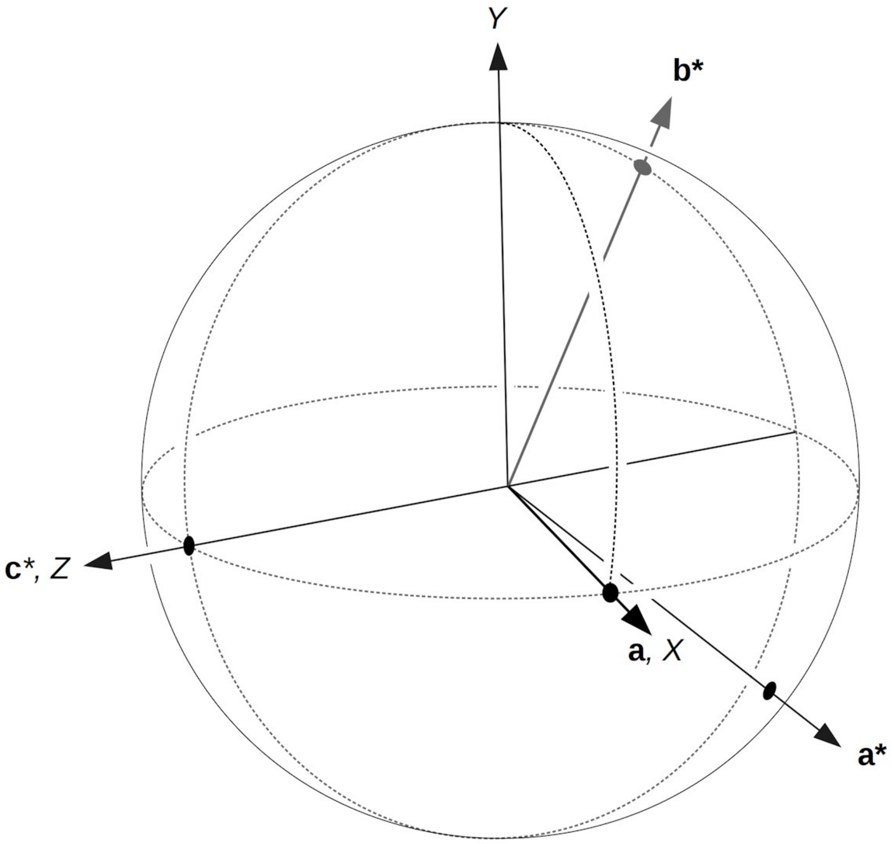
$$Y = qb\sin\gamma - rc\sin\beta\cos\alpha^*$$

$$Z = rc\sin\beta\sin\alpha^*$$

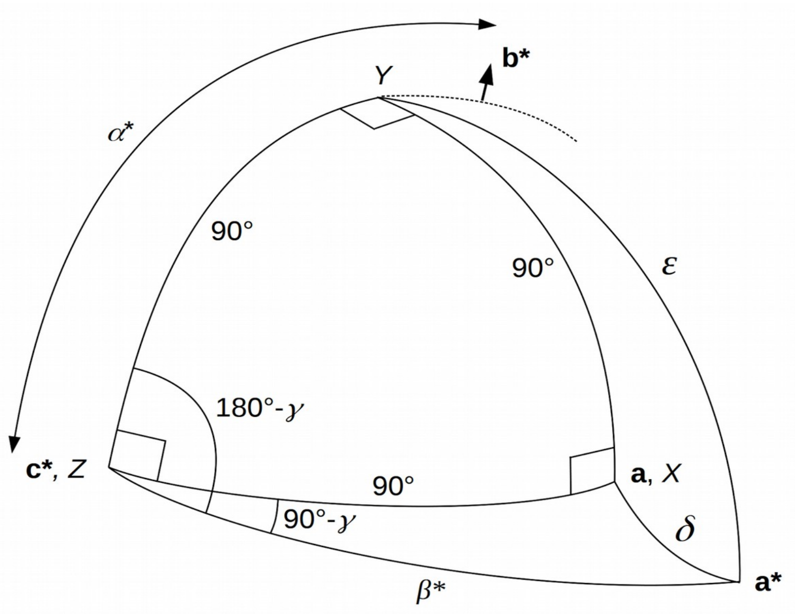
and its length will be $\sqrt{X^2+Y^2+Z^2}$ . Hence we can determine the direction cosines of each vector and the angle between them can be calculated by the same spherical trigonometry as with reciprocal lattice vectors.

## Angles between lattice planes and direction vectors

This is the hybrid situation in which we: *a*) calculate the (*X*, *Y*, *Z*) components of the crystal direction vector [*pqr*] with the orthogonalisation matrix for the real lattice, and *b*) calculate the (*H*, *K*, *L*) components of the reciprocal lattice vector, **S**. The intervening angle follows from the same spherical trigonometry as in the previous two cases. **However**, there is a problem with using the orthogonalisation matrix for the reciprocal lattice that we derived earlier since the reference frame is different from that which we used for the real unit cell vectors. Hence, instead, we need to orthogonalise the reciprocal lattice coordinates using the *X*, *Y* and *Z* axes as defined for the real unit cell and shown in the figure below.




Note that to be consistent with the coordinate transformations essay, this figure assumes that $\alpha^*$, $\beta^*$ and $\gamma^*$ are obtuse although the standard convention is for them to be acute. However, everything works out the same so it does not matter! Starting with $H$, since the $X$ axis is perpendicular to **b*** and **c*** , $H$ only depends on $h$**a***. To determine the component of **a*** on $X$ we need to consider the following spherical triangles in which the angle between **a*** and **a** is shown as $\delta$.




Application of the spherical cosine rule to the lowermost triangle gives the following:

$$\cos\delta = \cos 90°\cos\beta^* + \sin 90°\sin\beta^*\cos(90° - \gamma) = \sin\beta^*\sin\gamma$$

Hence: $H = ha^*\sin\beta^*\sin\gamma$ .

Considering the outer spherical triangle we get:

$$\cos\epsilon = \cos 90°\cos\beta^* + \sin 90°\sin\beta^*\cos(180° - \gamma) = -\sin\beta^*\cos\gamma$$

Hence, *h***a*** has a component of $-ha^*\sin\beta^*\cos\gamma$ on the *K* axis. Since the angle between **b*** and the *Y* axis is $\alpha$*-90° we can see that the component of *k***b*** on the *K* axis is $kb^*\cos(\alpha^* - 90°)$ or $kb^*\sin\alpha^*$ . In contrast, the **c*** vector has no component on the *K* axis since they are at 90° to each other. Hence:

$$K = -ha^*\sin\beta^*\cos\gamma + kb^*\sin\alpha^*$$

Finally, since **c*** is parallel to the *Z* axis and makes angles of $\alpha$* and $\beta$* with **b*** and **a***, respectively, we can see that:

$$L = ha^*\cos\beta^* + kb^*\cos\alpha^* + lc^*$$

So to summarise, we have the following matrix equation which should orthogonalise the reciprocal lattice coordinates using exactly the same reference frame that we have used for the real lattice.

$$\begin{pmatrix} H \\ K \\ L \end{pmatrix} = \begin{pmatrix} a^*\sin\beta^*\sin\gamma & 0 & 0 \\ -a^*\sin\beta^*\cos\gamma & b^*\sin\alpha^* & 0 \\ a^*\cos\beta^* & b^*\cos\alpha^* & c^* \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

The angle between the zone and the reciprocal lattice vector can then be calculated by the spherical trigonometry described earlier. Note that the Very Simple Crystallographic Calculator uses this matrix to orthogonalise the reciprocal lattice coordinates, rather than the one given earlier.

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